PONTIFICIAE ACADEMIAE SCIENTIARVM SCRIPTA VARIA

81

Symposium on

FUTURE TRENDS IN SPECTROSCOPY

June 27 - 28, 1989

PROCEEDINGS

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FOREWORD

On 27 and 28 June 1989, a Symposium on "Future Trends in Spectroscopy" took place at the Seat of the Pontifical Academy of Sciences, Casina Pio IV, on the grounds of the Vatican. The occasion for this Symposium was the 50th anniversary of the first publication of *Spectrochimica Acta*, the founding editor of which was the Vatican Astronomer, Father Alois Gatterer. Participants in the Symposium included representatives of the combined Editorial Advisory Boards of *Spectrochimica Acta* Parts A and B, with representatives from the Pontifical Academy, the Vatican Observatory and Pergamon Press.

This volume contains the papers presented at the Symposium, with summaries of the ensuing discussion. Professor Gerhard Herzberg was not able to be at the Symposium to present his paper in person, so we are grateful to him for providing the manuscript which appears here. The message to the participants from Robert Maxwell was presented by his wife, Dr Elisabeth Maxwell, whose presence at the Symposium was greatly appreciated. In addition to the texts of the lectures, this volume also includes a selection of "Classic Papers" from earlier issues of the journal. Thus, this volume presents both a retrospective and a prospective view of the exciting and evolving field of spectroscopy, whose applications span so many areas of science, from the cosmos to global environment to detailed studies of life processes.

LIST OF PARTICIPANTS

Dr D. A. Bekoe
International Development
Research Centre
Nairobi, Kenya

Professor R. Bacis
Université Lyon I
Villeurbanne, France

Professor M. W. Blades
University of British Columbia
Vancouver, Canada

Professor P. W. J. M. Boumans
Philips Research Laboratories
Eindhoven, The Netherlands

Dr J. A. C. Broekaert
Institute for Spectrochemistry
Dortmund, F.R.G.

Dr S. Caroli
Instituto Superiore di Sanità
Rome, Italy

Professor J. A. Coxon
Dalhousie University
Nova Scotia, Canada

Father G. Coyne
Vatican Observatory
Vatican City State

Dr R. Dardozzi
Pontifical Academy of Sciences
Vatican City State

Dr L. de Galan
Unilever Research Laboratory
Vlaardingen, The Netherlands

Professor H. Falk
Central Institute for Optics and
Spectroscopy
Academy of Sciences
Berlin, G.D.R.

Dr V. A. Fassel
Iowa State University, U.S.A.

Professor R. W. Field
MIT
Cambridge, MA, U.S.A.

Dr J. E. Griffiths
Armstrong State College
Savannah, GA, U.S.A.

Professor H. H. Günthard
Physical Chemical Laboratory
Zurich, Switzerland

Professor G. M. Hieftje
Indiana University
Bloomington, IN, U.S.A.

Professor J. A. Holcombe
University of Texas at Austin
Austin, TX, U.S.A.

Professor G. Horlick
University of Alberta
Edmonton, Canada

Dr T. Kantor
Institute for General and
Analytical Chemistry
Technical University of
Budapest, Hungary

Professor G. Kenney-Wallace
University of Toronto
Canada

Professor S. F. A. Kettle
University of East Anglia
Norwich, U.K.

Professor S. R. Koirtyohann
University of Missouri-Columbia
Columbia, MO, U.S.A.

Professor K. Laqua
Dortmund, F.R.G.

Dr M. Margoshes
Technicon Inst. Corp.
Tarrytown, NY, U.S.A.

Professor G. B. Marini-Bettòlo
President, Pontifical Academy of
Sciences
Vatican City State

Father M. F. McCarthy SJ
Vatican Observatory
Vatican City State

Dr J. M. Mermet
Université Claude Bernard
Lyon I, Villeurbanne, France

Professor D. J. Millen
University College London
London, U.K.

Dr F. A. Miller
Pittsburgh, PA, U.S.A.

Dr N. Omenetto
Commission of the European
Communities
Joint Research Center
Ispra (Varese), Italy

Dr I. Roelandts
University of Liège
Liège, Belgium

Professor A. Scheeline
University of Illinois at
Urbana-Champaign
Urbana, IL, U.S.A.

Professor N. Sheppard
University of East Anglia
Norwich, U.K.

Dr W. Slavin
Perkin-Elmer Corporation
Norwalk, CT, U.S.A.

Professor J. Steinfeld
Massachusetts Institute of
Technology
Cambridge, MA, U.S.A.

Dr R. E. Sturgeon
National Research Council
Ottawa, Canada

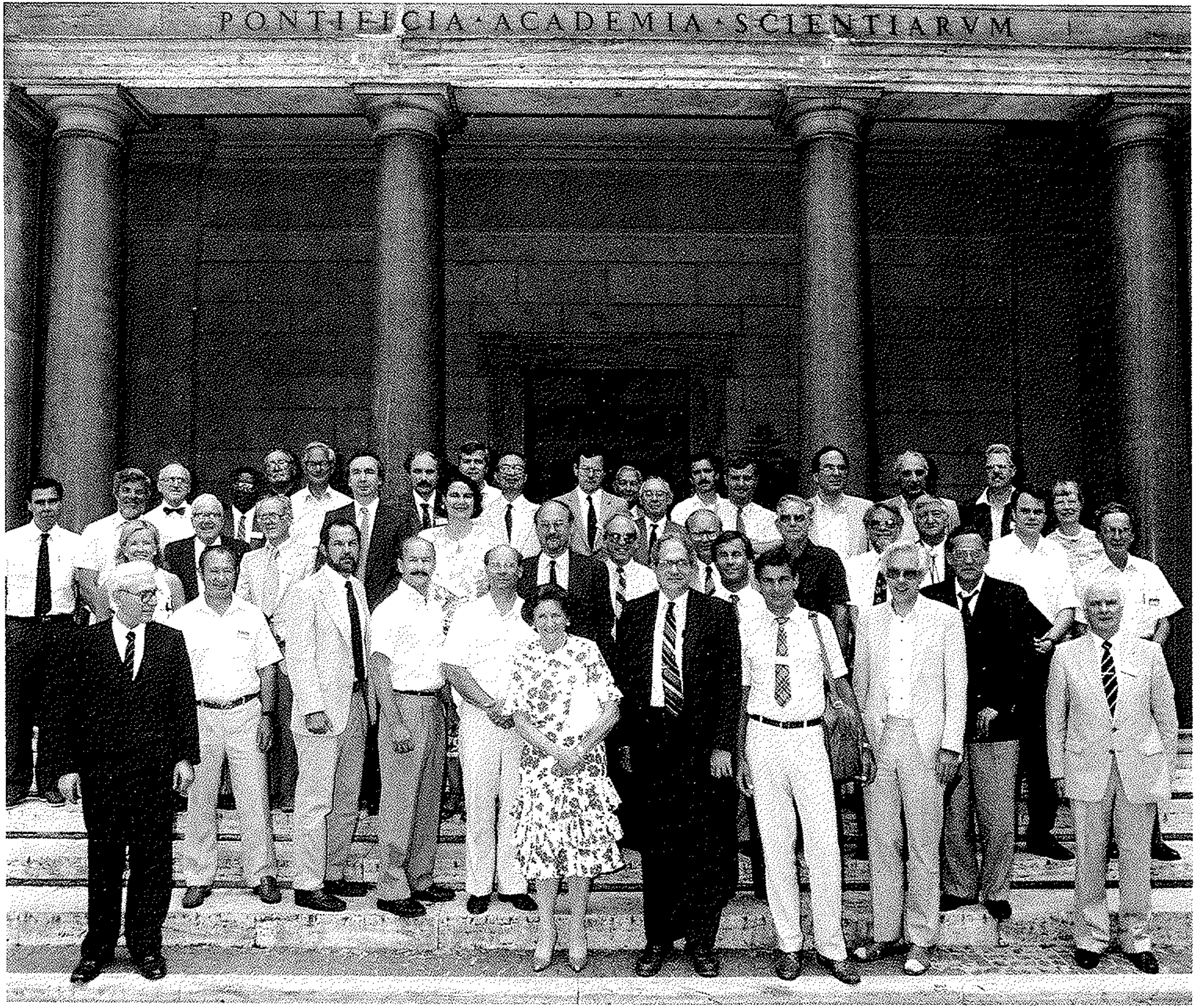
Dr R. L. Swofford
BP America Research and
Development
Cleveland, OH, U.S.A.

Professor S. C. Wallace
University of Toronto
Ontario, Canada

Dr M. K. Wilson
National Science Foundation
Washington, DC, U.S.A.

Professor J. D. Winefordner
University of Florida
Gainesville, FL, U.S.A.

Professor C. Zhang
Dalian Institute of Chemical
Physics, Dalian
People's Republic of China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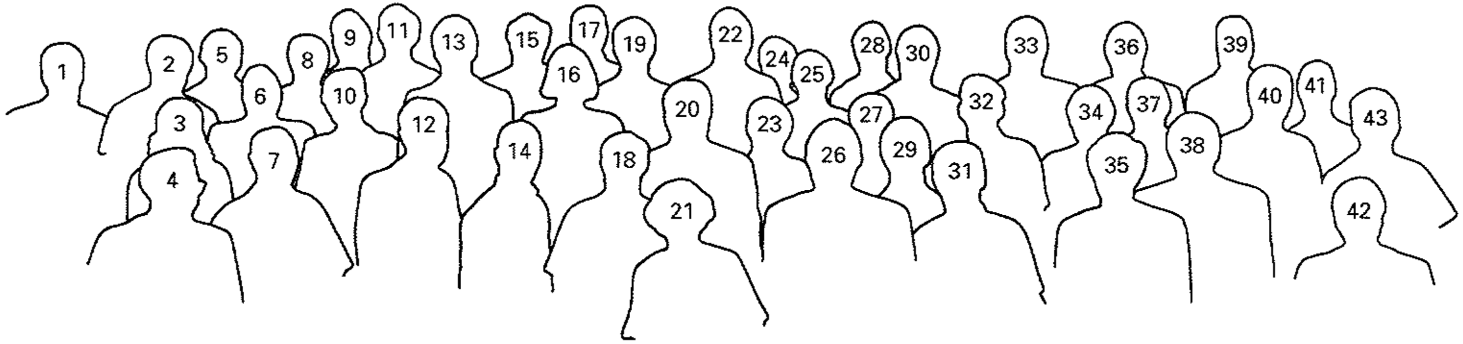

Key to photograph: (1) Dr S. Caroli, (2) Prof. S. F. A. Kettle, (3) Ms A. Moon, (4) Dr R. Dardozzi, (5) Dr M. Margoshes, (6) Dr F. A. Miller, (7) Dr T. Kantor, (8) Dr D. A. Bekoe, (9) Fr M. F. McCarthy, (10) Dr W. Slavin, (11) Prof. D. J. Millen, (12) Prof. J. A. Holcombe, (13) Prof. S. C. Wallace, (14) Prof. G. M. Hieftje, (15) Dr N. Omenetto, (16) Prof. G. Kenney-Wallace, (17) Dr R. L. Swofford, (18) Prof. G. Horlick, (19) Prof. Zhang Cunhao, (20) Dr P. S. H. Bolman, (21) Dr E. Maxwell, (22) Prof. J. A. C. Broekaert, (23) Prof. A. Scheeline, (24) Mr G. F. Richards, (25) Prof. N. Sheppard, (26) Prof. J. Steinfeld, (27) Prof. K. Laqua, (28) Prof. M. W. Blades, (29) Dr R. E. Sturgeon, (30) Dr J. M. Mermet, (31) Prof. H. Falk, (32) Prof. S. R. Koirtyohann, (33) Prof. R. W. Field, (34) Prof. J. D. Winefordner, (35) Dr L. de Galan, (36) Prof. R. Bacis, (37) Dr M. K. Wilson, (38) Dr J. E. Griffiths, (39) Dr I. Roelandts, (40) Prof. J. A. Coxon, (41) Ms D. Boumans-Postma, (42) Prof. P. W. J. M. Boumans, (43) Prof. V. A. Fassel.

MESSAGE FROM ROBERT MAXWELL ON THE 50TH ANNIVERSARY OF SPECTROCHIMICA ACTA

I AM VERY proud and pleased to send this message of greeting and celebration to all the Pergamon Editors and other distinguished scholars and guests involved in this historic Rome meeting.

The early history has now been documented by others; and the formidable role which this journal has come to play in modern spectroscopy at a global level is too well-known to everyone concerned to need any elaboration and superlative language from me.

Let me only say this. If Maxwell Communications (the parent company of the Maxwell Pergamon Macmillan publishing group) as we know it today as one of the top ten communication and information corporations operating at a global level can be seen as a mature oak forest, then *Spectrochimica Acta* was one of the first handful of acorns from which it grew and prospered. It was one of the first three journals published by Pergamon, whose more than 400 scientific, technical and medical publications remain a crucially important part of the world scientific communication system, which is so vital to the advancement of science.

In speaking of the early history of *Spectrochimica Acta* a special tribute is due to Pope PIUS XII, whose great personal interest in supporting international scientific collaboration was crucial at this time in providing a new publishing home for the journal after the traumatic disruption of the war. I learned the deepest respect for his interest in global science; and we at Maxwell Pergamon Macmillan continue to value enormously our relationship with the Pontifical Academy of Sciences, which we hope to widen still further in the years ahead.

Indeed, as we reflect on this long, enduring and fundamentally significant link between church and science, it is appropriate to recall that in the 50 years since *Spectrochimica Acta* was founded science has grown more powerful and more all-pervasive, while regrettably the influence of religion has diminished in many nations. Yet, the cooperation between men of God and men of science needs more than ever to continue.

In spite of—or perhaps as a direct result of—all the advances in the technology of higher living standards and the technology of mutual destruction, we as a global human community need to go back to the roots of any successful society, which lie in the ability, learned from childhood, to discriminate between right and wrong.

Unless the responsibility to teach that essential principle is fully accepted as the first duty of every family, then scientific progress will not be guided to the true betterment of mankind; and we need to remind ourselves, in this year in which we joyfully celebrate the bicentenary of the French Revolution and its historic Declaration of the Rights of Man, that rights logically imply duties and that the Duties of Man were never in more urgent need of being declared as loudly as his rights.

The late Professor Sir HAROLD THOMPSON, known to us all as Tommy, wrote some kind words about me on my 60th birthday, in which he recorded that in our early discussions some 40 years ago about scientific journals, "One thing was clear and dominant, namely his [my] foresight and recognition of the rapid expansion of science and technology, and the future needs of a proper communications system amongst scientists themselves, and for the general public. It would sometimes be of a new kind, and planned on a world scale". I vividly recall that my founding purpose in creating Pergamon was to provide a global communications system which would give opportunities for individual research workers to disseminate their results to fellow scientists throughout the world.

It needed no genius after the war to see that information would progressively become the most important product of all in the global economic system, because without it no problems, whether scientific, political or commercial, can be solved. It is this same simple idea which has inspired everything which Maxwell Communications has done and is doing to supply the world's most rapidly growing and perennial need and to build a successful world business on that basis.

The pleasure of it has lain in the fact that in this fundamental respect the imperatives of the business and the imperatives of service to science and our other professional, government and personal customers, have always pulled in the same direction. Greater still has been the pleasure and the inspiration of working over 40 years with the best brains and the finest characters to be found anywhere in the world.

I salute you all and regret only that I cannot be with you because the building of Maxwell Communications goes on as vigorously today as it did when Pergamon started out all those years ago.

ROBERT MAXWELL

WELCOMING ADDRESS

IT IS A GREAT pleasure to extend to you the welcome of the Pontifical Academy of Sciences here in the Casina of Pius IV, in the very heart of the Vatican Gardens and, I might say, under the shadow of the dome of Saint Peter's.

You represent here today, a very important branch of science, Spectrochemistry, which in the last century made possible great advances in practically every field of science. It has enabled us to penetrate into the phenomena which occur in the cosmos, as well as to establish the shape of extremely complex molecules and, at the atomic level, the properties and the behaviour of atoms in their excited state. In the last 50 years technology has made extraordinary progress in this field, and science has broadened the limits previously assigned to spectrochemistry.

The Editors of the fundamental scientific journal in this field, *Spectrochimica Acta*, with the sponsorship of the Publisher, Pergamon Press, have asked the Pontifical Academy of Sciences to allow them to organize a meeting here to examine "Future Trends in Spectroscopy" on the occasion of the 50th anniversary of the founding of this journal, which took place here in this Academy in 1939.

The initiative was due to two eminent Academicians, Fathers ALOYSIUS GATTERER and JOSEPH JUNKES, in collaboration with Father SALPETER, all of whom were working at the time at the Specola Vaticana in Castel Gandolfo, in the Laboratory of Astrophysics. Their main work, which may be considered as constituting a fundamental contribution to spectrochemistry, is the *Atlas of the Spectra of the Elements*, which was published after many years of enormous experimental work. The aim of this work was to make possible the analysis of the extraordinary collection of meteorites at the Specola.

I am old enough to have met Father GATTERER and Father JUNKES at Castel Gandolfo and in the Academy during those years. I also followed their interesting work indirectly through the information of my colleague GIULIO MILAZZO who, like me, was an Assistant at the University of Rome, and who very often went to Castel Gandolfo to work with the Fathers, using the most advanced spectrometer then available in Italy, collaborating in their work and co-authoring that part of the *Atlas* related to the Schumann vacuum–u.v. bands.

The *Atlas* was a great work. It was an incredible piece of luck that at the moment when the Astrophysical Laboratory was closed at Castel Gandolfo, all the chemical material used for the *Atlas* during those years, and especially the exceptional collection of rare earths, the lanthanides, came into my hands. Today they are here in the Academy as a constant reminder of the work done by the Fathers GATTERER, JUNKES and SALPETER.

The involvement of the Specola, and indirectly of the Academy, in spectrochemistry, and the need to publish research results in a rather specialized scientific journal, resulted in the initiative of Fathers GATTERER and JUNKES to establish such a journal of spectrochemistry. Thus was born *Spectrochimica Acta*, an international journal printed, at first, by Springer Verlag, whose pages were open to all the world's scholars in the field.

At the time of the journal's founding, the Academy had focused its interest on Cosmology and Astronomy, and the President, Father GEMELLI, had announced a meeting on "The problem of the age of the universe" to be held on 3 December 1939. Eminent astronomers had said they would attend it, but the war began in September, and the meeting was delayed for 10 years. However, the new-born journal went on, albeit with difficulty. Later, Pergamon Press took over the responsibility of publishing the journal, for which we are most grateful.

I should like to recall here that there is a long tradition of interest in spectroscopy at the Pontifical Academy. The first scientist and astronomer to use spectrochemistry for the classification of stars was Father ANGELO SECCHI who, in the last century, was Director of the Observatory, then located in the Collegio Romano, and also President of this Academy which was known then as Accademia dei Nuovi Lincei. The Academy honoured him on 11 July 1978 by celebrating the centenary of his death with an International Colloquium on Stellar Spectroscopy, held here in the Vatican. The commemorative address was pronounced by Pontifical Academician HERMANN BRÜCK.

It is my hope that also this present meeting, inspired by tradition, but looking to the future, may constitute another substantial advance toward the knowledge of truth and the progress of science.

Professor GIOVANNI BATTISTA MARINI-BETTÒLO
President
Pontifical Academy of Sciences

INTRODUCTORY REMARKS AT THE SYMPOSIUM, "FUTURE TRENDS IN SPECTROSCOPY"

MR PRESIDENT, Distinguished members of the Pontifical Academy and Vatican Observatory, Colleagues and Friends—

It is a great privilege for us to meet in these beautiful and historical surroundings to commemorate the 50th anniversary of publication of *Spectrochimica Acta*. Our profound thanks go to Professor G. B. MARINI-BETTÒLO, Ingegnere DON RENATO DARDOZZI, and the personnel of the Pontifical Academy of Sciences and the Vatican Observatory for permitting this meeting to take place, and for their more than generous assistance with the arrangements. We are grateful for the participation of members of the Pontifical Academy, particularly Dr DANIEL ADZEI BEKOE, who has joined us from Nairobi, and Professor GERHARD HERZBERG of the National Research Council of Canada; although unfortunately not able to be here in person, Professor HERZBERG has graciously contributed a paper on "Molecular Astrophysics" which appears in these Proceedings, and indeed was instrumental in initiating the contacts with the Pontifical Academy and Vatican Observatory which have led to our being here today. We appreciate the generosity of Pergamon Press and Maxwell Communications Corporation in underwriting this event, and we are indebted to the Pergamon representatives, Dr PIETER BOLMAN and Ms ANNA MOON, for organizing the logistics of the meeting, an effort in which they were ably assisted by Dr SERGIO CAROLI of the Istituto Superiore di Sanita in Rome.

As this Symposium begins, let us pause for a moment to remember our associates and colleagues who cannot be with us at this time. Among the losses we have experienced during the past several months, we note especially Professor RICHARD C. LORD [1] of M.I.T., Professor GEORGE PIMENTEL of the University of California at Berkeley, and Professor C. TH. J. ALKEMADE [2], late of the State University of Utrecht, The Netherlands. All of these individuals served with distinction on the Editorial Advisory Boards of *Spectrochimica Acta*. We especially miss the participation of MICHAEL J. CHURCH, late Editorial Director of Pergamon Press, whose initial enthusiasm for the Symposium contributed in an important way to its success, and whose untimely and sudden death at the end of 1988 shocked and saddened us all.

Our meetings at Casino Pio IV, the home of the Pontifical Academy of Sciences [3], address several objectives. By no means least, we are actually fulfilling a biblical injunction, for in the 25th Chapter of Leviticus we find written,

> "And ye shall hallow the fiftieth year . . . it shall be a jubilee unto you . . . ye shall return every man unto his possession, and ye shall return every man unto his family."

In returning to the place where *Spectrochimica Acta* had its origins, we seek not only to look back over the development of spectroscopy during these last 50 tumultuous years, but also to look forward, in an attempt to assess the likely developments in our field which will be represented in the pages of the journal during the coming years. While most of the distinguished invited speakers at the Symposium have commented on the difficulty of making such projections, it is nevertheless extremely useful to consider at least the near-term future of spectroscopy in the light of recent advances. In addition, there is also a sub-text we have to consider, a counterpoint to the theme of spectroscopic research and applications. This deals with the questions of distribution and dissemination of scientific information in an era when the technology of communication is undergoing rapid change. Masses of data can now be archived, retrieved, and transmitted using electronic network mail and databases, and indeed the organization of this very meeting would have been nearly impossible without extensive use of Telex and Facsimile transmissions! The challenges posed by this new technology to traditional methods of publication, and to control of the quality and reliability of the information so transmitted, are addressed in the paper by Professor BOUMANS in these Proceedings.

J. I. STEINFELD
Massachusetts Institute of Technology
Cambridge MA 02139, U.S.A.

REFERENCES

[1] Professor LORD's career has been reviewed in a special issue of *Spectrochimica Acta A*, "Topics in Molecular Spectroscopy" Vol. 42A, Nos 2/3 (edited by J. R. DURIG) (1986).

[2] Professor ALKEMADE's career has been reviewed in a special issue of *Spectrochimica Acta B*, "Physics and Spectroscopy: a Flaming Interaction" Vol. 43B, Nos 9–11 (edited by P. BOUMANS, W. SLAVIN and T. HOLLANDER) (1988).

[3] G. B. MARINI-BETTÒLO, *Historical Aspects of the Pontifical Academy of Sciences*, Pontif. Acad. Sci. Documenta No. 21 (1986).

IN MEMORY OF PROFESSOR GEORGE C. PIMENTEL

THE 50TH Anniversary Conference in the Vatican occurred shortly after the announcement of the death of Professor GEORGE C. PIMENTEL of the University of California at Berkeley at the sadly early age of 67. He was arguably the most eminent infrared spectroscopist of his generation and was very highly regarded for no less than four seminal contributions to infrared spectroscopy:

(i) his development and use of the matrix-isolation technique for studying the infrared spectra and structures of metastable, highly-reactive species such as free radicals;
(ii) his first successful detection of the infrared spectrum of a polyatomic free radical in the gas-phase using a specially designed fast-scanning spectrometer;
(iii) his first successful development of a chemical laser; and
(iv) his construction of a very compact and efficient interference-filter infrared spectrometer for successful deployment in a space probe sent to Mars to study the chemical composition of that planet's atmosphere and pole caps.

In the course of his spectroscopic research career, GEORGE PIMENTEL trained, stimulated and gained the warm affection of very many PhD students and postdoctoral colleagues. He inspired many of these to take up distinguished academic careers of their own. Although spectroscopy was his chosen and enthusiastically pursued field of research, GEORGE PIMENTEL's name was also very widely known to a wider community of chemists. He made outstanding contributions to the teaching of high-school chemistry in the U.S.A. and elsewhere through his work for the very influential CHEMSTUDY programme of the early 1960s. He was also the principal author of the widely-acclaimed report on "Opportunites in Chemistry"—universally known as the Pimentel Report—carried out for the U.S. National Academy of Science. In this he very effectively put the case, to scientific administrators and political figures, for the importance to the world community of chemistry and its vigorous future development. A second version of that report "Opportunities in Chemistry; Today and Tomorrow", co-authored with one of his daughters, may in the long run, be even more influential in persuading members of the next generation that chemistry is a very useful and a fascinating subject to take up as a career.

On being congratulated by a colleague on the award to him, in 1988, of the American Chemical Society's most distinguished honour, the Priestley Medal, GEORGE PIMENTEL's response was "Isn't it wonderful!" It was a response characteristic of the man, for it was equally that sense of wonder at techniques that could be developed, and at the secrets of Nature that they could reveal, that inspired both his highly original researches and his major influence in persuading so many to take up future careers in chemistry. He was a superb spectroscopist and a very fine man.

NORMAN SHEPPARD
School of Chemical Sciences
University of East Anglia

PART I
SYMPOSIUM PROCEEDINGS

THE 50TH ANNIVERSARY OF PUBLICATION OF SPECTROCHIMICA ACTA

A Historical Perspective by the Editors of Spectrochimica Acta:

PROFESSOR DR P. W. J. M. BOUMANS
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

PROFESSOR S. F. A. KETTLE
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

DR WALTER SLAVIN
Perkin–Elmer Corporation, Norwalk, CT 06859, U.S.A.

PROFESSOR JEFFREY STEINFELD
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

THE EARLY history of *Spectrochimica Acta* is intimately connected to two forces which have exerted considerable influence in contemporary Europe (albeit operating in quite different realms!): on the one hand, the Roman Catholic Church, specifically the Vatican Observatory and the Vatican Press, and on the other ROBERT MAXWELL and Pergamon Press. The interaction of these forces with each other and with the spectroscopic community presents a fascinating story, aspects of which are still not wholly clear.

As a result of numerous developments in spectroscopic instrumentation and applications during the 1930s, the need arose for a new research journal devoted to the theory, methods and results of investigations on the application of spectroscopy to chemical problems. This journal, known as "*Spectrochimica Acta*", was founded by Father ALOIS GATTERER, the Vatican astronomer, in 1939. The first issue of the new journal, which included papers received through 24 May 1939, was published by Springer Verlag in Berlin. Volume 1 consisted of six issues, the last dated 9 May 1941, with a total of 599 pages. The original Editors, in addition to Father GATTERER, included R. BRECKPOT (Louvain), W. GERLACH and G. SCHIEBE (Munich), and F. TWYMAN (London). The Editors were assisted by an Editorial Board, among whom was GEORGE R. HARRISON, then Director of the M.I.T. Spectroscopy Laboratory. The journal was polyglot from the outset, with the first volume containing papers in German (70% of the total), English, French and Italian. The first paper [1] dealt with spectral analysis of aluminum, and indeed the initial emphasis of the journal was on the use of atomic spectroscopy for elemental analyses. Also from the beginning, the journal included supplementary information of interest to spectroscopists, such as book reviews [2] and abstracts of articles appearing in other journals. The first erratum appeared in issue Number 4 [3], and the first advertisements in issue Number 6; Zeiss–Jena was, not surprisingly, one of the first advertisers.

The second volume of *Spectrochimica Acta*, containing a total of 441 pages, was published by Springer Verlag between 1941 and 1944 under, to say the least, adverse conditions. Nearly all the papers were in German, with a few in Italian or Spanish. The circumstances attending the re-appearance of the journal following the 1939–1945 war are unusual, and perhaps unique in the history of scientific publishing. Volume 3 began appearing in 1947, under the imprint of Specola Vaticana, printed by Tipografia Poliglotta Vaticana—in other words—the Vatican Observatory and Press. Many of the original Editorial Board, including Father GATTERER, remained on the masthead, and the sub-headings were now in Latin; for example, contributed articles were "Commentationes". The circumstances leading to this change were explained in a Foreword to Volume 3 [4], in English, French and German, and we quote from the former:

> "The tragical developments of the second World War involved the interruption in publication of the newly founded journal, *Spectrochimica Acta*, during 1944. At this time, volume two of the journal was just completed."
>
> "Numerous efforts were made to bring the journal back to life again. The hindrances were, however, too numerous and the difficulties too large, so that these efforts were temporarily unsuccessful. Frequent and urgent appeals continued to come in from spectrochemists of the entire world, inquiring into the possibility of continuing publication, in some form or another, of the international journal, *Spectrochimica Acta*."
>
> "In view of these widespread inquiries the undersigned editor [Father A. GATTERER] decided to present Pope PIUS XII with a plan to have the journal published by the Vatican Observatory, in agreement with the Springer Publishing Company."
>
> "The Pope, who takes great personal interest in sponsoring scientific cooperation between all nations, agreed heartily to this proposal. The agreement with the Springer Publishing Company was promptly reached, and the Vatican Press—Tipografia Poliglotta Vaticana—expressed their readiness to undertake the printing and distribution of the journal."

As if to make up for lost time, the "Vatican Volume" rebounded to nearly 700 pages. The journal included summaries of spectroscopic work which had been carried out in Great Britain [5], Belgium [6], France [7] and the U.S.S.R. [8] during the war years, when publication had been difficult or impossible. Also appearing in Volume 3 was the first conference report published in *Spectrochimica Acta:* this consisted of the abstracts of an American Chemical Society Symposium on "Color and Electronic Structure of Complex Molecules", held in Evanston, Illinois, in December 1946. Since the symposium participants included R. S. MULLIKEN, K. F. HERZFELD, W. PRICE and M. KASHA, among others, it must have been a memorable event!

Commercial publishing interests enter the picture with Volume 4 (1950). Butterworth–Springer Ltd was formed in April, 1949, with the purpose of maintaining the Springer Verlag tradition of publishing high-quality technical books and journals. Dr PAUL ROSBAUD, who was to play an important rôle in the journal's development, was instrumental in setting up this activity. Within 2 years, however, Butterworth's interest was bought out by ROBERT MAXWELL and restructured as Pergamon Press [9, 10]. Dr ROSBAUD moved from Butterworth–Springer to Pergamon as Scientific Manager. The first three journals published by Pergamon were:

Spectrochimica Acta
Journal of Atmospheric and Terrestrial Physics
Geochimica and Cosmochimica Acta.

The transfer from Butterworths to Pergamon evidently took place midway during the publication of Volume 4. Numbers 1, 2 and 3 of that volume appeared under the imprint of Butterworth–Springer, 4, 5, and 6 Bell Yard, London WC2; as of issue Number 5, the publisher is given as Pergamon Press Ltd, 2, 3, and 5 Studio Place, London SW1. Due to inconsistencies in binding procedures among various libraries, some copies shows Butterworths as the publisher of Volume 4, while others indicate Pergamon.

Despite the transmutation of the publisher, the Editorial Board and scope remained unchanged from the previous volume published by the Vatican, even to the Latin subtitle, "Commentarium Scientificum Internationale Tractans de Re Spectrochimica". In a brief Foreword [11] the Editors express

> "their deep and sincere gratitude to His Holiness Pope PIUS XII for his generous assistance in reviving this Journal at the end of the War"

and indicate their readiness to get on with the job of publishing the journal. A full menu of articles, abstracts, book reviews (including a review of CHARLOTTE MOORE'S Atomic Tables) and meeting reports brought Volume 4 to 545 pages.

Volume 5 brought further changes. VELMER FASSEL joined the Editorial Board in 1952, eventually becoming "Editor-in-Chief" (in fact, if not in name) in 1956. Sir

HAROLD THOMPSON, who was to influence the journal for the next 30 years, was brought into the Editorial Board shortly thereafter [12]. On a somber note, Father A. GATTERER, the Founding Editor of the journal, passed away in February 1953 [13]. Beginning a long tradition, papers from the Second Colloquium Spectroscopicum Internationale (Venice, 1951) appear in Numbers 1 and 2 of Volume 5. Papers from the Third CSI [High Leigh, Herts, U.K. (1952)] were published in Volume 6, along with abstracts from the 1954 "Pittsburgh" Conference, which actually met in Pittsburgh at that time! Meanwhile, the mastheads reveal Pergamon floating between 4 & 5 Fitzroy Square, London W1; 242 Marylebone Road, London NW1; and the Studio Place address.

FOIL MILLER was added as a Co-editor beginning with Volume 6 (1953). During the ensuing years he and VELMER FASSEL, along with PAUL ROSBAUD [14] and PATRICIA WAKELING in Pergamon's U.S. office, devoted a great deal of effort to trying to improve the journal by attracting better papers, speeding the review process, and superseding irregular publication with a regular monthly schedule. The latter was accomplished with Volume 16 (1960). Both FASSEL and MILLER wanted to publish some of their own work in the journal and, to maintain high standards and objectivity, they agreed to submit their papers to each other, with the further stipulation that the papers would receive exceptionally rigorous scrutiny. A consequence was that each rejected a manuscript by the other! Both papers were eventually published, however, after major revision [15].

Partly as a result of the efforts of FASSEL, MILLER and others during the early and mid-1950's, major changes to *Spectrochimica Acta* took place in 1957. These are explained in an Editors' Note appearing at the beginning of Volume 9 [16]:

> "The changing emphasis in spectroscopy over the past ten years, caused especially by the vast increase in measurements on molecular spectra of many kinds, has made it desirable to reorganize the operation of this journal. Originally it was mainly directed to problems of atomic emission spectroscopy and spectrographic analysis, and it is not intended that the importance of this aspect shall now be diminished. However, the impact upon chemistry, whether organic or physical, of molecular spectroscopy—emission or absorption, ultra-violet, infra-red, or Raman—has been so great that many of their applications are now routine both for analysis and for work on molecular structure. They are equally significant in research, whether it be pure or applied.
>
> It is therefore proposed to widen the scope of this international journal so as to cater for all the above lines of work. Also, it is hoped to include up-to-date reports on spectroscopic meetings held in different countries, general information of interest to spectroscopists internationally, reports of commissions, and other features. The Editorial Board has been reconstituted so as to include recognized authorities on most aspects of the field, and its members will be replaced from time to time after a period of office. It is hoped that the journal will provide a rapid means of publication of spectrographic data of many kinds."

In the reconstitution referred to above, a number of now-familiar names make their appearance on the Editorial Board, including the late R.C. LORD (M.I.T.), G. PORTER (Sheffield), N. SHEPPARD (Cambridge) and M. K. WILSON (Tufts). The close personal relationship which developed between Publisher and Editor is revealed by surviving fragments of their correspondence [17], such as:

> "I have been most impressed by the remarkable increase in the number of molecular papers for submission to *Spectrochimica Acta*. You will also be pleased to know that the number of subscriptions. . . has gone up by 200 and the number continues to rise. The fact that the Journal is in this splendid state is undoubtedly due to your hard work on its behalf" [18].

This relationship was not always without friction, to wit:

> "I so enjoyed our meeting and frank discussion in your rooms at St John's. On reflection I am quite certain that both our points of view are right. . . . I look forward to ever improving relations and am, etc." [19].

Spectrochimica Acta flourished under the stewardship of Professors THOMPSON, FASSEL and MILLER. A large number of important publications in atomic and molecular spectroscopy appeared in its pages, as well as reports on leading spectroscopy conferences. Volume 11 in its entirety consisted of papers presented at the 6th Colloquium

Spectroscopicum Internationale (Amsterdam, 1956), and abstracts of the "Columbus" [20] and "Pittsburgh" meetings appeared regularly. The journal's success gave rise to imitators, which were not looked upon kindly by the Publisher [21]. Another important change occured in 1960: with Volume 16, the Publishers' address changed from Fitzroy Square, London, to Headington Hill Hall, Oxford, where they have prospered, with few exceptions [9], ever since.

FOIL MILLER retired from the Editorship in 1963 [22], with M. KENT WILSON assuming the U.S. Editorship effective with Volume 20. Professor MILLER was presented with a gold medal at the conclusion of his tour of duty, which elicited the following comment [23]:

> "I was mightily pleased with the handsome gold medal which you ordered to be struck in appreciation of my services to *Spectrochimica Acta* . . . Many people have seen and admired the medal . . . A typical comment was that of Professor Bryce Crawford, 'Captain Maxwell knows how to do things with the right touch!'"

By Volume 22 (1966), the journal was publishing over 2000 pages anually. Most of the papers were now in English, although contributions in French and German continued to appear. This led to certain pressures, as a "Notice to Authors" [24] makes clear:

> ". . . It will no longer be possible to print excessive and elaborate mathematical detail such as that sometimes involved in normal coordinate analysis . . . Authors writing in English, but whose native language is not English, must themselves ensure that the text is satisfactory, since the Editors can no longer undertake to rewrite the paper."

These problems are not entirely unfamiliar, 25 years later!

By the mid-1960s, the pressure to split the journal into two separate sections became irresistible. In addition to the large volume of papers being published, many European atomic spectroscopists had felt for some time that *Spectrochimica Acta* had in some sense "abandoned its roots" in analytical atomic spectroscopy. Accordingly, the journal was divided into Part A (Molecular Spectroscopy) and a new Part B, covering the atomic analytical subjects. The Editors of Volume 23A (which ran to over 3000 pages!) were H. W. THOMPSON and M. K. WILSON, and M. MARGOSHES and K. LAQUA were named Editors of Part B [25]. Since that time, the two parts of the journal have proceeded along independent lines, with separate Editors and Editorial Advisory Boards. However, the Editors of each part are now listed as "liaison members" of the others' boards, and planning for this Golden Jubilee issue has led to even closer interaction among the Editors.

We now proceed rapidly to the present. After a meeting [26] between R. MAXWELL, Sir H. W. THOMPSON and Professor J. I. STEINFELD, the latter succeeded to the U.S. Editorship in October, 1983 [27]. It was a considerable shock to all concerned when Sir HAROLD THOMPSON passed away suddenly at the end of 1983 [28]. Volume 41A Numbers 1 and 2 (January, 1985) appeared as a memorial issue to Tommy, as he was widely and affectionately known in the spectroscopic community. Tommy's contributions to *Spectrochimica Acta* were further recognized by ROBERT MAXWELL in the form of the Sir HAROLD THOMPSON Memorial Award [29]. This award, consisting of a cash prize and a presentation wine decanter, is made each year to the authors of the paper published in *Spectrochimica Acta,* Part A which, in the judgment of the Editorial Board, represents the most significant contribution to spectroscopy reported in the journal during the preceding year. The recipients to date of this award have been:

D. H. WHIFFEN, for "Spectroscopic constants evaluated by the numerical contact transformation" [30];

I. MILLS, for "C–H local modes in cyclobutene: FTIR studies, 700–9000 cm^{-1}" [31];

D. J. GARDINER, for "The use of Raman intensity measurements to monitor pressure and temperature induced changes in conformational equilibria" [32];

D. MCKEAN, for "Vibrational anharmonicity and Fermi resonances in CHF_2Cl" and related papers [33].

A similar award, known as the "Pergamon/Spectrochimica Acta Atomic Spectroscopy Award", was established by *Spectrochimica Acta*, Part B in 1987 [34]. The first authors who received the award [35] were T. HASEGAWA and J. D. WINEFORDNER for a series of three articles:

"Spatially resolved rotational and vibrational temperatures of a neutral nitrogen molecule in the ICP" [36];

"Rotational, vibrational and electronic excitation of a neutral nitrogen molecule in the ICP [37]; and

"Spatial distribution of atomic and molecular species in the inductively coupled plasma" [38].

The European Co-editorship of *Spectrochimica Acta*, Part A was accepted by Professor SIDNEY KETTLE later in 1984 [39]. During the interim, MICHAEL J. CHURCH, late Editorial Director at Pergamon Press, stepped in as virtual Co-editor of *Spectrochimica Acta*. In this, and innumerable other ways, MIKE CHURCH was an invaluable member of the Pergamon family, and his sudden and untimely death late in 1988 shocked and saddened us all.

Changes were also taking place at *Spectrochimica Acta*, Part B. Professor LAQUA was replaced by P. W. J. M. BOUMANS effective with Volume 27B (1972), and M. MARGOSHES by V. G. MOSSOTTI the following year. After a few lean years in the mid-1970s, *Spectrochimica Acta*, Part B was extensively reorganized when PAUL BOUMANS was appointed as Editor-in-Chief, effective from July 1979. This position gave him the opportunity to consolidate his previously initiated "face-lifting" campaign, including a reorganization of the Editorial team and the Editorial Advisory Board [40], and the establishment of a "hot" communication line between the Editor's offices and all branches of the Publishers'. This line has remained "hot" to the present day, with "critically damped sparks" flowing in both directions across the English Channel at regular intervals. In 1980, the North American Editorship passed to HORLICK [40] and, since 1983, it has been safely entrusted to WALTER SLAVIN [41]. To facilitate communication with the Chinese spectroscopy community, ZHANXIA ZHANG was nominated as Assistant Editor in 1987 [34]. H. W. WERNER and H. OECHSNER have become Editors for surface and in-depth analysis [40(b), 42], but the attempt to bridge the gap between the "classical" spectroscopy community and those involved in the characterization of surfaces, interfaces and thin films has so far met with substantial resistance.

The flow of manuscripts rapidly increased once the atomic spectroscopy community became aware of the changes taking place in *Spectrochimica Acta*, Part B. Since 1983 the annual volume size has been intentionally kept at 1500–1700 pages, which is considered optimum for maintaining the standards of the journal. From the early 1980s onwards, *Spectrochimica Acta*, Part B has been generally recognized as the premier journal for analytical atomic spectroscopy. Its emphasis lies on the fundamental aspects of the field, without neglecting, however, the practical and instrumental sides. An "Instrument Column", authored by Assistant Editor J. A. C. BROEKAERT, has been a common feature since 1981 [43], while the present Golden Jubilee year sees the start of three new columns: "News on Reference Materials", "News on Fundamental Reference Data for Analytical Atomic Spectroscopy" and "News on Standard Procedures and Normalization", edited by I. ROELANDTS, A. SCHEELINE and S. KAEGLER, respectively. *Spectrochimica Acta*, Part B continuously widens its scope and its readers' horizons by not only passively publishing articles on new topics as received, but also actively pursuing entries into new fields. One such field is laser spectroscopy, which, since 1987, has been the focus of a new column, "Topics in Laser Spectroscopy", with K. NEIMAX as Guest Editor [44]. Most recently, *Spectrochimica Acta*, Part B has seen the publication of a special issue on "Total Reflection X-ray Fluorescence Spectrometry", guest-edited by R. KLOCKENKAMPER.

The introduction of such new features, in both Parts A and B of *Spectrochimica Acta*, as well as publication of special issues dedicated to eminent spectroscopists (KAISER, Walsh, L'vov, Laqua, Fassel, Alkemade; Thompson, Sheppard, Lord), devoted to particular conferences, or to research in a particular region or laboratory [45], testify that *Spectrochimica Acta* maintains its enviable position, not as an "eminence grise", but as a journal with the drive and energy of eternal youth, looking at the past with satisfaction, but primarily directed toward the future. This is also reflected in the Editorial Advisory Boards; since 1983, numerous changes have been made in the make-up of these boards, with J. Winefordner chairing the Board for Part B. The journal's aspiration to eternal youth is thus reflected in its Editorial Boards, which regularly see the departure of those whose term of office have expired, and welcome new members: spectroscopists who are willing to accept the challenge which the duties of nomination place upon their shoulders!

Both individuals and institutions have the desire to return to their roots. In the case of *Spectrochemica Acta*, we are privileged to be able to do so, not only by means of this historical survey, but also by the 50th Anniversary Symposium on "Future Trends in Spectroscopy", which we have been permitted to hold in the Vatican, under the auspices of the Pontifical Academy of Sciences. The Proceedings of this symposium, in the form of papers contributed by the invited speakers and the Editors' summaries of the ensuing discussions, are included in this special issue sent to all subscribers of *Spectrochimica Acta*, Parts A and B. Also included in this issue are reprints of selected "classic" papers from past issues of the journal, which in the Editors' opinion have had a significant impact on the practice of spectroscopy. We look forward to publication of more "classics" in the coming decades of the journal.

Acknowledgements—We thank the "referees" of this article for their valuable insights and comments, particularly F. J. Miller, V. Fassel, M. K. Wilson and M. Church. We are deeply grateful to the Pontifical Academy of Sciences for permitting us to hold the 50th Anniversary Symposium in the rooms of the Academy at the Vatican. Particular thanks are due to Professor G. Herzberg for providing the contact with the Academy, His Excellency R. Dardozzi, Director of the Chancellery of the Pontifical Academy of Sciences, and Dr S. Caroli of the Istituto Superiore di Sanita (Rome), for facilitating the arrangements. Finally, we express our gratitude to Robert Maxwell, Chairman of Maxwell Communications Corporation and Pergamon Press, without whose vision and energy none of the events described in this account would have come to pass!

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[15] Letter from V. Fassel to E. Maxwell, 24 October 1988.
[16] *Spectrochim. Acta* **9**, 1 (1957).
[17] S. F. A. Kettle, in Ref. 9, pp. 490–492.
[18] Letter from R. Maxwell to H. W. Thompson, 3 July 1957.
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[20] *Spectrochim. Acta* **16**, 1245 (1960); *ibid.* **18**, 1397 (1962).
[21] "I was interested to read about Academic Press planning another journal on Spectroscopy which might be a definite competitor for *Spectrochimica Acta*, and I trust that Foil, Velmer, and you will use your good

offices to prevent this unnecessary duplication." (Letter from R. Maxwell to H. W. Thompson, 27 January 1960). On the other hand, Maxwell did not hesitate to inaugurate two new journals, later named "*Infrared Physics*" and "*The Journal of Quantitative Spectroscopy and Radiative Transfer*", without forewarning the editors of *Spectrochimica Acta*. The latter initially viewed them as competition for their journal, and a great deal of heated correspondence ensued until the titles and subject areas were carefully defined.

[22] *Spectrochim. Acta* **19**, 2137 (1963).

[23] Letter from F. Miller to R. Maxwell, 4 September 1964.

[24] *Spectrochim. Acta* **19**, 2137 (1963).

[25] *Spectrochimica Acta A* appeared in regular annual volumes thereafter, but Volume 24B did not appear until 1969. This accounts for the numbering mismatch between Parts A and B, which persists to this day.

[26] "I very much look forward to meeting with you on July 4 . . . July 4 is not a public holiday in England." (Letter of R. Maxwell to J. I. Steinfeld, 26 May 1983, after the latter had expressed concern about the meeting date).

[27] *Spectrochim. Acta* **39A**, No. 10, i (1983).

[28] *Spectrochim. Acta* **40A**, No. 2, i (1984).

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[30] Volume **41A**, p. 1 (1985).

[31] Volume **42A**, p. 21 (1987).

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The dissemination of the results of scientific research in the era of electronic media

P.W.J.M. BOUMANS

Philips Research Laboratories, P.O. Box 80.000,
5600 JA Eindhoven, The Netherlands

Abstract—This paper is the extended text of a lecture presented during an "on-invitation" symposium: *"Future Trends in Spectroscopy"*, organized on the occasion of the 50th Anniversary of the founding of *Spectrochimica Acta.* This symposium was held under the auspices of the *Pontificia Academia Scientiarum* in the Casina Pio Quattro in Vatican City.

The lecture considers the future of scientific publishing primarily from the point of view of the *actual* behaviour of authors, editors, reviewers, publishers, and readers. In this scope the author discusses (a) aims and format of scientific publications, (b) new approaches to conventional scientific publishing, *i.e.*, in "hardcopy journal format", (c) the implications of desktop publishing (DTP) and camera-ready copy (CRC) for author, editor, reviewer, and publisher, and (d) the truly electronic publication, *i.e.*, a publication on an electronic medium, such as a diskette, which does not only contain text and graphics, but also executable programs, source codes, data files, and parameter sets. The paper includes a tutorial discussion of issues such as word processors, scientific word processors, DTP, WYSIWYG (What You See Is What You Get) *versus* ML (Markup Language), procedural markup *versus* descriptive markup, text *versus* graphics, and standard generalized markup language (SGML).

As to conventional scientific publishing the author concludes that the "DTP-CRC approach" is *not* a viable alternative. The most promising appears an approach in which the author produces the "author's primary electronic manuscript" (APEM) in ASCII format with graphics in a format such as Computer Graphics Metafile (CGM) *without* procedural markup but *with* a minimum of descriptive markup, for example, in SGML codes. The "APEM-SGML approach" is considered (i) to provide for a balanced distribution of tasks among authors, editors, reviewers, and publishers, (ii) to eliminate the necessity of rekeying documents, and (iii) to give publishers additional "handles" to exploit the information via on-line and CD-ROM databases. This appears to be the solution that will make every shoecobbler stick to his last and thus feel entirely comfortable.

As to the truly electronic publication, the author feels that there must be excellent perspectives for an electronic spectroscopy journal and proposes to investigate the viability of a journal *Spectrochimica Acta Electronica* (SAE), as a supplement of Parts A and B.

1. INTRODUCTION

THIS SYMPOSIUM on *"Future Trends in Spectroscopy"* has been organized to celebrate the Golden Jubilee of *Spectrochimica Acta,* one of the leading journals for the dissemination of results of scientific research. It is not surprising therefore that the program includes a lecture dealing specifically with the communication of results of research. We are all concerned with this topic, and it is stringent therefore that we carefully reflect on the possibilities offered by new media and take up a position. If we would look back at fifty years of *Spectrochimica Acta* and limit ourselves to the mere publishing aspects, we would establish that hardly anything essential has changed in the past fifty years, except perhaps for the replacement of lead by laser. It is unlikely that this steady state will be maintained in the next fifty years, or even in the next five years.

Computers have drastically modified the way in which we perform our research and the personal computer (PC) is also rapidly invading our offices and exerting an increasing influence not only on the way in which we *obtain* research results but also on the way in

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which we *report* these results. It is the latter aspect, scientific publishing, which forms the major issue of this lecture.

I have reflected about this issue, made some analyses, and developed a bit of a philosophy, which has various backgrounds. First, the background of a scientist and author with more than 35 years of experience, an author who did and still does the essential part of his research work personally and who wrote and writes virtually all his papers personally from the first "a" to the last "z". Another foundation of my philosophy is 18 years' experience as Editor of *Spectrochimica Acta B,* the experience of an Editor whose only secretaries are two computers and two laser printers, a mainframe facility in the lab and a PC at home! The third background is recent literature on electronic publishing and some personal experience with the use of "script" software on a mainframe computer and desktop publishing software on a PC, as applied to the production of scientific manuscripts. Finally, I mention my dialogue with the Publisher, in particular with the present Managing Director, Dr. Pieter Bolman, as an essential and vital part of the background of my philosophy.

The purpose of this lecture is to communicate this philosophy, stimulate you to reflect about the future of *Spectrochimica Acta,* and, perhaps awake you from the dream that we might continue along the same line as in the past fifty years, which essentially implies that Authors may submit manuscripts without bothering a trifle about the way in which the final articles are edited, produced, and disseminated.

An essential thesis as the basis of this lecture is that communication is an interactive, not a one-way process: *i.e.*, the message should come over to the recipient in a form he understands enabling him to respond. This is equivalent to saying that *the way in which results of scientific research are reported is, in principle, equally as important as obtaining those results.*

2. THE SCIENTIFIC PUBLICATION: AIMS AND FORMAT

Discussions on scientific publishing usually centre on the question of how the transmission of information can be made more efficient, more rapid, and less expensive. This question is then approached by considering the various technical means that are at present available or will become so in the near future. Searching for an adequate technical answer *is* an important issue, but not the only point of concern. This will become clear if we consider the purposes of scientific publications and the interests of the various "parties" involved: Authors, Referees, Editors, Publishers, Readers and other Users of information, such as Librarians and Documentalists, and "third parties": vendors of computers and desktop publishing (DTP) software. Each of these groups will look at the issue from a different point of view.

Starting-point for discussing this matter again is a thesis, a thesis on the aims of scientific publications, which are

(a) disseminating information to promote scientific and/or technological advancement,

(b) establishing the Authors' prestige and reputation.

I believe that *the latter aim is equally important as the former.*

If dissemination of information were the only goal, we might devise an information network differing from the present one, which is primarily based on scientific journals in hardcopy format [1]. However, neither science nor scientific publications are made by an ensemble of information robots, but by a community of scientists, who want to show their identity and wish to exchange not only data, results, and ideas, but also feelings. Scientists aim at recognition and take pride in the quality and quantity of their publications and in the impact these publications have on the development of science. This pride roots in the satisfaction associated with creativity, on the one hand, and in the feeling of power inherent in the possession of knowledge. Prestige, reputation, satisfaction, and power are the prime motivations of scientists. Therefore it is unlikely that the near future will see the classical journal format being replaced by "electronic journals" consisting of manuscripts stored in electronic form in a database from which "Readers" may extract information when they need it. Authors want to see a hard proof of their work in the form of articles distributed via a reputed journal and exhibited on the bookshelves of the libraries: the galleries of the scientists! Authors want to push their products upon the community rather than passively wait to see whether the community will be so kind to retrieve these products from a database. *Honni soit qui mal y pense,* but it would be naive to deny it! Therefore, I do not believe that the near future will see an essential change in the way in which the results of scientific research will be exhibited to the public. *The classical journal format has an eternal life!*

Yet major changes in the field of scientific publishing can be expected in the near future. They concern:

(a) the way in which manuscripts are created and transmitted, and the manner in which the final hardcopy articles are produced;

(b) the form in which the information contained in the articles is stored and made retrievable, in addition to their temporary storage as hardcopy journals in the library galleries;

(c) the publication of truly electronic journals as an expedient for disseminating information that can not adequately or not at all be transmitted to the "Reader" by the conventional hardcopy journal.

Anyone who critically examines the various attempts that are being made to introduce innovation in scientific publishing will soon discover that *chaos is virtually complete and that really viable approaches are still far off.* This is so in spite of what champions and protagonists of DTP and camera-ready copy (CRC) are trying to make us believe. This again is a thesis and you may be surprised to hear this pronounced by me. I immediately add another one: *Order appears to emerge from the chaos if we recognize that the era of DTP in science is concomitantly at its start and at its end.* This paradox will be clarified further on in this lecture. Perhaps you will already feel where I am heading to when I pronounce this metaphor:

> DTP in science is not a still-born child, but a very healthy one, which, however, should be kept under the Author's patronage, to be caressed and to please him, but should not grow up under the Author's supervision to be then entrusted to and photographed by the Publisher. Instead we should think in terms of twins, one of whom is freely educated by the Author such as *he* likes it, whereas the other one gets a rigid professional education at the Publisher's boarding school.

This has nothing to do with technological feasibilities, but primarily roots in *psychological arguments,* dictated by the *actual* - not the ideal — *behaviour* of Authors, Referees, Editors, and Publishers.

In order that you will clearly see the points I just made and those I shall make later on, I start with some citations under the heading "Fictions and facts". I do this including the details, for it is precisely the details which are so enlightening.

3. NEW APPROACHES TO CONVENTIONAL SCIENTIFIC PUBLISHING: FICTIONS AND FACTS

3.1. *Fiction or fact?*

In 1987, Raymond Dessy [2] published an authoritative, tutorial article "Scientific word processing", from which I cite here the Prologue:

> "This Fall the Chemical Institute of America, with the support of the Federal Bureau of Information, will begin publication of the Electronic Edition of its Journal of Chemistry. Each subscriber will initially receive a CD-ROM disk for use on a personal computer. The CD-ROM will contain a scientific word processor to be used for manuscript preparation. Separate style sheets for Introduction, Experimental, and Results and Discussion will allow prospective Authors to develop their material in the format required by the Journal. Style sheets for references, tables, forms and graphs will also be included. With the built-in scientific word processor, the user can enter appropriate text and data, and be assured that the result is editorially acceptable. The CD-ROM will also contain templates for all of the normal chemical and biochemical core structures, including the CAS Ring Index. The scientist can use these to sketch out desired structures and reactions. IUPAC names will be generated automatically.
>
> Articles may be submitted to the Editors on diskette or by modem. The review process will be "on-line". Reviewers will receive their copy by modem and will append their comments on electronic PostIt^{TM} notes for return to the Editor.
>
> Accepted manuscripts will appear in a monthly interactive CD-ROM version. The interactive format will allow readers to scan the electronic documents using their own customized access program. This format will also let Authors use photographs and images within their text. The CD-ROM will include a "current awareness" file containing all of the Titles and Abstracts for chemical and biochemical papers published in the preceding period. A full-text relational database will allow subscribers to search for pertinent references."

Dessy then concludes: *Real? NO. Technically possible today? YES."*

This citation will be further commented upon implicitly in this lecture. Dessy himself does not add additional comments, but provides after the prologue an excellent, tutorial overview of the various *technical* possibilities and covers, among many other things, the distinctions between word processors, scientific word processors, and desktop publishing software, as well as technical aspects of "graphics".

3.2. *Technology pioneers among Pergamon journals*

During a "Communication Innovations Seminar" for Pergamon Editors associated with the celebration of Pergamon's 40th Anniversary and Robert Maxwell's 65th birthday in June 1988, various lecturers presented keynotes on new approaches to publishing. The essentials are summarized in a new Pergamon Newsletter for Editors *"Innovating"* [3], from which I extract the following information.

(a) *Cancer Communications* [4]

This new journal will publish the results of original experiments in areas of basic cancer research and will use the newest technologies in all phases in order to complete all journal processes in the least time possible. Manuscripts, reviews, and proofs will be communicated from one person to another by the fastest method that the Editors, Reviewers, and Authors can devise with their own equipment. The Editorial Office stands ready with a multitude of state-of-the-art hardware and software configurations designed to reduce to a minimum the various time periods involved in publication. The Editor, Barabara Renkin, challenges those scientists who consider submission of manuscripts to *Cancer Communications* to configure their hardware and software to be compatible with at least one of the configurations supported by the Editorial Office.

The Editorial Office is prepared to receive manuscripts transmitted by:

- direct telecommunication from the Author's to the Editor's computer,
- public or private EMail,
- floppy disk sent by overnight or two-day mail,
- facsimile machine,
- in hardcopy by overnight or two-day mail.

The reviewing process also is speeded up by using the fastest available and most convenient method of transmitting manuscripts to the Referees, supported by telephone calls to determine availability to referee a paper.

Suitably revised manuscripts and those accepted without revision will be transferred to the computer hard disk by one of the following methods:

- Text on paper will be read by optical character recognition (OCR) software while being scanned. Line drawings and halftones will be scanned into one of the graphics programs on the computer disk and enhanced, sized, and transferred to the word processing program for appropriate placement in the manuscript.
- Floppy disks will be read-in by a disk drive that matches the Author's floppy disk drive.
- Computer-to-computer communicated manuscripts will be on the hard disk when they arrive in the office.

These are my comments: *"Technically feasible? YES. Real? FEASIBLY. Psychologically realistic? NO."*

If it works, we have a small Publisher under the wings of "the" Publisher, but no longer an editorial office in the common sense of the word. We also have terribly good and obedient Authors and extremely exemplary Referees. Perhaps our medical colleagues behave differently from scientists, but I must still meet the Author who follows all manuscript prescriptions to every detail and I am still waiting for that wonderful Referee who eagerly confirms his availability to review a bitnet-transmitted manuscript next day! Psychologically a reviewer cannot bypass seeing the manuscript slowly creeping upwards in the pile until the point is reached that the water has risen to his teeth. Would that change if the manuscript is hidden in a stack of computer files instead of displaying itself on the reviewer's desk like a time-bomb? I do not see that computers and computer networks will help Referees more easily over the threshold to start with a manuscript of which they intuitively know beforehand that the story is poor and will take a lot of time for reviewing. *The crux of all lies with the Author*, but this point requires a far more careful inspection. Let me, however, first continue the review of innovations among the Pergamon journals.

(b) *Leonardo adopts desktop publishing* [5]

Leonardo is an art journal addressing the application of science and technology to art. They decided to experiment with new publishing technologies in order to learn how to use these technologies to face attrition among their Authors and audience. As an art journal they were also under pressure from Authors and Editors to improve the visual appearance and accessibility of the journal.

They decided in mid 1987 to convert the production to desktop (DTP) preparation or camera-ready copy instead of delivering typed manuscripts to Pergamon for typesetting. From the available hardware/software choices they eventually chose Ventura Publisher on an IBM computer in preference to Aldus Pagemaker on an Apple Macintosh computer. For various reasons, including the absence of large numbers of equations in the manuscripts, they did not consider "TEX". They contracted a designer to implement a new layout design. Manuscripts were typed in their office and converted to ASCII files. In addition they also accepted ASCII files on diskette from some of the Authors. They sized all the illustrations and chose for sending them to Pergamon for re-shooting and paste-up. They first applied it to conference proceedings published as a supplement and decided to switch all production to DTP from 1989 onwards. An issue of 120 pages of text was said to be produced in roughly 50 hours of layout work. The final copy was delivered on diskette to a local electronic typesetter, who produced the camera-ready copy, since their own laser printer did not provide sufficiently high resolution.

This story again reflects activities of a "daughter Publisher under the wings of mother Publisher". However useful the approach for mother and daughter may be, it is no more than an example of journal production put out to contract. Clearly, scientific Editors will not be eager to take up this gauntlet!

(c) *Rapid publication typeset quality CRC journals — The Applied Mathematics Letters Experience* [6]

Ervin Rodin, Editor-in-Chief of *Computer & Mathematics with Applications* reported experience with the new journal *Applied Mathematics Letters* (first issue January 1988), which is devoted to two purposes: (i) to publish short (1-4 pp) technical papers, and (ii) to do so in uniform typeset form, yet within 3 months of acceptance by an Editor. This aim is achieved as follows.

They have established a large Editorial Board, with complete editorial autonomy. Most papers are reviewed by the cognizant Editor himself. This arrangement would allow one to publish CRC papers of any sort very fast, but this is incompatible with the goal of producing a uniform, typeset journal of papers which are full of complicated mathematical formulas. To achieve both targets, the 3-months limit and uniform, typeset quality, they have adopted TEX, which is a scientific, mathematical word processing and typesetting program.

TEX (pronounce as "tech") was developed and placed in the public domain by the mathematician Donald Knuth [7,8] of Stanford University. It has been adopted as the standard by the American Mathematical Society for all their publications [9]. It is available for most mainframe computers, IBM compatible PCs, and the Macintosh. A review by Abikoff [10] explains in a tutorial, nontechnical way the essentials of TEX and covers the macro packages AMS-TEX and LATEX as well as the PC versions MicroTEX and PCTEX, which are essentially implementations of the same program TEX (also see [11]).

Two points are crucial here. First, the input file for TEX, the source code, is a straight ASCII file, which can be produced with any editor that does not insert any special formatting codes into the text. Second, TEX produces from the source code a device independent or DVI file. This implies that one can prepare a TEX manuscript on any computer, and that anyone, on any computer which runs TEX can revise it or print it out.

Rodin [6] further reports that they are receiving an increasing number of manuscripts by either electronic mail or on diskette. When these are submitted in TEX they can immediately print it out in a beautiful typeset version. They can easily change such things as margins and page size and produce a final CRC product to be sent to Pergamon Press.

However, the majority of the manuscripts received at the time that Rodin's report was written was still in hardcopy form. These manuscripts are retyped in their office using TEX software. Authors are encouraged to submit their manuscripts in TEX by the promise of publication within 3 months from the date of acceptance. Those who submit otherwise receive a "penalty" of having to wait an additional 3-6 months.

An interesting feature of the approach recounted by Rodin is the use of a technical word processor which can handle mathematical formulas, formats a text in a fixed style, and stores all formatting instructions in a DVI file. This relieves the scientific Editor of the often cumbersome style corrections, which he cannot always avoid, in spite of the existence of script editors at the Publisher's. It also appears convenient for an Editor that he can produce in his office an article with a physical appearance similar to that of the final article and that he can directly interact with the text via the computer so that his finishing touch, for example, some linguistic corrections in the revised manuscript, is indeed the last touch.

One may dispute the final step of the editorial procedure: the conversion of the DVI file into CRC, to be delivered to the Publisher. It means again that the editorial office becomes part of the Publisher's production department. This need not be a problem if the required resources are made available. These last remarks will apply *a fortiori* to the retyping of manuscripts that are not submitted in the required TEX format. Generally, one might wish to keep scientific editing and technical production separated. The above approach in principle permits this, since either the DVI file or the source file can also be directly used by the Publisher to produce a high-quality typeset paper with the aid of a phototypesetter.

The above survey concerned some experiences of Pergamon Editors with new approaches to the production of journals in classical format for the dissemination of research results.

Another approach having a broader scope and more fully exploiting the potentials of electronic media will be considered in section 7.

4. THE DESKTOP PUBLISHING AUTHOR PRODUCING HIS OWN MANUSCRIPT — HOW FAR DOES HE GO? — HOW FAR SHOULD HE GO? — — WHICH ARE THE BENEFITS OBTAINED? —

4.1. *An author's confession of faith*

An analysis of the new approaches discussed above indicates that there are some benefits when the Author produces the manuscript himself. These benefits appear to be primarily at the side of the Publisher, who shifts ever more tasks to the Authors and the Editors by letting the former type, correct, and typeset the manuscripts. Where do the Author and the Editor stand?

An even superficial glance at literature and advertisements nourishes the belief that the Author will enter paradise when he adopts DTP for the production of his manuscripts, while the Editor will feel himself allotted an easy-chair in heaven. What to think about this? I shall approach this by recounting a brief autobiography, a type of dialogue between an Author and an Editor who share the same office and continuously juggle with their different caps!

As an Author I have always typed the manuscripts of my articles, chapters, or books myself, and not just once, but usually I retyped them twice or thrice. I could easily do that because I learned typing with 10 fingers when I was eighteen, and I did so because my pen could only produce horrible hieroglyphs or cuneoform characters — and still has not made any progress! The vital benefit was that it enabled me to assemble concepts of texts from different, handwritten or typed sheets, and rags of blotting paper, with multiple corrections, additions, and deletions, and with only rough references to whichever personal records, often hardly specified amidst the apparent disarray, inaccessible for anyone except myself. Perhaps it has been my computer-like memory rather than the 10-finger typing craft which has enabled me to reshape the disarray into scientific documents which most of the time have been recognized by the international scientific community as clean products of the human mind. The 10-fingers typing craft enabled me to produce a typed text with reasonable speed and thus to see the text rapidly pass in review. Consequently, I never retyped a text such as it stood in the hand-corrected preceding version, but reshaped and changed it again during typing until it reflected the logical and consistent train of thoughts I wished to see, without gaps or jumps.

In summary, I have always felt myself a text moulder; creeping into a typist's skin has made this task more comfortable and has turned out to be a well repaid investment. Needless to say that the advent of software for word processing fitted my state of mind and my way of working as a hand-tailored suit. A mainframe and a PC have replaced both the typewriter and the piles of paper. I now hardly produce any handwritten text, everything gets straightly from mind to computer, where I can mould the texts and combine them with whatever experimental data stored in the same computer or called up from disk or tape. There also is a most beneficial interaction between formulating the text and interpreting the data since the process of formulating acts as a critical reviewer and often compels me to reexamine, reorder, or even revise the data by performing new calculations or additional measurements.

The philosophy behind this approach is that I consider the *writing of an article not as a separate procedure that follows on an experiment or a theoretical computation, but as an integral and indispensable part of the creative scientific process in its entirety.* This is seldom a straightforward process, but usually a heavy struggle, whereby it may often happen that new ideas arise as a result of letting the formulation pass a ruthlessly critical sieve. The computer forms a great help in that it permits the Author to compose and mould a text until it is conceptually entirely satisfactory. Note well *the computer is only a help in the mental process of creating a text; it does not add anything essential, but makes it easier to assemble fragments, shift and delete parts, and apply corrections and additions.* A neat printout further facilitates a critical judgment of the results and makes it more attractive and effective for the Author to critically re-read the product of his mind for the umpteenth time. As a creative process, writing up a text remains a strenuous and fatiguing act, which demands strong concentration from the Author and therefore also calls for regular breaks during which the mind finds some relaxation, is enabled to distance itself from the contents of the text, and subconsciously digests it. Any experienced Author will be familiar with these mental "jams" and will have devised effective means to deal with these crises. There may be many such means.

Personally I experience in particular the benefits of the breaks during which I occupy myself with the purely graphical design of the text, including the interactive corrections via preview of the processed text on the screen or the hardcopy printout. In other words, I do not feel that spending some time as a graphic artist means lost time, first, because it can be used as the indispensable relaxation, — but there may be also other ways for that — and second, because it may also lead to direct improvements in the scientific clarity of the manuscript. Two examples may illustrate this.

If an Author has to fit a set of tabular data neatly on a page, he will be far more critical as to which data he should omit than when he saddles the Editor and/or printer with the impossible task of having to fit a square mile of data on an acre!

Personally I experienced this: when describing an approach in terms of mathematical equations, the preview showed that the formulas did not look very attractive to a reader, whence I changed the whole set-up by, *inter alia,* using a smaller number of indices. The complexity had not mattered in the underlying computer program, but I felt that it would stand in the way of effective communication when maintained in the final manuscript. Clearly, I might have also come to that conclusion via a handwritten text or even before that stage, but just imagine the resultant chaos!

In short, I see many advantages in an Author composing his own manuscript on the computer while acting at the same as an amateur graphics designer:

- working on separate fragments in "any" order of preference;
- arranging fragments in an optimal composition;
- multiple interactions between the editing of fragments;
- easy interactions with and import of external data;
- frequent screening of the text in near-to-final form;
- refreshment of the author's concentration power in the editing intervals;
- direct and immediate feedback from "graphics designer" to scientist, and conversely, since decision making about content and "look" are in one and the same hand.

It will be obvious that with this state of mind I consider the computer along with scientific word processors as a gift from heaven! I should immediately add, however, that I am also fully conscious that the adequate exploitation of this heavenly gift requires considerable investments, and compels one to learn (and keep perpetually learning!) a great many tricks. I went through that school for a variety of reasons including my interest as Editor in the use of electronic media for the production of scientific articles. For this latter reason, in particular, I went so far as Author of my own articles that I devised on the laboratory's mainframe IBM 3081 computer the precise rules for producing an article in exactly the style of *Spectrochimica Acta B* (SAB). The IBM "Script/VS" employed for this purpose uses procedural markup language ‡, analogous to (but different from) that used in TEX and also has a convenient mathematical formula formatter. Once you are familiar with it, you can hardly imagine that there would be someone not happily using it, but this seems to

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‡ *Procedural* or *specific* markup is a means of identifying *how* the information will appear in finished form; this type of markup provides instructions for formatting the document. Procedural markup contrasts with

apply to whatever software you have got accustomed to. It is always the finest and most comfortable software ever devised, so that you almost think that you made it yourself, but all you actually did was make considerable efforts to learn its use and then it seems to have become part of yourself. Perhaps the enthusiasm is also an unconscious way of protecting yourself against having to pass the valley once more to familiarize yourself with the routine use of another software package.

To conclude, as an Author I found it beneficial in all respects to produce my manuscripts on the computer and as an Editor I could convince this Author to exercise so much patience and perfectionism that manuscripts resulted which were virtually 100% SAB style. Additionally, in our laboratory we are privileged in that we can produce the final output using an electro-erosion printer, resulting in CRC of such a high resolution that only professional graphic artists see the difference in the final printed article. Thus I published in the past year three articles of substantial length in SAB, in which the Publisher had only to paste the separately added figures.

4.2. *Some crucial questions*

I have told the above confession in detail to present a background for the formulation of some questions which I consider essential for the assessment of present and future developments in scientific publishing. The point I wish to make is not principally which technical means are or will become available but *how we can and should use them optimally* vis-à-vis *the actual states of mind, behaviours, and targets of Authors, Editors, and Publishers.*

I'll treat this by considering four questions:

(a) Does my philosophy as Author reflect that of the average Author?

(b) Would it be feasible to let Authors meticulously produce their manuscripts themselves down to the last minute detail so that the Publisher can reproduce these manuscripts as CRC by either direct photocopying of the Author's hardcopy manuscript or phototypesetting of the Author's electronic manuscript? Would it be desirable and scientifically beneficial?

(c) How do Authors, Editors, Publishers, and Readers look at the present developments of the use of electronic media and how can we achieve an optimum balance between the tasks allotted to Authors, Editors, and Publishers?

(d) What can Editors and Reviewers gain by receiving MSs on an electronic medium?

4.3. *The Author and his manuscript*

The first question: *"Does my philosophy as Author reflect that of the average Author?"* My experience as Editor tells me that this is certainly *not* so.

There is a broad distribution of Authors ranging from text moulders to producers of stories which have neither head nor tail. There are recruits and veterans, soloists and ensemble players, and novices enjoying the patronage and blessings of a senior tutor. There are handwriters with either a secretary, PC or mainframe at hand, and there are genuine PC or mainframe writers having pen and secretary entrusted to an archeological museum! Most manuscripts are now produced with at least a word processor, and an increasing number with a scientific word processor that adequately handles mathematical formulas. DTP manuscripts in the sense of texts with graphics integrated, have not yet been submitted to SAB and this format actually is discouraged by the present manuscript requirements (MSR) of the journal, which prescribes the separation of text, tables, and graphics. Laser printers are replacing dot matrix or daisywheel printers, although the era of the old-fashioned non-electrical typewriter has not yet vanished either. Evidently, there is a big difference in the physical appearance of the manuscripts from "first-world" or "third-world" countries, the latter including Eastern European countries. It also appears that the lack of ease to mould a text, inherent in third-rank facilities, has its repercussions on both the scientific content and the physical look of the manuscript.

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descriptive or *generalized* markup, which identifies document elements, such as paragraphs, headings, parts to be emphasized, etc., *without specifying the ultimate presentation* (see section 5 for further explanations).

As to style, there are Authors who follow the journal's MSR carefully, whereas others snap their fingers at them. Even those Authors who meticulously produce manuscripts which are virtually SAB style drop a few stitches so that reproduction of their manuscripts as CRC is illusive as it is incompatible with the requirement of a uniform and consistent journal style.

Should we compell them to dot the last "i"s and cross the last "t"s? Definitely no! If you ask me whether I submit my manuscripts to other journals also in precisely the style required by that journal, my answer is: "I once found out how to do it for SAB, but since I publish only exceptionally in other journals, they will have to accept 'my style'. If they wish to change it, then that is their business!" Generally, as Authors, we can always say this, because we only need *journals* and not necessarily a *particular journal*. If a journal asks too much or if an Editor changes our personal style of writing into dull ready-made uniformity, we say 'goodbye'. Each particular journal needs us more than we them. In other words: the Author is the journal's customer, and the customer is king, provided that the scientific content of his paper meets the journal's standard, and the organization and physical appearance of the manuscript reasonably link up with the journal's MSR.

The conclusion is that DTP and consequently CRC will not work: the Author does as he likes. Few authors have the talents for or interests in graphics design, and if authors have, they may lack patience and/or time to produce immaculate DTP manuscripts. Many authors like to "play" a bit with powerful DTP software packages, but once their curiosity has been satisfied, they are not willing to accept the consequences of having to embark upon serious fumbling and fiddling with "cut, paste and crop". If one sees as Editor how Authors at present submit their computer-produced graphics with abundances of illegible letterings, impossible scalings, and an overdose of redundancy, one can only conclude with respect to the use of DTP for scientific publications: *"Voi che entrate, lasciate ogni speranza!"*

Curiously enough, this conclusion need not be incompatible with my trumpetting the benefits of the Author producing his own manuscript with the aid of a scientific word processor or even DTP facilities. Let him exploit as much as possible the full benefits of these expedients to produce a "final" manuscript for himself, for his internal Referees, and for initial submittance to a journal. *Let him also produce, however, a "stripped" file, i.e., a file in straight ASCII format, which can be processed by professional graphic artists to yield an output in whatever style.* This ideal is within reach, as I shall explain below.

On the other hand, DTP appears ideal for the production of books, in particular books written by one author or a small group of authors. It will already meet more problems with multi-authored treatises. However, this is an aspect of scientific publishing beyond the scope of the present lecture, which confines itself to journals.

4.4. *An Editor's views at the Author's manuscript*

Any reader will prefer *studying* a text using a hardcopy in which he can put markings and annotations. Therefore Editors and Referees will prefer hardcopies of the manuscripts. These may be the DTP products composed by the authors provided that they satisfy the general style and organization requirements of the journal. These manuscripts may be submitted as hardcopies or via electronic media, diskette or electronic mail. The hardcopy form has the disadvantage of the sluggishness of the mail, while the electronic form, in particular electronic mail, still copes with problems in the transfer of graphics, but this is not likely to remain so. What primarily matters with the electronic media is the availability of both adequate facilities and *staff* for producing hardcopies in the Editors' and Referees' offices. Otherwise the delays in the mail will be replaced by delays in the offices. By contrast, transmitting the *reviews* via computer networks does not meet these objections and will always be beneficial.

What can an Editor gain by receiving a manuscript on an electronic medium?

For a journal like *Spectrochimica Acta B* there is no straightforward answer to this question, for various reasons. First, virtually no manuscript can be accepted without at least minor revision by the Author. This means that the Author has to rework some part(s) of the text and/or graphics and will resubmit a new version. One might thus think this is clear-cut pie: the Editor sends his Editorial Report along with the reviews, and the Author prepares a new electronic version of the manuscript which he submits together with his revision report, so that the Editor's task is confined to a final check. This is the ideal picture of the "operation of an Editor's office". If it were realistic, an SAB Editor would lead the comfortable life of a louse! Actually an Editor could fill a whole book with stories about what he has to do with the manuscripts before they appear as clean documents in the journal. Scientific content, organization, journal style, language, unambiguity and clarity to a printer (symbols!), and overall physical appearance pass the Editor's judgment. It makes no sense to tell an Author in a general way "that he has to improve the manuscript in this or that respect"; many Authors should be told concretely and in detail what they precisely have to do. If an Editor does not include this "message" with his editorial report, he only postpones his own execution and will see a virtually unaltered manuscript joyfully land again on his desk two or three months later! Telling this is not to claim an Editor's martyrdom or the role of a hero, it is only to indicate that it is not a simple job to maintain a journal's high standard and concomitantly (i) save as much as possible of what seems scientifically sound and (ii) give Authors a fair chance to establish their reputations, in agreement with the belief in the dual purpose of scientific communication. It would be all much simpler if dissemination of information were the only goal! Then, computers might take over many tasks from Authors, Editors, Referees, and Publishers: this would bring us, however, to the inhuman world of scientific robots.

Again that question: *"What benefits can an Editor obtain from a manuscript on an electronic medium?"*

If we abandon the possibility that the Author produces the final electronic DTP text but instead submits "stripped" electronic files to be handled by the Publisher, then there is no need for an Editor's finishing touch to the electronic files of the revised manuscript. Minor final corrections can then be sent on hardcopy to the Publisher in much the same way as happens at present with manuscripts for typesetting. Alternatively, these corrections could be easily sent in a separate electronic message to either the Publisher or the Author, whereupon the latter transmits the truly final electronic manuscript to the Publisher.

A rather different situation arises with the "troublesome manuscripts", the Editor's nightmares, requiring substantial linguistic and/or organizational editing. At present I do this by handwriting between the lines and in the margins. The Author then gets this version with my style "suggestions" for checking and retyping if he agrees. This is feasible in the first stage, and thus can be done along with the preparation of the editorial report, if the manuscript does not require extensive major revision with respect to the scientific content. If it does, then it is the *revised* manuscript which is stylistically edited by the Editor and subsequently checked and retyped by the Author. Even then a final check (and final corrections!) by the Editor remain indispensable!

The irony is in fact that as Author of my own manuscripts I have worked myself completely beyond the "era of my own handwritten disarray", while the Authors of my dear journal keep tearing me back into the "stone age". On the one hand, one might wish to attack the manuscripts in a modern way and to interact with them on the computer, on the other hand, I am afraid that it might easily lead to loss of the Authors' identities, which is certainly undesirable. But even if this can be avoided, it remains questionable whether it would lead to a gain in time and efficiency.

You may also dispute whether severe linguistic revision of the English grammar in scientific articles is required. Some Editors shift off the load by the statement that a scientific journal is not a literary journal. I agree, but the heart of the problem is not the *correct* writing of *English*, but *correct writing* in whatever language. I receive manuscripts from Russian authors, which can be easily corrected by adding or deleting some "articles", cutting a few long sentences in parts, or changing an expression. Those manuscripts follow a clear line and reflect a logical train of thoughts. I also receive manuscripts in which the reading and recasting of every sentence is a true torture. The majority of these manuscripts stem from third-world countries, but not alone: also Authors with an English mother tongue know how to torment an Editor!

What can an Editor gain from electronic media? For the time being, he is likely to lose more than he can gain, because he will also be saddled with all the technological problems inherent in the diversity of soft- and hardware.

We should also ask here: "What do we, the scientific community, thus, Authors, Editors, and Referees, *want* to gain?"

Generally we wish to increase efficiency and productivity, and reduce the time between submittance and appearance of an article. For a fundamental journal such as SAB, maintaining a high standard is more important than extreme speed of publishing, but a substantial reduction of the turn-around time is certainly desirable. Since the largest fraction of this time is consumed at the Publisher's, it is primarily at that end where the benefits of electronic media should be optimally exploited, the more so because a scientific document in an appropriate electronic form, once it has been accepted by an Editor, has become a merely mechanical assembly of codes, which can be processed by machines. This contrasts with the preceding phases of the document in the Editors' and Referees' offices. There the document is subjected to mental scrutiny, *i.e.*, a process which cannot be hurried at will, since it requires the mental disposition for absorption and digestion. The latter also applies to the next step: the Author's revision of the mansucript, which, to my experience, often also is a lengthy process. All we may speed up in the *pre*-publisher's part of the turn-around cycle are some trivial time losses in the mail. The future may solve this problem technically, but I'm somewhat sceptical about the staffing problem, if I see faxes cross the Atlantic in 2 minutes and take two days to travel from the 7th to the 8th floor within the laboratory! I wonder whether I am the only person complaining about such problems? We should not deny them in a society where not the ideal, but the actual behaviour of *people* is the deciding factor. However, let us now examine the position of the Publisher.

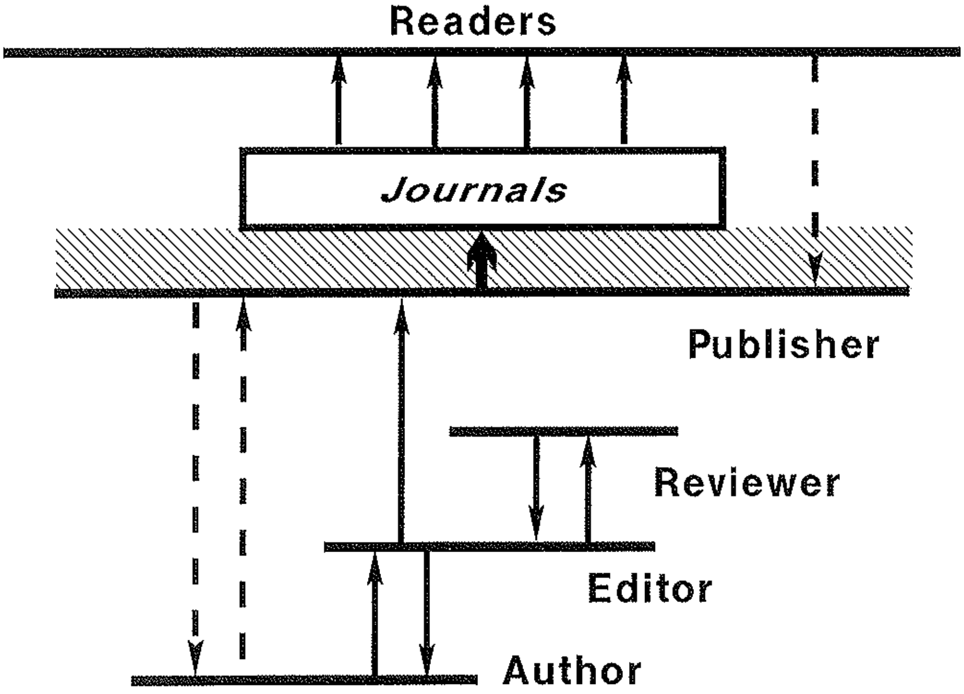

Fig. 1. "Level diagram" representing the present interaction between the parties involved in scientific publishing.

4.5. *The Publisher and the Author's manuscript*

The Publisher is an entrepreneur whose goal is to make money. His product is information, which he buys from the Authors in exchange of fame and which he sells to the Readers in exhange of pecunia. The balance between the receipts and the production and overhead costs makes up his profits. Part of the latter has to be used for investments in order to face competition and thus to ensure the continuity of the entreprise. The whole business operates according to the rules of capitalist economy...... just be a good bookkeeper and...... a clever entrepreneur.

In the past years Publishers have sought means for better controlling the ever increasing production costs, one of the attempted remedies being the promotion of author-produced CRC. Generally this approach has not been accepted, since the degradation of the overall physical appearance of a journal is felt to entrain the scientific standard in the same downward direction. I have explained that DTP is not likely to provide better perspectives. The principal argument for the Publisher to abandon this approach is that he will lose the Authors as suppliers of information. He will also lose them, however, if he does not keep pace with modern production methods and sharply reduces the turn-around time of manuscripts. A clever exploitation of electronic media will enable him not only to keep his clientele at the suppliers side but also permit him to expand his enterprise in the direction of the information users, the "Readers".

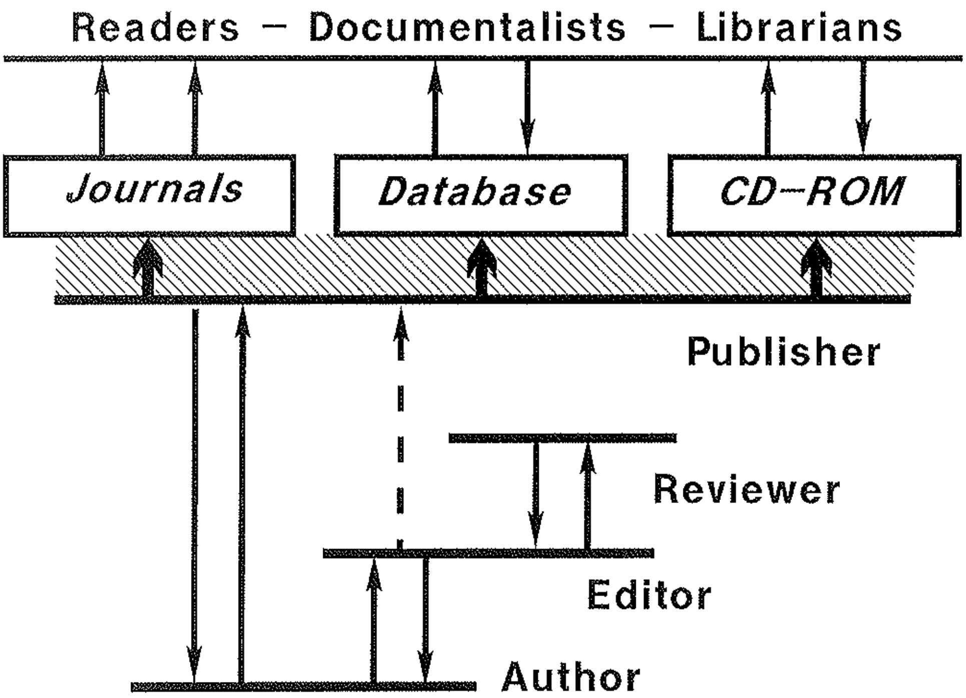

Fig. 2. "Level diagram" representing the future interaction between the parties involved in scientific publishing.

As a spectroscopist I wish to illustrate this with the aid of two "level diagrams". The first one (Fig. 1) characterizes the present situation. The Authors form the ground level, the Editors the resonance level, and the Referees a metastable level; the Publisher is near the ionization limit, while the Readers float in the region of free-bound transitions. At present, the Author interacts virtually exclusively with the Editor, and the Editor additionally with the Referees. Once these interactions are finished, there is a one-way flow from Editor to Publisher, followed by a very weak interaction between Publisher and Author in the proof stage. Finally there is one-way traffic between Publisher and Readership, the only feedback being possible cancellations of subscriptions.

The future is likely to see a somewhat different "level diagram" (Fig. 2). The initial part of the picture, representing the interactions between Authors, Editors and Referees, will not essentially change. For the next stage, however, we can expect a far stronger and more direct coupling between Author and Publisher: the Editor gives his "nihil obstat" or "imprimatur" on the basis of the revised hardcopy manuscript, which will not be reproduced in that form by the Publisher. In contrast, the Author will send electronic files to the Publisher, files stripped of all DTP whistles and bells, but provided with codes that identify the *type of information*, so-called *"standard generalized markup language"* (SGML), to be further dealt with below. The Publisher can then encode the electronic manuscript for phototypesetting, saving the effort and costs of the rekeying of the text. This stage might require some direct interactions with the Author.

It is in the Publisher's interest to create effective communication lines with the Authors, not only to achieve more efficient and faster production of "classical journals", but also to get a firm grip on the same information for dissemination via such media as CD-ROM ("complete journals") and electronic databanks, from which Readers can retrieve information, as is symbolized in the upper part of the diagram. The use of SGML by the Author is likely to substantially facilitate the recognition, storage, and retrieval of information.

This lecture has now reached the point where some technical explanations may be enlightening.

5. A TUTORIAL INTERMEZZO

5.1. *Introductory remarks*

The views on the future of scientific publishing presented in the previous sections were primarily based on an analysis of the *behaviour* of the various groups of persons involved in the creation and dissemination of scientific documents. I approached the problem from that side and not from the viewpoint of information science or technology, for various reasons. Evidently, as I speak as a spectroscopist, it would be pretentious to emulate experts in information science or technology. Crucial it is, however, that I wish to express a view which can be appreciated by other scientists for whom publishing is an important issue and which they want to address in an optimum way using modern media but without becoming the slaves of these media. Perhaps the sting lies in the words "optimum" and "slaves", two terms which may be defined rather differently depending on whether a scientist is computer-literate or computer-illiterate. Probably, the latter group will have completely vanished within ten or twenty years, but I would not be happy to cater to them at present! This latter group, however, comprises many leading Authors and Editors and it is of paramount importance therefore that they, too, take up a position with respect to future developments of electronic media for disseminating results of scientific research. A problem may be to collect, in spite of many other priorities, the required background information. All roads lead to Rome, but only a few appear to conduct the traveller with minimum efforts to the right spot. Whether he will ever arrive is doubtful since the "roads to Rome" spring up like mushrooms. I mention only a few tutorial reviews from which I extracted some technical information relevant in the present context.

5.2. *Word processors, scientific word processors, and desktop publishing*

An authoritative tutorial review *"Scientific Word Processing"* by Dessy [2] discusses the distinction between word processors (WP), scientific word processors (SWP), and desktop publishing (DTP) with special emphasis on various aspects of graphic display, in both a historical and future perspective.

Word processors are defined as programs intended to handle the standard business and correspondence chores that require text entry, mail-merge, and limited database access.

They can implement the basic emphasis features of boldface, underline, and font change ‡. WPs may also include spelling checkers, thesauri, and sub- and superscript features. Minimum configuration PCs, low resolution monochrome displays, and ASCII printers are usually sufficient.

Scientific word processors are defined as packages that provide extensions which include a rich set of the fonts used in manuscript preparation, including Greek, continental, fraktur, script, chemical and mathematical symbols. They also include sketch pad facilities and utilities to construct tables and forms. They require screens and printers with medium resolution.

Desktop publishing may be defined [3] as the use of software packages on desktop computers to produce disk-based camera-ready artwork of articles and other types of written and illustrated documents for publication. The types of computers currently used for DTP are mainly IBM PCs and compatibles and Apple Macintosh computers. With the need to emulate typeset quality the systems require high resolution displays and printers. Laser printers are required to take advantage of all the detailed layout features. The software systems are powerful and complex.

The software is usually designed to import text files, produced with separate word processing software, and illustrative material ("art work") from a graphics package or a scanning device. These elements are then combined onto a page layout grid. Once the text, graphics and layout are all present on the screen, the user can apply different fonts, lay out tables, label diagrams, create footnotes linked to the content, etc. The desktop publisher thus creeps into the multiple skins of typesetter, layout artist, graphic artist, compositor, and production editor. Tutorials and reference manuals teach him how to use the software.

The success of the "enterprise" will depend on the time the user can spend on learning and, above all, on his *capabilities and talents as a graphic artist,* which is a professional skill that cannot be learned on a rainy afternoon from a tutorial and a reference manual!

Under the title *"Technical Word Processors for Scientific Writers"* Gerson and Love presented in *Analytical Chemistry* [12] a tutorial overview of software facilities available by mid 1987. The authors addressed the distinction between "WISYWYG" (What You See is What You Get) and "ML" (Markup Language) approaches and assessed the product features of the software packages in terms of price, category, capabilities, file formats imported and exported, output devices, and benchmarks with which the various products were challenged: three sets of mathematical equations and two chemical structure diagrams.

Reviews of this type explain many software features in a tutorial, non-technical way and are therefore highly useful for both readers wanting to orientate themselves in a general way and readers wishing to choose a package that suits their purpose. Also numerous reviews in computer or mathematical journals, *e.g.*, [11,13], provide such information.

What matters in the present context is not so much the details of the capabilities of the various packages in creating scientific documents to be produced at the Author's end, but the *ease and convenience with which the computer files created by the Author can be transmitted to the Publisher*. Discussing this matter requires some explanations of the differences between WYSIWYG and ML, between procedural and descriptive markup, and between text and graphics files.

5.3. *WYSIWYG versus ML*

There exist two ways of integrating text, math, chemical structure drawings, and graphics [12]. The first, WYSIWYG, is the more popular one. WYSIWYG programs are word processors with extra features, which enable the display of special characters on the screen and printout, usually by directly accessing "alternate keyboard" character sets. Mathematical expressions are displayed on the screen as the user creates them. The user formats the equation by positioning the cursor where he wants a symbol to appear in relation to the rest

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‡ *Fonts* are collections of characters with a consistent size and style. Font characteristics determine what a printed font looks like. These characteristics include orientation (upright as in roman or slanted to the right as in italic), character height or type size (vertical height or point size), style or typeface, stroke or type weight (light, demi bold, bold, etc.), and type width (ultra condensed, condensed, expanded, etc.).

of the equation and then accesses the alternate keyboard character. Some programs, however, incorporate abilities for automatic formatting of the equations. Chemical structures are created in a similar way as math expressions. — For chemical structures, also specialized graphics programs are often used. --

WYSIWYG systems may be more difficult to implement in view of hardware requirements such as screen resolution and graphics cards. A WYSIWYG system requires the user to remember which alternate keyboard character contains a special character. A major advantage is that it provides immediate visual feedback. However, it may be tedious to use for constructing complex mathematical equations or chemical structures, unless it is provided with automatic formatting features.

An ML system uses in-line codes that are interpreted by a program called a "formatter", which instructs either the printer to print special characters or the computer's graphics card to display them on the screen. The ML formatter is an extra program used in addition to a standard word processor. In fact, any word processor that can create an ASCII file can create the so-called "source file" containing the text plus the ML codes. *This source file is an ASCII file, which can be transported without any difficulty between different computers.*

Math equations and expressions are created with the aid of a mnemonic set of code words. The program then automatically formats the equations or expressions either embedded in the text or positioned on separate lines, depending on the instructions given by the user. Equations and expressions can also be defined in the form of "macros" and stored in a library. The name of the macro is then used throughout the source file as a replacement of the defined sequence of instructions. Few ML systems can construct chemical structure drawings. Graphics programs using pull-down menus, icons, and a mouse appear preferable.

In view of hardware and software requirements, an ML system is usually easier to implement than WYSIWYG systems. An ML system requires the user to remember a set of mnemonic control words. Compared to WYSIWYG packages, the initial ML systems had the disadvantage of the lacking immediate feedback, but this situation is rapidly changing since ML packages more and more include a "screen driver", in addition to a "printer driver" to display the formatted text and math formulas on the screen. This utility permits the user a preview, which is not interactive, however: making corrections requires the user to return to the source file and change the source codes.

Since both systems, WYSIWYG and ML, have their advantages and disadvantages, the user's choice will primarily depend on his own preference. The available hardware, including screen resolution and memory space, may also play a role. Essential in the present context is not *how* an Author creates a manuscript and *how* the hardcopy produced with the Author's printer will look, but *what type of file in machine-code* the Author can make available to the Publisher.

5.4. *Procedural markup versus descriptive or generalized markup*

Generally, a word processor comprises an *editor*, a *processing program*, a *printer driver*, and often a *screen driver*. This is schematically illustrated in Fig. 3. The editor enables the Author to enter text and symbols, *i.e.*, formatting instructions as alternate keystrokes (WYSIWYG) or code words (ML). In this way the Author creates the *source code* or *source file*. The processing program uses the formatting instructions in the source code and its own built-in instructions to create a sequence of non-specific printer instructions. Screen and printer drivers contain built-in screen-specific and printer-specific instructions, which interpret the non-specific printing instructions and enable the computer to display the final, formatted document on the screen or to produce a printout.

The common denominator of source codes produced in the above way is that they contain *procedural markup*, which conveys *how* the information will appear in the finished form.

For example, if the Author gives the instruction to format a word in boldface, he inserts the code associated with the alternate key "bold" in a WYSIWYG system or types a code word, *e.g.*, ".bf b12", in an ML system, the latter code telling the word processor to change from the current font to 12-point boldface. The codes inserted in the two systems differ in that the ML code consists of a sequence of ASCII characters, which can be recognized by any machine, whereas the WYSIWYG code is specific for the word processor used and thus requires recognition instructions when imported in a different environment.

Most Authors will be hardly aware of how their word processor operates and generally need not bother about this point when the creation of the document by the printer is truly the final step, as happens when the document is intended for dissemination as CRC or will be completely rekeyed at the Publisher's. If, however, the Author would deliver the

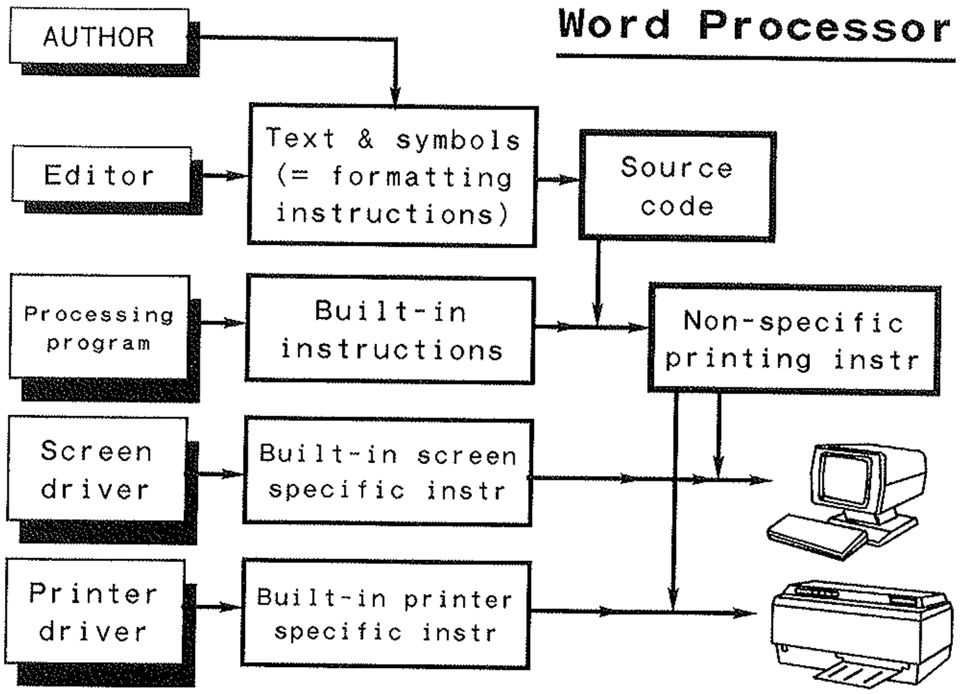

Fig. 3. Schematic representation of the operation principles of a word processor.

document in electronic form to an Editor or Publisher, it will be generally required for the latter to have closely similar hardware and software available in order to reproduce the Author's document, although conversion features may allow some margins.

Clearly, in the era of electronic media the rekeying of an Author's manuscript at the Publisher's is an intolerable waste of resources. Reproducing the Author's manuscript as CRC is not a viable alternative either, as I have argued above. The remaining alternatives are either direct procedural markup of the Author's electronic text by the Publisher or conversion of the Author's hardcopy into an electronic document using an optical character reader, followed by procedural markup. The latter approach may be indispensable, at least in a foreseeable future, to deal with manuscripts from "third world" countries.

Letting the Publisher mark up the Author's electronic text implies that professional typesetters, layout artists, graphic artist, compositors, and production editors deal with the markup, while a phototypesetting machine produces final documents of high technical quality. Which DTP hardware and software the Publisher wants to use for this purpose is the Publisher's, not the Author's business. The latter's prime concern is then *how to provide a "clean" electronic text, preferably as a straight ASCII file, which the Publisher can conveniently handle.* It will depend on the type of software and procedural markup the Author uses and the extent to which he "embellishes" his document for display on his screen or printout at his printer, which efforts the Author has to make to convert his document so as to strip off the "whistles and bells" and insert a minimum of *descriptive or generalized markup.*

Descriptive markup does not specify the actual processing to be performed, but describes generic characteristics of the document as a whole or of separate document elements. It may also define *what* is to be emphasized, without specifying *how* the emphasis should be formatted in the final document (*e.g.*, bold, italic, underlined). One form of descriptive markup is *standard generalized markup language* (SGML).

Essential is the concept of separating the *format* of a document from the *content*. This concept was introduced by a group of interested industry representatives in 1967 [14]. With their support and that of the Graphic Communications Association (GCA) it was developed, first to GCA GenCode and subsequently to SGML. The SGML methodology has expanded over the past several years and received major recognition through the U.S. Department of Defense *Computer Aided Logistics System* (CALS) initiative.

SGML is a set of rules to be used in different applications for defining documents or document components [14]:

- The structure of document types (*e.g.*, technical reports, technical manuals, training manuals, journals, books).
- The logical components of the document types independent of the format of those components (*e.g.*, title, section heads, paragraphs, footnotes, references).
- References to document contents that cannot be keyed from a keyboard or are external to the document (*e.g.*, special characters, graphics, drawings).
- A database publishing system.

In summary, SGML is a set of rules which provide for the definition of types of documents, the identification of elements that constitute documents, the descriptive tags for those documents or document elements, and a means to reference data external to documents. Using the SGML rules to define the structure and structural elements of a particular kind of document is called "developing an SGML application". Such an application establishes the specific document descriptions and related tags for an industry (*e.g.*, publishing) or use (*e.g.*, technical documentation in a particular branch). Applications include the Association of American Publisher's *Standard for Electronic Manuscript Preparation and Markup* and the U.S. Air Force Logistics Command's *Automated Technical Order System* (ATOS).

Evidently, this lecture is not intended to serve as an introduction to SGML, for which the interested reader should consult the literature. I would mention here in particular the following sources:

- ISO 8879, *Information Processing -- Text and Office Systems -- Standard Generalized Markup Language (SGML)* [15].
- Numerous publications and tutorials by Joan M. Smith, Senior Consultant in the Standards Division of the National Computing Centre, U.K., *inter alia*, [16--23].
- *"Pointers to SGML Information"* [24].
- *"Application Development and Surprise"* [25], which describes a commercial product "SoftQuad Author/Editor" as an SGML application.
- The text of a talk by Juri Rubinsky as part of "SGML: A New FIPS", a Graphic Communications Association Seminar (1989) [26].

SGML is particularly suited for document interchange among systems with differing text processing languages that involve different devices and for processing more than one application, such as journals, books, directories, catalogues, and databases. Publishers are thus recognizing the value of electronic manuscripts for use in more than a single product, *e.g.*, journals and searchable databases, since this perspective provides new product options. It obviously also helps Publishers to reduce costs by eliminating the need to rekey documents produced by external authors.

When the SGML marked-up document is transmitted to the Publisher's computer it is run through a so-called *SGML parser*. This is software that is designed to analyze a string of characters, recognize it as markup or document contents, and handle it properly [14]. The parser can perform multiple functions, serving as "tag or syntax checker" to validate the prespecified document structure and allowable tags or syntax. Another function is *to actually add tags or document content* where it can be determined, thus minimizing actual keystrokes. Graphics are treated as external non-SGML files. The parser eventually

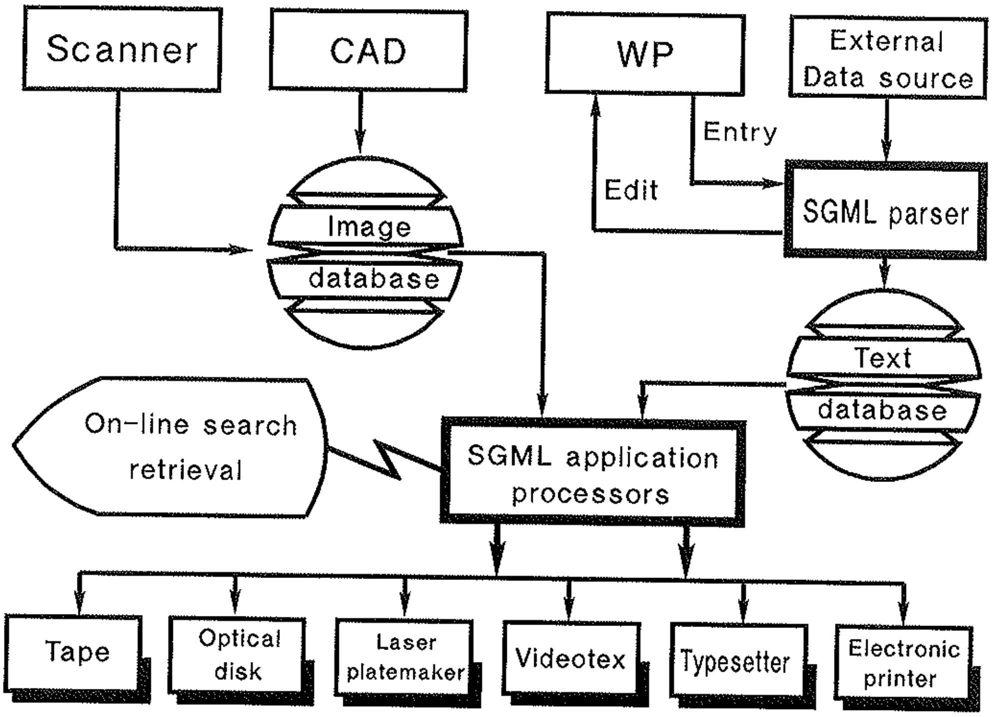

Fig. 4. Flow chart representing the "data flow" in a system operating on the basis of Standard Generalized Markup Language (SGML). WP = Word Processor; CAD = Computer Aided Design.

delivers the fully marked-up SGML document from which the data for the database and the application files can be derived (Fig. 4).

The entire approach gives the Publisher full and efficient access to the Author's document and permits him to let information scientists, typesetters, layout artists, graphic artists, compositors, and production editors handle the document and its information content in whatever way. The Publisher can thus produce an array of products: hardcopy journals, electronic journals, on-line databases, and CD-ROM databases. Electronic journals and CD-ROMs will make indexed data for complete volumes as well as as detailed, non-indexed data in separate articles, including graphics, available to Readers and Documentalists.

SGML champions [14] further wish to make us believe that the use of SGML-based generic tags (a) allows authors greater control over the creative process by producing text that can be used for more than one purpose, (b) simplifies and expedites manuscript exchange between Authors and Editors, and (c) provides a "standardized vehicle" for Editors to interact with Authors, resulting in better-quality products.

Although there is certainly substance in these statements, the implementation of SGML in the Authors', Editors', and Reviewers' environments appear less simple than the SGML protagonists wish to make us believe. I have argued above that Editors and Reviewers prefer the handling of manuscripts in hardcopy form and that most Editors will prefer receiving those hardcopies directly from the Authors. The latter, on the other hand, will ever more use scientific word processors or even DTP packages to produce neat manuscripts. Editors will appreciate this gesture provided that Authors also submit additional, double spaced copies with separate figures and tables to be "butchered" by the Editors' red, blue, and green pens.

Will the Author let himself pull back and abandon the fine software package he has so eagerly learnt using? *Should* he be pulled back *or* can he continue along the line adopted and *yet* eventually deliver to the Publisher a machine-readable document which complies with the requirements for descriptive markup and thus is free from procedural markup? I believe that providing an adequate response to this question can and will lead to a major breakthrough in our publishing habits and customs. This is the heart of the problem: integrating the *"dressing"*, *"undressing"*, and *"redressing"* of electronically created scientific documents. If this problem can be satisfactorily solved, then we shall achieve a balanced distribution of the tasks among all interested parties: Authors, Editors, Reviewers, and Publishers, as information suppliers, and Readers, Librarians, and Documentalists, as information consumers. It is only such a balanced distribution that will make every shoecobbler stick to his last and thus feel entirely comfortable. Finding the best ways is a chore for information scientists and technologists, both hardware and software developers, while the Publishers, too, should play an active role, as to both *research* and *guidance,* as I shall further discuss in section 6.

5.5. *"Text" versus "graphics"*

Conventionally, *artwork* is produced by the Author *separately* from the document text, submitted to Editor and Publisher as a *separate* part of the document, and finally *separately* handled by the latter. The conventional procedure is to compose complete documents by pasting artwork, after appropriate reduction, into open spaces left within the text. This approach is still widely used, but the situation is rapidly changing.

A major change at the Author's end is the generation of graphics by computers, both on-line and off-line, with the aid of graphics programs which can realize the boldest dreams. Creating graphics has become an essential and integral part of present-day research work. However, creating *graphics* is not the same as creating *artwork* to be included in scientific documents. The ease with which plotters and printers can produce large numbers of diagrams with parameter variation tend to affect the Author's critical selection power while the ease with which data (including the lettering and numbering of the axes) can be inserted into the diagrams tempt the Author to produce graphics swarming with illegible redundancy. Authors are easily inclined to overlook the differences in the aims of graphics in the research phase and artwork in the final publication. In the research stage, diagrams should be labelled with all data that facilitate identification and interpretation, whereas in the publication stage clarity is paramount.

Personally I also use graphics programs in which options permit me to omit all inscriptions in the final manuscript production stage. I then produce with a separate computer program letterings of adequate size and in accordance with the journal's manuscript requirements. Ultimately I paste them personally at the appropriate places in the figures. Waste of time? No! We have an excellent professional graphics department in the laboratory, where I could have this done. Generally, however, providing them with the detailed instructions would consume more time than when I do it myself. In addition, — and this is perhaps more important — I mentally integrate the diagrams and their inscriptions with the text. There is a continuous interaction: creating the artwork may lead to changes in the text, and conversely. Recently, I have also had available an image scanner, "drawing and charting galleries" and various DTP packages available, which might make me replace scissors, tape, gum, and correction fluids by electronic "cut, paste, crop, pan and zoom" procedures. Whether it will go faster remains to be seen. Essential is that it will yield artwork in electronic form. Will that be useful in the scope of the problem we are considering here: the dissemination of results of research in the era of electronic media?

Again I have introduced the subject by looking at *behaviour* rather than technology. Creating graphics is a craft; creating artwork is an art! Some Authors have an artist's gifts, others may develop hidden talents by using a computer, and perhaps the great majority of the Authors are mere scientific craftsmen and wish to remain so. For this reason and because of the diversity among the available technical facilities, both hardware and software, it is likely that the type of "artwork" produced at the Author's end will keep covering a very broad array of graphic documents, ranging from primitive hand-drawn diagrams, via complex but unretouched graphics as expectorated by the computer, to sophisticated, computer-generated artwork of genuine design quality, the latter being then available in the form of both high-resolution hardcopies and images on electronic media.

- All is serene in the exchanges between Authors, Editors, and Referees, if we accept the thesis that everyone will remain happy with hardcopies and the mail or fax!
- All is serene at the Author's end if he does as he likes!
- All is serene at the Publisher's end if he continues as he does!

The crux is the Publisher's desire to economize the production of his journals and to expand his range of products with various forms of databases. The Publisher should then be able to deal with all elements of the "artwork array". Clearly, the lower end of the range does not offer a challenge: a poor hand-drawn diagram simply demands redrawing. The elements of the array involving computer files constitute a different cup of tea if the Publisher wishes to avoid complete redrawing or rekeying. Memory space, resolution, speed, and transferability of graphics files between devices and programs are issues which make dealing with graphics far more complicated than handling text files, which simply consist of strings of characters.

Two categories of graphics must be distinguished:

(1) *bitmapped graphics* and

(2) *object graphics*.

Bitmapped graphics, also named *paint graphics*, *images*, or *pixel-based graphics*, are stored in the computer as patterns of bits. Such a digital pattern has a one-to-one correspondence to the pattern of dots in the image.

Object graphics, also called *draw art* or *line art*, are stored by the computer in the form of a compact mathematical description. Object graphics have several advantages over bitmapped graphics. When printed on a high-resolution output device such as a typesetter, diagonal lines in object graphics remain smooth, whereas such lines in bitmapped graphics become jagged. Object graphics also have the advantage that they can be scaled to any size and still look equally well, whereas bitmapped graphics deteriorate markedly when they are scaled to a larger size.

A brief but lucid overview of the technical aspects of graphics in the present and future perspective is presented by Dessy [2], who also points to the considerable problems associated with the lack of standardization as to both hardware and software. This lack also exists with respect to text files, but their format is generally far less complex, so that the exchange of text files between different systems is much simpler. In fact, many word processors include conversion features, which make import and export of text files in foreign formats a cinch. Although the situation with respect to graphics files is rapidly improving, much work remains to be done. Discussing this topic is beyond the scope of this lecture. A tutorial introduction *"Scientific programming with GKS: Advantages and Disadvantages"* by Flerackers [27] gives the layman in this field at least some insight into the status of graphics standardization, refers him to the key literature, and puts him up to a few acronyms in the huge and dark forest of "cryptographics".

A format which is becoming common for storing picture information is the standard of the American National Standards Institute (ANSI): Computer Graphics Metafile (CGM). Many graphics programs support the CGM standard and thus can import and export CGM files with the aid of conversion utilities.

Important in the present context is the notion that graphics require a *special* and *separate* treatment, not only in the era of conventional scientific document processing, but also in the era of electronic media.

Bitmapped and object graphics, have in common that they are generated and stored at the Author's end and must subsequently be transmitted to the Reader. There is, however, an interesting third type, closely related to object graphics, but with a much wider scope: graphics generated by the Reader on his computer using a program and a database, both released by the Author and disseminated as a truly *electronic publication* by the Publisher. This approach, already brought to life recently in some other fields of science, obviously also wells up in our spectroscopic environment with its vast databases and numerous graphical representations of spectra. Therefore this approach deserves special attention and emphasis. I'll discuss it in the last part of this lecture, but prior to this, I'll attempt to assemble the pieces of the jigsaw puzzle of conventional scientific publishing via hardcopy journals.

6. NEW APPROACHES TO CONVENTIONAL SCIENTIFIC PUBLISHING: A BALANCED DISTRIBUTION OF TASKS

— THE "APEM" APPROACH —

If I would have to comply with Professor Steinfeld's request to the invited speakers, my view should cover a future of not less than 50 years! His request reminds me of the fact that we are on an historial spot where in the time of the Roman Republic, more than 2000 years ago, the Pontifex Maximus was responsible for ensuring that the wishes of the gods were made known. He had the assistance of Augurs who were expert in interpreting the signs by which deities communicated their will to the earthy world in the voice of thunder or by flashes of lightning, by movements in the entrails of sacrificed animals, or by the flight of birds. If the Augurs would still be alive, I might let them cut open my computer and look whether its bowels move in the right way. This would be certainly accompanied by lightning and allow me to proceed with predicting the future of scientific publishing in the next 50 years! Unfortunately for me, but fortunately for my precious and priceless ally and companion, I was not able to seize the flaps of the ghostly coats of the Augurs when I saw them flying about the Forum Romanum, last night. I thus will have to face the verdict alone, here at the Forum Spectroscopicum.

1. The main constraints of the classical way of producing and disseminating scientific documents are
   (i) *repeated rekeying* of the texts by persons who do not understand the contents, such as secretaries and typesetters,
   (ii) *lack of convenience in the retrieval of information* in the framework of *complete journal volumes* when this information is not covered by keywords in subject indices or databases, and
   (iii) *lacking text search capability:* rapid localization of and access to detailed information within the separate publications.

   These constraints can be removed by the following approach.

2. The *basis* of all future publications will be *the author's primary electronic manuscript,* which will be produced where it should be produced: *at the author's keyboard;* the latter will replace the author's pen and secretary.

   — Here the term "author's primary electronic manuscript" or APEM specifically refers to documents consisting of text and graphics that will eventually be disseminated via *hardcopy journals.* It should not be confused with the term "electronic publication" (EP), the topic to be dealt with in the next section. —

3. The APEM is *not* the finished product, but the *rough product,* and forms the centre of all communication channels and production lines, as pictured in Fig. 5.

   Note first that the APEM should be *free of display-oriented, procedural markup.* Its format should thus be as simple as possible, preferably straight ASCII text with separate graphics files in a format such as computer graphics metafile, CGM. The separate files should be readily accessible for editing and retrieval. It will be convenient when they contain a minimum of *descriptive markup,* for example, in SGML.

   In principle, the Author can use the APEM in combination with a word processor or a DTP program to produce hardcopies of the manuscript in an appropriate format for internal use and for the Editor and the Reviewers. This MS may be as simple as most present-day MSs, but may also be a "Whistles and Bells MS", as symbolized in the figure. After revision, the APEM is transmitted to the Publisher, who can then do with it what he wants. The author, too, can use his APEM for other purposes, for example, his own database.

4. There appears, however, to be a snake in the grass, which comes into focus if we note in particular the bold arrows connecting the APEM via the "Author's DTP" with his "Whistles and Bells MS". These arrows point out *reversibility.*

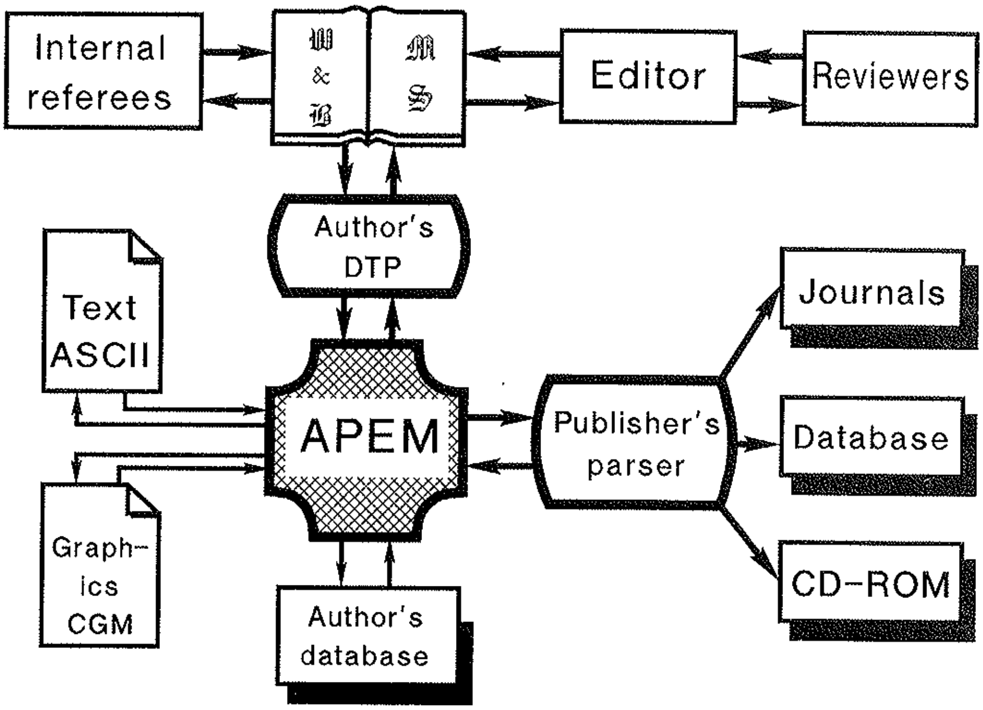

Fig. 5. Schematic diagram illustrating the central position of the APEM, the Author's Primary Electronic Manuscript, in the format of ASCII text files and Computer Graphics Metafile (CGM) graphics files.

Commonly, an Author will *not* produce a *"primitive"* text, but use a word processor or scientific word processor and produce an initial document provided with procedural markup codes. For simple text files this need not be a problem, since word processors usually have utilities to convert the encoded files into straight ASCII files. For technical documents including mathematical expressions and/or chemical formulae more difficulties may be encountered, in particular with WYSIWYG based formatters. Documents produced with ML based formatters, such as TEX, will be far easier to deal with, since they are in straight ASCII format.

More problems might arise when the Author uses a DTP program, but this is not necessarily so (Fig. 6). For example, a DTP program such as VENTURA Publisher [28] imports *separate text files, image files,* and *line art files,* produced with any of a broad choice of word processors and graphics programs. The DTP program combines the various files with a *"style sheet"* and stores all instructions in a so-called *"chapter"*, while leaving the *original* text, image, and line art files *intact.* In other words, *the Author may do whatever he wants to produce a hardcopy of his document, but the orginal files remain at his and anyone else's disposal.*

5. It is beyond the scope of this lecture to discuss the various ways in which scientific word processors and DTP programs operate. *It is likely, however, that for scientific publishing only those processors and programs will survive which can deliver, in addition to embellished CRC products, APEMs in straight ASCII and CGM or comparable formats.* These APEMs will form the *nuclei of all further interactions.*

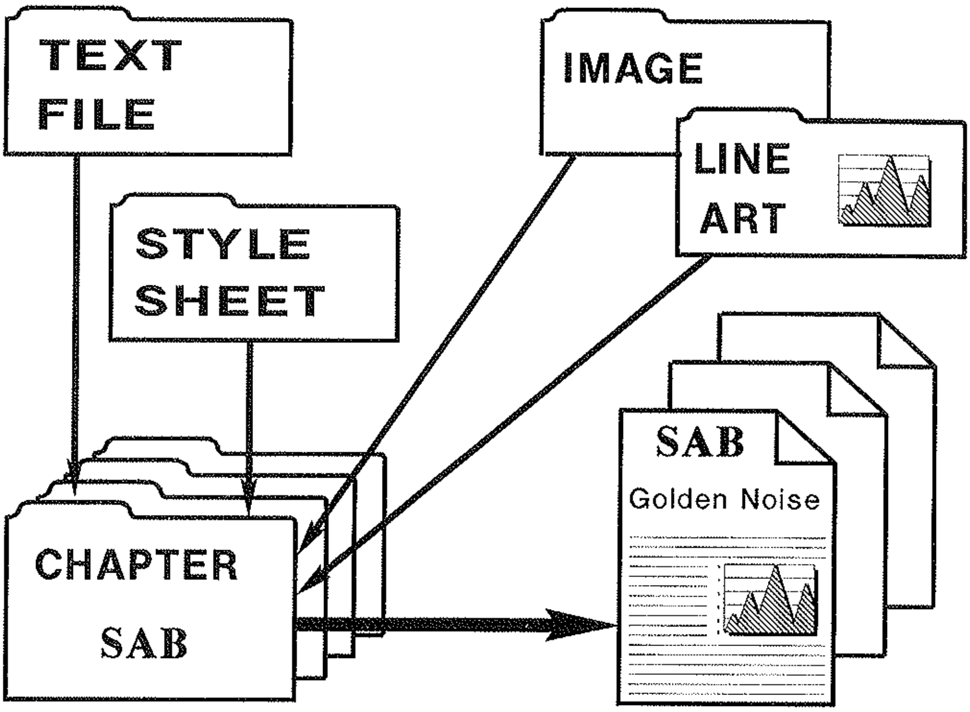

Fig. 6. Schematic diagram representing the operation of a DTP program such as VENTURA Publisher, which leaves the separate files intact and stores all instructions for the import and formatting of the various files for the DTP output in a file called "chapter".

6. Authors, Editors, and Referees will keep interacting via *hardcopies derived from the APEMs by the Authors*, except for the exceptional situations where Authors, Editors, and Referees can come to a mutual agreement upon the use of particular software and hardware facilities so that texts and graphics transmitted by networks or mailed on electronic media can be printed in the Editors' and Referees' offices with the same speed and ease as required for opening an envelope. For the time being, this appears to be an illusion! However, secretaries, being released from the task of having to type Authors' manuscripts, might be "promoted" to computer operators, which in fact means rebaptizing them as "typesetters"!
7. Unless we will enter a paradise of virtually absolute standardization, the APEM approach appears incompatible with an exchange of manuscripts on electronic media between Authors, Editors, and Referees. This statement does not imply that the APEM approach is doomed even before it can take shape; neither is it in contradiction with the successful approaches to the use of electronic media for the production of CRC manuscripts in the Authors' or Editors' offices discussed in section 3.2. In the latter situations, the Authors' and Editors' offices are pure and simple annexes of the Publisher's production department. This is precisely what the majority of Authors and Editors do *not* want! Those approaches can be only considered as short-term solutions to a basic problem, because they completely *rely on the tuning and compatibility of display-oriented, procedural markup of documents* at both the Authors' and the Editors' ends, the latter acting in fact as disguised Publishers.
8. *The APEM approach can provide for a long-term solution, since it is the pivot of the axis Author—Publisher.* This is at once clear if we realize ourselves that an Author can easily

encode the APEM with *descriptive markup,* such as SGML, which requires a minimum amount of work at the Author's side, while it provides the Publisher with a wealth of information on a document, which, in addition does not require rekeying.

9. Implementation of SGML-based electronic publishing systems appears relatively easy in those situations where Authors use ML approaches, also for mathematical expressions and chemical formulas, but may give more problems with WYSIWYG software. *R & D aimed at this implementation belong in the Publisher's domain.* Neither Authors nor Editors will consider it their tasks to be involved in the details, except for the details directly related to the Author's adding of SGML codes to the APEMs, for which the *Publishers should provide clear prescriptions.*

   The Publisher with the broadest coverage of the leading software and hardware and with the best guidance to Authors will reign the future market of scientific publishing and information communication.

To conclude, the essential difference between the production of hardcopy journals at present and in the future can be reduced to the difference symbolized in the level diagrams of Figs 1 and 2.

Author and *Publisher* will directly communicate and interact using an electronic document which essentially is only once keyed and descriptively encoded with SGML at the Author's side and is parsed, procedurally encoded, and printed at the Publisher's side.

Editors and *Referees* will maintain their positions as supervisors and guards and guardians of the pure doctrine, in the same way as they do at present.

The communication between *Authors, Editors,* and *Referees* may be speeded up to a certain extent by the use of electronic mail for reviews, editorial reports, and brief messages. Generally speaking, it is doubtful, however, that electronic media will also be used for the exchange of the scientific manuscripts themselves. This may happen only in situations where standardization can be pushed so far that Editors and Referees can print scientific documents with SGML markup without great expenses and efforts.

Publishers will see the desired return on investment reflected in reduced production costs of journals and in the marketing of databases of various types.

Readers and *Documentalists* will get convenient access to both general and detailed information.

The *Author*, finally, is crowned *king,* albeit king with an empty treasury, and will see his articles produced and disseminated more efficiently and more rapidly, with little extra effort on his side. The library shelves are maintained as his exhibition gallery, while, on the other hand, the impact of his work on the scientific community may be enhanced by the fast and convenient dissemination via improved databases *and* truly electronic publications, as explained in the next section.

7. THE TRULY ELECTRONIC PUBLICATION: DO WE NEED IT, DO WE WANT IT IN SPECTROSCOPY?

7.1. *A pioneer: Tetrahedron Computer Methodology*

During a "Communication Innovations Seminar" for Pergamon Editors in Oxford, June 1988 (cf. section 3.1), Todd Wipke announced the start of a "new international electronic chemistry journal in hardcopy plus disks": *Tetrahedron Computer Methodology* (TCM), which has been thereafter also featured in *"Innovating"* [29]. In the meantime, TCM has entered its second volume [30].

TCM focuses on new computer methods for handling chemical information, representing chemical entities, designing algorithms, and solving problems – particularly those relating to organic chemistry. TCM is the first chemical journal published and distributed completely electronically. Authors prepare manuscripts with graphics embedded using ChemText^{TM} or Microsoft Word^{TM} or with any word processing program as an ASCII file with camera-ready graphics. Authors may submit these electronic manuscripts to the Editor-in-Chief. Using ChemText, the journal produces uniform CRC directly from the author's file. These documents are disseminated as hardcopy. Thus far the approach is similar to those made by *Cancer Communications* [4], *Leonardo* [5], and *Applied Mathematics Letters* [6], discussed in section 3.1. However, TCM is distributed with *floppy disks,* in addition to the hardcopy format. The disks contain not only texts and, where possible, graphics of the printed version, but also *additional key information such as executable programs, source code, data files, and parameter sets.* The electronic materials are equivalent to the experimental section in a conventional paper. They are part of the paper and are refereed with the paper. In this way, scientists can publish material that cannot be printed, or which is the most useful to the Reader in computer-readable form.

Readers can reproduce published computer chemistry "experiments", apply a new algorithm to their own data, or use their own three-dimensional display software to view a molecular model, published in TCM, in ways not pictured in the printed article. Through a sequence of molecular coordinates a Reader might even observe animated molecular dynamics.

The electronic version of TCM *text* offers the Reader on a PC *full text search capability.* Further, the Readers can easily *transfer* references, molecules, reactions, and figures into their own personal documents or databases.

The first issues of TCM [30] provide additional information in Editorials, Instructions to Readers, and Instructions to Authors.

Thus far the description of this approach, which has encouraged me to consider whether we need and want a similar journal in spectroscopy.

7.2. *Electronic Supplement of Spectrochimica Acta?*

Hardly any of today's scientific investigations is performed without extensive and intensive use of one or more computers. Only a small fraction of the results can be embedded in a journal paper of the classical, printed form. In many instances this is adequate and sufficient. However, there also exist many situations in which the author has compiled data and developed models and computer programs with which the data can be manipulated in such a way that an "infinite" number of diverse situations can be visualized. A printed publication can only cover the underlying (mathematical) model in a generalized form, part of the data, and a few examples to illustrate the approach. Readers who want to use the data and explore the models developed must then rekey the data from the published tables (or exceptionally obtain them on an electronic medium "by writing to the Author") and make considerable efforts to retranslate and recast the mathematical formulas of the publication into a computer program. This is an absurd waste of precious time. The same applies to mere data compilations.

The conclusion is that there should be established adequate and "well structured" ways for Readers to obtain programs and data on electronic media in order that they can explore published approaches more efficiently and incorporate them effectively in their own research work.

The pioneering approach made by *Tetrahedron Computer Methodology* appears to be useful and adequate, and we may consider to which extent the Molecular and Atomic Spectroscopy Communities feel a need for following this example in such a way as to propose to Pergamon Press the start of an electronic supplement of *Spectrochimica Acta:* SAE, *Spectrochimica Acta Electronica.*

A prerequisite for such a proposal is to establish the market of attractable electronic manuscripts in the Authors' domain and the market of subscriptions in the Readers' domain. To wet the appetite I shall describe below an application from my own work which would excellently lend itself as a "tryout", but this is only one example, the main issue being that I wish to solicit response from the spectroscopy community, in the form of ideas, opinions, and criticism.

A major problem for research workers in an industrial organization may be the odium that sticks on "making software available to third parties", where the sting is in the term "software". Making a clear distinction between "electronic publication" and "software" appears indispensable to pull down possible "psychological and political barriers" that may exist in industrial organizations with respect to the dissemination of research results on electronic media. The following definitions may be helpful to settle this point.

- *Software* is a commercial product, which is brought onto the market with the purpose of making direct financial profits. Being a commercial product, software should fulfil a particular specification and the vendor should guarantee the customer that the software does what the specification promises. Otherwise, "no cure, no pay". In order for software to fulfil a specification, development by software engineers is required. The "power" of the software package and the degree of development are reflected in the price.
- An *electronic publication* is *not* the author's commercial product, but an extension and partial replacement of a classical publication, having the purpose to provide the "Reader" (*not* the "Customer" or "User") with information that may or may not be communicated in printed form, but can be far more effectively or even exclusively disseminated in electronic form to enable the "Reader" picking up the thread of the work immediately and manipulating the Author's data in the way described by the Author in the accompanying printed text. The "Reader" does not pay the Author, but gets the electronic publication as part of his subscription to the journal in which the electronic publication appears. On the other hand, the "Reader" has no claims: neither the Author nor the journal guarantee more about the correctness of the data and the proper operation of the program under the conditions used by the Author than at present is guaranteed with respect to what is published in classical form: all what the Reader is guaranteed is that the Author did his or her best to perform the research work in a scientifically correct and reliable way and that the Editor consulted Reviewers to separate the wheat from the chaff and to remove major flaws and smooth unevenesses in what is eventually accepted. This also implies that the program in an electronic publication should not necessarily work on any of the possible devices a "Reader" may use. It is made available such as the Author prepared and used it on *his* device. If a "Reader" wishes to make it operational on another device, — or wants to add whistles and bells —, it is up to him to make the required adaptations, in the same way as he will have to adapt at present, for example, an analytical procedure to his specific instrument when he wants to use a "literature procedure" devised for a different instrument.

  The objectives of an electronic publication should be precisely the same as those of a classical publication: spreading scientific or technical information and establishing the Author's prestige and reputation, but *not* making money by the author.

  Making money as such is a noble objective, but if applied in the present context, this will transfer the concept of "electronic publication" to the "software" domain, with the consequences of requiring specifications, development, guarantees, vendor organizations, etc. We then transfer the matter from the scientific to the commercial domain.

7.3. *Spectrum simulation in analytical atomic spectroscopy as an example of a possible electronic publication*

Emission spectroscopic trace analysis requires the availability of a database which permits selection of those analysis lines that yield the lowest possible detection limits. The latter depend on (a) the intrinsic properties of the lines, (b) the source characteristics, and (c) the structure of the background spectrum as dictated by the sample composition. This structure may give rise to what is commonly known as "line interference". Line interference is inherent in emission spectroscopy and therefore constitutes a persistent problem, which can be alleviated, to a certain extent, by the use of high-resolution spectrometry. However, part of the problems connected with line interference stem from (a) the lack of quantitative spectral data appropriate to each of the common excitation sources, such as arcs, sparks, inductively coupled plasmas (ICP), microwave induced plasmas, glow discharges, and hollow cathode discharges, (b) the intransferability of available data between different spectrometers, and (c) the lack of insight into the quantitative effect of line interference on the detection limits.

The absolute ideal would be to have available the transition probabilities of "all" spectral lines as well as quantitative models for calculating the spectral emission distributions for the various sources. An interesting attempt to spectrum simulation using this approach has been made by Burton and Blades for spectra emitted from an ICP [31,32]. However, the approach is currently limited by both the lack of accuracy and the limited availability of transition probabilities for all elements. The simulated spectra are only as complete and accurate as the gA-values used to generate them.

In Philips Research Laboratories we also made an approach to spectrum simulation, but different from the Burton and Blades *ab initio* approach. Our purpose was to measure spectra emitted from an ICP at high resolution and to derive physically resolved spectral data from these measurements. The convolution of the physically resolved spectra with the instrument function should then yield effective spectra for any specified spectral bandwidth. In agreement with a conclusion drawn at a Workshop [33] (*cf.* secton 7.4), we did not measure complete spectra, but confined ourselves to 80-pm wide spectral windows centred about prominent analysis lines. To cover a maximum of pitfalls during the design and development of the measuring and simulation procedures we chose the complex spectra of rare earth elements (REE) for the exploration of the approach. We thus measured spectra of 14 REEs as interferents in the spectral windows of 26 prominent lines of Ce, La, Nd, Pr, and Sm. To cover also very weak lines we exploited a dynamic range as large as 10^6, but this demanded some sacrifice from the resolution, so that we eventually obtained what we called "pseudo physically resolved spectral data", which for the time being are entirely adequate and can be treated in convolutions as truly physically resolved data, except at very small spectral bandwidths.

We have recently described the approach in detail with examples [34], published the complete data [35], and assessed [34,35] the results for internal consistency and *vis-à-vis* classical data compilations [36—39] and a recent compilation for an ICP [40,41]. The papers also address the quantitative effect of line interference on the detection limit, and the spectrum simulation program delivers the numerical data needed for the calculation of the relevant detection limit.

In summary, the publications [34,35] describe the approach and its evaluation, show examples, and cover the underlying data. *The only shortcoming is that the Reader is doomed to passiveness whereas the subject in fact urges him to activity!* The Reader would absorb the quintessence of the approach far more easily if he could himself specify parameters, choose examples from the infinite variety of possibilities, and watch the outcome on the computer screen. Not only would this facilitate his job as a Reader, it could also fruitfully contribute to the development of new ideas and induce cross-fertilization. Obviously, the spectrum simulation program is just one example of results of scientific research that would be excellently suited as a truly electronic publication.

Recognizing that this wealth of spectroscopic data including the simulation program may be important for the spectroscopy community as a benchmark and milestone as well as for its didactical value, we have redesigned and extended the program and data to make it operational on PCs using a compiled version on diskette. This user friendly program permits (a) simulations as described in the papers [34,35], (b), superposition of simulated spectra for any sample composition, and (c) calculation of the true detection limit according to [34,40,42,43], in all instances with the spectral bandwidth as a freely selectable parameter.

Within the scope of the 26 REE analysis lines and the 14 REEs as interferents the database is more comprehensive than whatever previous data compilation. However, vis-à-vis the complete data set spectrochemistry actually needs, it is not more than a drop in the ocean! Perhaps, however, a small droplet of heavy water!

A rare but salient curiosity is the closure of a circle: it is not only that 50 years ago *Spectrochimica Acta* was founded, but also that at that time Gatterer and Junkes in the Vatican Observatory at Castel Gandolfo started with an extensive analysis of rare earth spectra, the results of which were published as *Atlas der Restlinien*, Vol. II, *Spektren der seltenen Erden*. Specola Vaticana, Vatican City (1945) [36] — [Atlas of prominent lines, Spectra of rare earth elements] — This Atlas comprises two volumes, 32 × 40 × 3.5 cm each, with tables and photographs of spectra. I thus bring back a bit of "rare earth", in the guise of some thousands of little bits on a thin floppy, to the ground where the diggings began!

7.4. *Which types of information might be covered by a possible electronic supplement of Spectrochimica Acta?*

I now return to the starting-point and raise the question: "Which types of information might be covered by a possible electronic supplement of *Spectrochimica Acta?*"

First, the power of such a supplement should lie in the publication of programs with data that enable the *Reader* to become *actively involved* in the communicated work, with a minimum of additional programming. An important issue is that the leading scientists of the Molecular and Atomic Spectroscopy Communities should not only nod approvingly, but also seriously reflect about and *define concrete examples* where this approach could enrich scientific communication.

Second, an electronic supplement would also be suited for the communication of *mere data*, such as transition probabilities, tables of normal-coordinate calculations, and whatever atomic or molecular spectral data in either numerical or graphical form. The electronic supplement could in part also become an extension of a column recently introduced in *Spectrochimica Acta B:* "News on Fundamental Reference Data", composed by Alexander Scheeline [44–46] and supported by the National Institute of Standards and Technology (NIST) [formerly: National Bureau of Standards (NBS)]. This column is a follow-up of a Workshop: "Needs for fundamental reference data in analytical atomic spectroscopy", Scarborough, Ontario (1987), the Proceedings of which were published in *Spectrochimica Acta B* [47].

A third role of the electronic supplement could be to provide for a gradual built-up of an efficient subject index for *Spectrochimica Acta, Part A* and *Part B* as well as for *Spectrochimica Acta Reviews* (SAR), the successor of *Progress in Analytical Spectroscopy* (PAS).

Clearly, there will have to flow still a few billion litres of water downstream the Tiber before it will be all realized, but I consider it as a personal challenge to pursue the idea, and therefore I solicit your opinions, ideas, and comments.

8. CONCLUSION

To end this lecture, I do not want to explicitly repeat theses, proposals, or scattered conclusions. I rather would prefer to condense the entire philosophy a bit playfully into a few pictures, taken from that immense museum called "Italy". Let it be at the same time a homage to our hosts.

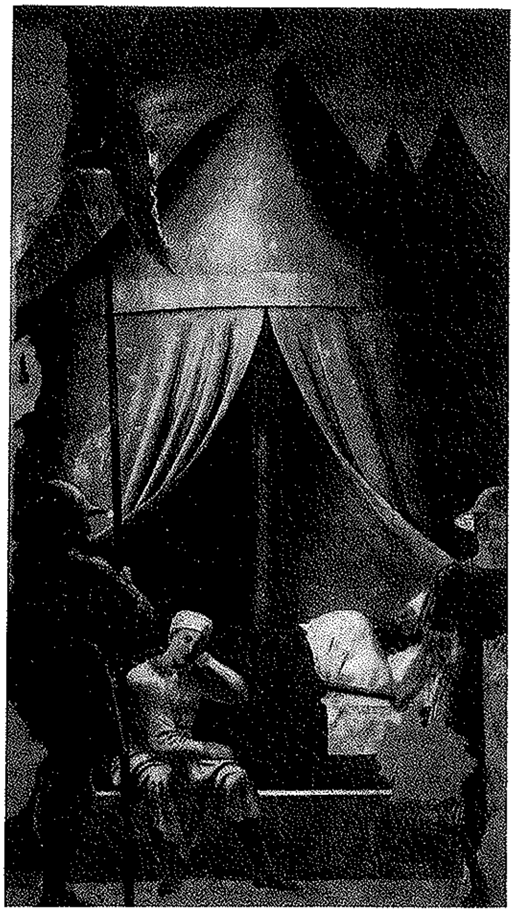

Fig. 7. Fresco by Piero della Francesca: *"Constantine's Dream"* (Arezzo, San Francesco).

We shall look at a few paintings of Piero della Francesca, a painter from Borgo Sansepolcro, reckoned among the Florentine painters of the Quattrocento, the 15th century. Piero and his confrères had understood how to communicate with their audience. In that time [48], paintings were made in commission, and the principals were tradesmen. These merchants had a good knowledge of mathematics, in particular geometry, and were capable of accurately computing the surface area of an army tent (Fig. 7) or a mantle (Fig. 8). They also eagerly computed the volume of sacks or bales of merchandise having an arbitrary, non-standardized form. For these calculations they reduced the volume of an irregularly shaped bale or sack to a composite of geometrically regular bodies, such as

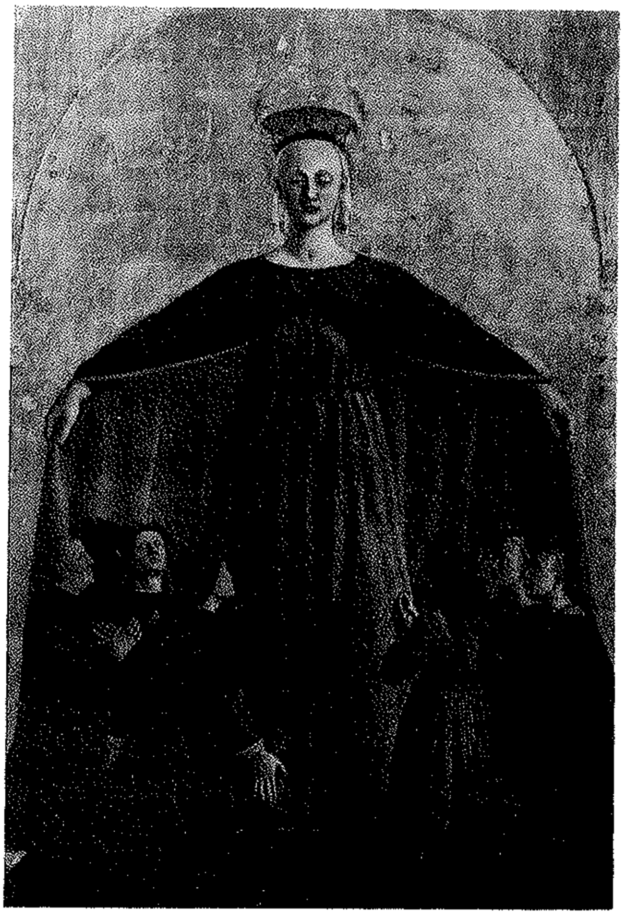

Fig. 8. Polyptych of the Misericordia, detail of the Madonna of Mercy, by Piero della Francesca (Sansepolcro, Museo Civico).

cylinders, segmented spheres, and truncated cones. When the merchants watched a painting, they looked for striking shapes that they could geometrically analyze so as to demonstrate their computing abilities among colleagues. This enabled them to proudly *reveal their understanding of the painting.*

The painters went along with this mentality and combined their own knowledge of mathematics with their artistic talents and embedded in their pictures sophisticated, geometrically analyzable shapes such as columns, cisterns, brick towers, and head-coverings. This is illustrated in the painting reproduced in Fig. 9, also from Piero della Francesca.

To conclude, *the message the painters wished to communicate was put into a form understandable for the recipients, who were thus apt to respond.* The recipients understood the structures that were hidden behind the objects they observed in the paintings, structures that were well thought and carefully worked out, as is illustrated in the study of a vase by Paolo Ucello, shown in Fig. 10.

Apparently there seems to be hardly any gap between such sketches of the Quattrocento artists and the magic pictures we call up on the screens of the present and the future: the Electronocento, in which era we shall ever more use electronic media to hand our messages to our audiences (Fig. 11). If we then also keep in mind the philosophy of the Quattrocento

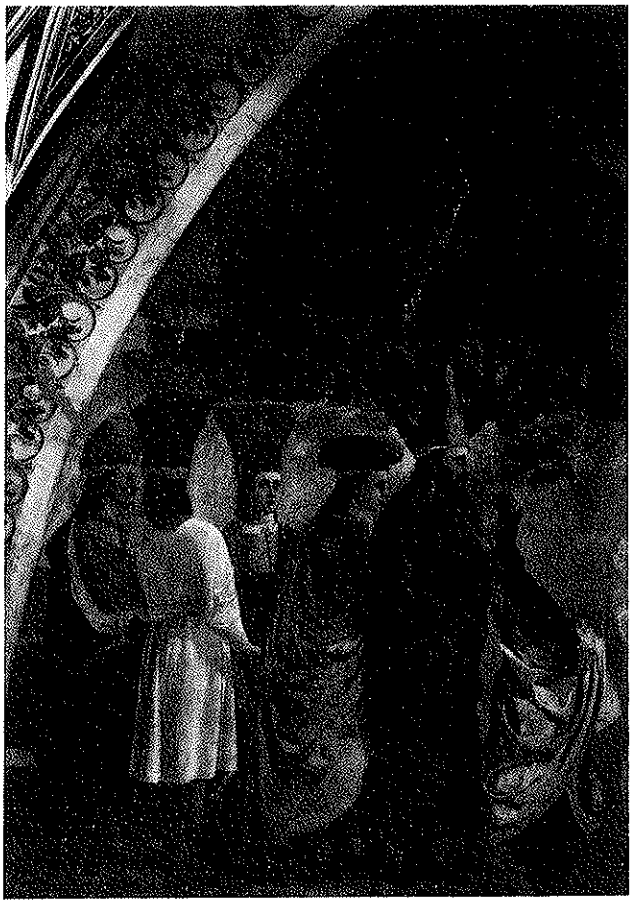

Fig. 9. Fresco by Piero della Francesca: "*Exaltation of the Cross*" (Arezzo, San Francesco).

artists, we may create a sparkling electronic, yet human, communication among scientists. Let our Golden Spectrochimica Acta play a pioneering role to realize this!

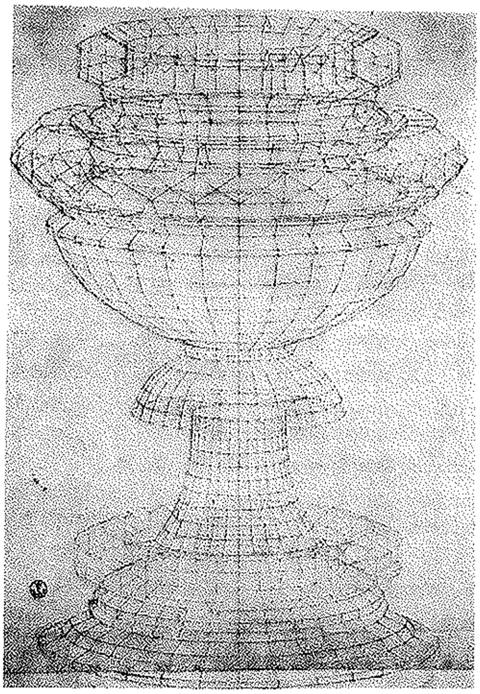

Fig. 10. Paolo Ucello: geometrical study of a vase (Florence, Uffizi).

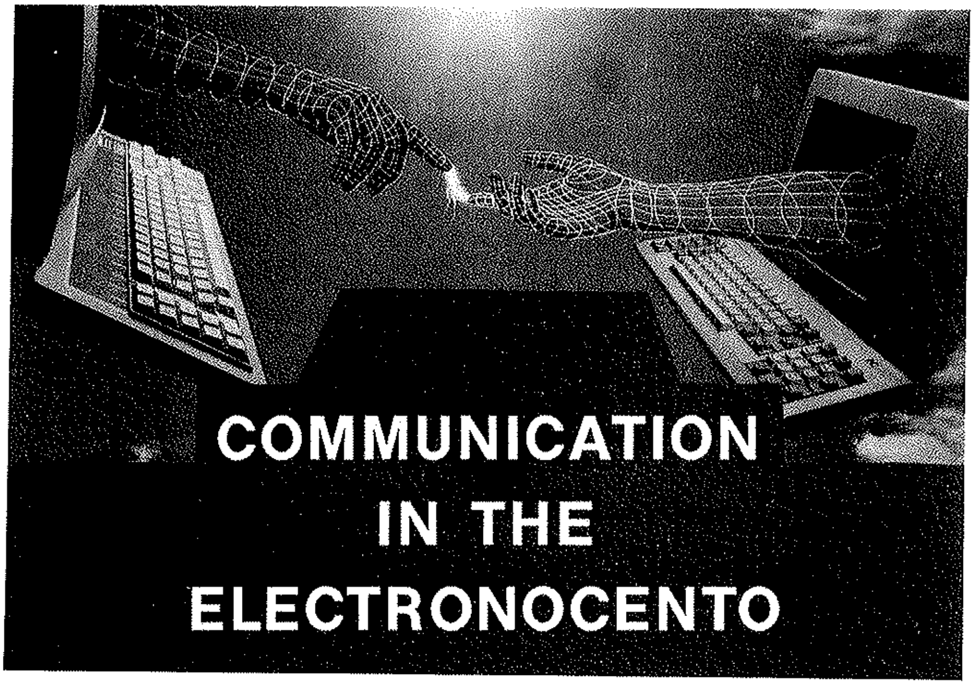

Fig. 11. Adapted from Michelangelo Buonarroti (Capella Sistina, Vatican City).

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Remarks on Scientific Publishing

DANIEL ADZEI BEKOE*
International Development Research Centre, Nairobi, Kenya

THANK YOU very much, Mr Chairman. I have two tasks to perform this afternoon: first, to say a few words on my own behalf, and second, to say a few words on behalf of the President of the Pontifical Academy. On my own behalf, I just wanted to provide the Proceedings of this meeting with a backward perspective in time to complement the forward prospectives. Some of us may not be aware that 50 years ago, there were very few universities or institutions of scientific research in sub-Saharan Africa, which is the area I know best. Since then, there has been a phenomenal increase in the number of such institutions; there are over 60 or 70 at the present moment. Not only has their number increased, but at least initially they were provided with the resources needed for their development. In the past 15 years, however, there has been a crisis in various aspects of life on the African continent, and scientific life is no exception. This crisis takes various forms, such as walking into a University library and finding that the most recent issue of a journal is 5 to 10 years old, and since then no later issues have been received, nor is there any prospect of seeing an up-to-date journal for the next several years. These matters stare one directly in the face, and I thought that, as we look forward to the next 50 years, we might spare a few moments to consider their implications.

These matters all result from the current economic crisis in Africa and its impact on governmental programmes. As we proceed with the development of various aspects of life in these countries, we find that fewer and fewer resources are devoted to the so-called "non-productive sector", and more and more attention is being paid to the "productive sector". The inescapable problem is that these two sectors interact: what may now seem to be non-productive may, in fact, be the basis of new production in the next few years. One therefore has to exercise great care to ensure that whatever macroeconomic policies are pursued, somewhere within the system attention is being paid to ensuring that the economy will not be left behind in coming years.

Scientific journals are an important aspect of this problem. After discussion with a number of organizations for many years, we are beginning to see some action. Organizations such as the International Council for Scientific Unions, the American Association for the Advancement of Science, the Academy of Sciences of the U.S.S.R., and a number of other bodies working together or separately are putting together programmes to ensure that scientific journals reach the libraries of institutions in the Third World. This has resulted from the joint efforts of these organizations, of Third-World representatives who have come together and discussed how the delivery mechanism is to be organized, and last but not least of the publishers of these journals, many of which are scientific associations themselves. A number of publishers have made available copies of journals, after the normal commercial press runs are completed, for distribution to institutions in the Third World. Various mechanisms are available for bringing the materials together in one location and arranging for them to be disseminated to focal points in different countries with the help of multilateral and bilateral agencies. While some of these agencies have kindly agreed to pay some or all of the costs involved, one is finding that more and more, we must turn to private publishers for assistance. What sort of help are we likely to get from private publishers? I could not resist the temptation to raise this issue before the present audience, especially given the large number of publications in which Pergamon is involved, as well as the number of publications which emanate from other private publishers in Europe. I will not go much

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* Member, Pontifical Academy of Sciences.

beyond raising the question here; I hope that as these various mechanisms proceed, we shall receive the cooperation of all concerned to ensure that normal levels of activity will be able to resume before too long. I say this because I believe that the current crisis is only a temporary phase—it would indeed be a pity if it were to be a permanent situation. We would like to think that, when the time comes and the crisis is resolved, we will be able to look our friends in the face and say, "Thank you very much for helping us out during a temporarily difficult situation!"

Even if we can assure a regular supply of journals in the future, there has already built up a number of serious gaps in various collections. This is where I believe some of the newer technologies, such as CD ROM, can indeed help. We have already seen evidence of what this technology can do, using either floppy-disk or hard-copy distribution. I think the beauty of some of this new technology is its potential for significant cost savings, by eliminating the great expense of having to mail hard copies over long distances. We should try to explore all of these various possibilities to reduce the costs of scientific communication.

Now, Mr Chairman, I would like to turn to the second part of my duty here and, in the absence of the President of the Academy, to say to Dr Elisabeth Maxwell, and through Dr Maxwell to Mr Maxwell and to Pergamon Press, how grateful the academy has been for the opportunity to host this very important and exciting meeting. We have received a feast of presentations which is by all standards rather rare. I hope that it will not be long before we see these papers put into print so that we can read them in the comfort of our homes, either electronically or in hard copy. A number of people have stood before us and said how intimidating it is to predict the future, and have then proceeded to do exactly that. I think that this is something which man lives for. Without a forward look, we would all be missing something in life and, even if we cannot be so sure that our predictions about the next 50 years are going to be very accurate, the exercise is still rewarding.

Lastly, on the question of communication. I was talking to a member of the group on the first day of our arrival here. He was saying how difficult it is now for one chemist to talk to another. I replied, "True, how true". Yesterday I was talking to another member of this group and he was saying how difficult it is now becoming for one spectroscopist to talk to another spectroscopist. I wish that within the next 50 years, whatever difficulties we may encounter, the problems of communication will be greatly minimized. So, on behalf of the President of the Academy, I would like to extend our thanks to Dr STEINFELD, to the invited speakers and participants, and to Pergamon Press for making this occasion possible. Thank you all very much.

Opening Remarks to the Symposium, "Future Trends in Spectroscopy"

GEORGE V. COYNE, SJ
Director, Vatican Observatory

NOT INFREQUENTLY for groups that assemble for scientific meetings in the Vatican there can arise some confusion about the relationship of the Pontifical Academy of Sciences to the Vatican Observatory (Specola Vaticana). I thought it would, therefore, be useful to make a few remarks concerning those two independent entities within the Vatican. Precisely at this time both entities are in a period of transition. I should like to follow up the biblical allusion made by Professor STEINFELD and tell you of the remark made by Eve to Adam as he started to leave the Garden of Paradise. Although the sacred author has not actually recorded the phrase, Eve is said to have whispered: "Adam, I think we are entering into a period of transition". As to the Academy a new President, Professor MARINI-BETTÒLO, and a new Council have just recently been appointed. As to the Observatory, after having initiated a new research institute in Tucson, Arizona in 1981, we are now engaged there in the construction of the Vatican Advanced Technology Telescope, which will be the first of a new generation of telescopes leading up to a 16 m reflector. However, even though both institutions are in a period of transition, their institutional structure remains well defined. I would like to make a few remarks about those structures. I will not enter into the history of the two institutions. These are amply documented in writings and you have just heard a brief historical résumé from Professor MARINI-BETTÒLO; in the following contribution, Father MCCARTHY provides a historical summary of the Astrophysical Laboratory, associated at one time with the Vatican Observatory.

The Academy and the Observatory are two distinct institutions within the Vatican. The Academy is a unit under the administration of the Secretariate of State, the Observatory under a different unit, the *Governatorato*, the Interior Ministry, if you will, of the Vatican. So with respect to budget, personnel, etc. they report to different units. The Academy is precisely that, an Academy. It promotes research. The Observatory is a research institute. It does research. Some of its current most active areas of research are: general relativity, the observational limits of cosmology, modelling of quasars, rates of star formation in the local group of galaxies, stellar spectroscopy, polarization in cataclysmic variables, metallic variation in the Milky Way. Both the Academy and the Observatory sponsor meetings and publish books which report the most recent research in various areas of the natural sciences. There are close institutional relationships between the two institutes. The Director of the Vatican Observatory is *ex officio* a member of the Academy. The Academy organizes many Study Weeks. About every 8 years one of these Study Weeks is on a topic in astronomy or astrophysics and the Observatory is very much involved in the organization, the conduct, and the resulting publication of those Study Weeks. Since 1958 these have included Study Weeks on the following topics: Stellar Populations, Active Nuclei of Galaxies, Astrophysical Cosmology and Large-scale Structure of the Universe.

There have been many personal ties between the Academy and the Observatory. Father DANIEL O'CONNELL, SJ was at one time both Director of the Observatory and President of the Academy. The second president of the Academy was ABBÉ GEORGES LEMAÎTRE, one of the founding fathers of the Big Bang model in cosmology.

It is with pleasure that we welcome you here. You help to remind each of our two institutes, the Academy and the Observatory, of some common, precious memories of the Astrophysical Laboratory with which we have both had close association in the past.

Spectral studies at the Vatican: Laboratory analysis and telescopic observations

MARTIN F. MCCARTHY SJ
Specola Vaticana, Città del Vaticano

Abstract—A review is presented of studies of spectra at the Vatican Observatory in the past century and a half. These began with the pioneer research of ANGELO SECCHI at the Collegio Romano in grouping stars according to their surface temperatures into four spectral types. Work continued under GATTERER, JUNKES and SALPETER in the Astrophysical Laboratory at Castel Gandolfo, where the chief work was the production of the Vatican Spectral Atlases of elements and molecules. Now (1989) stellar spectroscopy occupies the Vatican astronomers who use the largest telescopes with improved image processing techniques to classify spectra of faint stars and galaxies.

INTRODUCTION

SPECTRAL STUDIES in the Papal States began in the middle of the last century with Father ANGELO SECCHI SJ working at the Observatory of the Collegio Romano which had been erected atop the Church of St Ignazio in downtown Rome.

SECCHI was a careful observer who knew his equipment and its limitations, who could formulate carefully his experiments and observations and took great pains in communicating results achieved. That he was a skilled artist in those days before photography made its entrance into our sciences is attested by the careful sketches he made of solar phenomena and by the very clear and accurate drawings he produced to illustrate his famous four types of stellar spectra [1]. SECCHI set a fine example for all of us in stellar astronomy by his faithful and constant turning to concrete confirmatory evidence from the laboratory. This is beautifully illustrated in the case of his finding evidence for carbon in the stars [2].

All of SECCHI's figures are the results of visual estimates made at the telescope and we admire his success in representing nature so correctly and beautifully. Even in the mid nineteenth century, SECCHI, unlike his successor at the new Vatican observatory, Father JOHN G. HAGEN SJ of variable star fame, was not opposed to the use of photographic processes in astronomy. We note SECCHI's use of photography [3] at the time of the total solar eclipse he observed from Spain in 1860. No, SECCHI was not all opposed to photography in solar or stellar physics; however he chose not to wait for the predecessors of Kodak, Afga and Gaevart to appear in order to furnish him with the proper receiver. He went ahead with the best wide angle camera yet devised, the human eye, and he coupled that with the excellent telescopes by CAUCHOIX and MERZ to give his colleagues and all of us new insights into the physics of the stars including the sun.

SECCHI's work in observational spectroscopy ended with the "troubles" of 1870, although he continued his analysis and publications until 1877; he died in 1878. Spectroscopy continued in Italy under RESPIGHI and ABETTI. When astronomy returned to the Vatican it was to a new observatory established by Pope LEO XIII on Vatican Hill and no longer atop the old Collegio Romano. SECCHI's instruments had been transferred to the new Italian observatory and these and SECCHI's original drawings of solar flares and prominences are visible today at the Monte Mario Observatory where relations with our Italian colleagues are, and have been, both happy and cooperative. As noted above, Father JOHN HAGEN was interested in visual observations of variable stars and this led to the production of eight volumes of *Atlas Stellarum Variabilium* [4]. HAGEN did all of his own work, without photographic aids. Father GIUSSEPE LAIS of the Oratorian Fathers, introduced photography to the Vatican with the *Carte du Ciel* [5]. This was the Vatican's contribution to the international project of mapping the heavens with the same type of telescope installed in several different latitudes to insure complete and overlapping coverage. LAIS, however, was recording the direct images of the stars and not spectral ones.

Indeed spectroscopy returned to the Vatican agenda only after the transfer in the early 1930s of the Specola (or Vatican Observatory) from the even then, light-saturated Rome to the cleaner and darker skies of the Castelli Romani at the Papal Palace at Castel Gandolfo. Here, two divisions of the always small Vatican Observatory staff began to function together in the new site thanks to the generosity of Pope PIUS XI; the traditional astronomy observatory with new telescopes and plate measuring equipment, offices and darkrooms was established on the rooftop of the papal palace, while the basement floor was dedicated to a branch of our science, which was quite new at the time: laboratory astrophysics [6].

Let us look first at this brand new branch of laboratory astrophysics and then see how it has aided the progress of the older astronomical observatory.

ASTROPHYSICAL LABORATORY AT CASTEL GANDOLFO (1933–1977)

Astronomy at the Vatican started for a very practical reason: the Julian Calendar needed reform [7]. This specific work was carried out by a team, the leaders of which were Dr L. LIGLIO of Ciro in Calabria and Father C. CLAVIUS of the Collegio Romano. They represented astronomers on the commission appointed by Pope GREGORY XIII. We regard 1582 as the date marking the beginning of serious astronomical work sponsored at the Vatican [8].

The astrophysical laboratory of the Vatican had an equally practical purpose. Father ALOIS GATTERER SJ, called from Austria by PIUS XI in 1933 to aid in the research work of the new observatory at Castel Gandolfo, decided to study the physical and chemical nature of meteorites. He recognized long before others that this was one of the most interesting problems in current astrophysics. His choice was greatly facilitated by the fact that the Vatican had been given a large and precious collection of meteorites as a gift by Marquis DE MAUROY and his wife [9]. This collection is larger and more precious today by reason of the numerous additions in the form of gifts made to the Curators of the Vatican's collections, especially under Father E. W. SALPETER [10] and through modern improvements in classification and storage [11]. It is noteworthy that some of the last studies reported from the Laboratory were devoted to meteorities [12].

Academician GATTERER's first experiments in 1935 revealed the peculiar difficulties to be overcome in the analysis of meteorites [13]. It was this: the great abundance of lines, especially of iron, makes the identification of the weaker components most difficult and at the time this difficulty seemed insuperable.

Further GATTERER acted now, just as Father SECCHI had done some 75 years before; he used the equipment he had at hand, worked very well with it, and had the courage to leave to other times and persons what he could not hope at that time to cope with: the identification of such faint and crowded lines. What GATTERER together with Academician JUNKES decided to do was to photograph the entire available arc and spark spectrum of iron at high dispersion. This was the beginning of the Vatican Atlas Project.

It has always been a source of merriment in our community at Castel Gandolfo that at the same time as our spectroscopists downstairs in the Laboratory (ground floor of the palace) were moving to higher and higher dispersions in their spectral work, upstairs in the dome, we were moving to low, lower and then to the very lowest dispersions to pick up and discern fainter stars with limited but identifiable spectral features.

GATTERER and JUNKES used three different exposures to bring out all parts of the Fe spectrum with sufficient clarity on a single plate. These were enlarged eight times so that the wavelength of each line which appears clearly can be indicated on the plate. The authors felt that a glance at the plate provided all that was necessary for a rapid identification in the comparison spectrum and for an easy wavelength determination in the adjacent research spectrum by means of the method of interpolation.

The first two atlases were published in 1935, two years after the Laboratory was dedicated and presented: *The Spark Spectrum of Iron* (4650–2242Å): 13 Plates; *The Arc Spectrum of Iron* (8388–2242 Å): 21 Plates. See the Appendix for a fuller listing of the Atlases as noted by JUNKES and SALPETER [14].

Of great concern to GATTERER and JUNKES was the detection of small amounts of impurities in a basic element for spectrochemical analysis; high purity was a fundamental requirement. Spectral purity was attained by standard samples of "spectropure" substances prepared by HILGER (London), by the American Society for Testing Materials, by the United States Bureau of Standards (Washington) or by the Molybdenum Co. (Austria). Later Father GATTERER [15] succeeded in a simple yet satisfactory manner in purifying the carbon electrodes and he reported this in one of the early issues of *Spectrochimica Acta.*

Typical of the auxiliary instruments designed by the Laboratory in the early days when working with the often very irregularly shaped meteoritic samples was a practical arc and spark holder moveable in all directions and easily adjustable for all samples even for the heavy iron meteorites. This was designed by the master mechanic of the Vatican Observatory, Brother CARL TREUSCH, and is described by GATTERER [16] in the first volume of *Ricerche Spettroscopiche* published by the Laboratory.

GATTERER designed the projection comparator for exact and rapid comparison of two spectra photographed on different plates; the enlargement was 20 times; the spectra to be compared could be brought into very exact juxtaposition by means of the adjacent iron spectrum. This projection comparator and its use are described, also by GATTERER [17].

We note that besides the major productions of the Laboratory, which were the Spectral Atlases listed in the Appendix, there was a very steady contribution to the current literature which deserves reading and consultation even today. We have mentioned the two principal places cited; the laboratory's "house journal": *Ricerche Spettroscopiche della Specola Vaticana* Vols 1–3, and *Spectrochimica Acta*, now celebrating its 50th year. Father GATTERER served as Editor for the analytical section.

Several colleagues have mentioned to us through the years that one of the features of the Vatican Observatory has been that it has always been "small but good". Often the staff have wished that it could be "just a little bit larger" but we try to be grateful for all the fine colleagues we have working alongside us.

Now let us speak of the scientific staff of the astrophysical laboratory and specifically of Father ALOIS GATTERER SJ (1886–1953), Father JOSEF JUNKES SJ (1900–1984) and Father EDWIN W. SALPETER SJ (1912–1976). Each was trained in Austria or Germany, each entered the Jesuit order in his own homeland, each was ordained to the priesthood and came to the Vatican Observatory assigned by Superiors for scientific research work. All did special studies in physics and chemistry at the doctorate level. GATTERER and SALPETER at Innsbruck; JUNKES at Innsbruck and Basel. Because of World War II, SALPETER was sent to Argentina where he studied theology, was ordained and later taught physics in Buenos Aires. In 1947 SALPETER came to work at the Vatican where Father GATTERER and Father JUNKES had preceded him by some 13 years.

They formed a splendid team in the Laboratory at Castel Gandolfo. GATTERER was the clear leader of the project; he planned the laboratory, set the project goals, first for the studies of the meteorites, then directly for the difficult and important work of the Atlases, each of which had its own problems, obstacles and challenges. Father JUNKES was the "worker–theoretician" of the group, who also served for several years as the religious superior of all the Jesuits at Castel Gandolfo. JUNKES was happy in the shadow of Father GATTERER, always his helper and most content when he could find spare-time for calculations involving ray-tracing for crossed-prisms and for deriving effective wavelengths. SALPETER was the "instrumentalist" of the group, who "made things work" even for us, the astronomers. He supervised the details of the daily production of the atlases and their quality control as these were stockpiled for the future to fill requests and orders. Three laymen assisted faithfully over the years in the Laboratory working on the mailing, packaging and shipping of the atlases. The person who "made it all work" and coordinated everything was Brother CARL TREUSCH, our master mechanic. He was trained with Zeiss at Jena and is best is known as the one who first mastered the art of photographing the elusive "Green Flash" and recording it for posterity.

The study of the "Green Flash" was not a part of the formal work programme of the Laboratory or of the Observatory but rather a "post-work" or "pre-work" hobby or "divertimento at twilight" performed in order to test (we had received a gift of many rolls of Kodak colour film) whether or not this elusive and controversial phenomenon could be recorded. It was recorded very succesfully and after encouragement had come from Professors MINNAERT and MENZEL and other friends, Father O'CONNELL decided to present TREUSCH's photographs in a book which was based on the colour film observations of the Green Flash. All these TREUSCH had made with the telescopes atop the papal palace. The text was O'CONNELL's, the photographs were all by TREUSCH [18]. Other staff members from the Laboratory and from the Observatory added their encouragement and proofreading and enjoyed what had become a "fun task" at dusk at Castel Gandolfo: looking for the flash. These photos were later widely reproduced in *Scientific American* [19] and elsewhere.

We cannot present here anything like the full details of the work of the laboratory. Some of it was routine and some was drab, and there were small crises and adventures and failures and successes. Each Atlas was different; each offered a new challenge, and some required new or modified instrumentation. There were concerns about "order-separators", "predispersers" and problems with hollow cathodes and glow discharge patterns from the Grimm lamps. There were new and special problems associated with certain elements such as thorium and some compounds such as hafnium oxide.

What cannot be minimized and must be stressed is the active spirit of wholehearted collaboration, consultation and communication which marked the three laboratory astrophysicists; GATTERER, JUNKES and SALPETER. This spirit stamped their works and days at Castel Gandolfo with marks of excellence. To attempt completeness in listing collaborators with proper acknowledgements would be to court disaster by omission and would offend many dear and deserving friends of the Laboratory and Fathers GATTERER, JUNKES and SALPETER. Here I can only mention professors MILAZZO, INTONTI, KIESL and RITZL. This, at least, balances Italy and Austria, the home bases for two prominent groups of colleagues who engaged in earnest research with our three Vatican spectroscopists. Across the Atlantic, C. M. SITTERLY, W. F. MEGGERS and C. C. KIESS were most esteemed co-workers and friends.

This spirit of cooperation shared between co-workers became concrete through active participation in colloquia and conferences. GATTERER, JUNKES and SALPETER recognized the dangers facing a small staff from effects of isolation; however, thanks to the same assistance from the Holy See which made the Laboratory's foundation and productivity so effective, our three Vatican astrophysicists found it possible to share in the growth of their science by participation in meetings, assemblies and colloquia. Again, a full enumeration would be dangerous and incomplete, especially for the early years. Let me name here only six samples of organizations in which the Vatican team participated as members or as representatives of the Holy See: the International Astronomical Union; the Colloquium Spectroscopicum Internationale; the International Union of Pure and Applied Chemistry; the Swiss Society for Applied Spectroscopy; the Italian Metallurgical Association; and the World Meteorological Organization.

The end of the Laboratory can be told briefly. In 1976, Father SALPETER died quite unexpectedly. Father GATTERER had died some 23 years earlier. Now Father JUNKES was 76 years of age and in gradually declining health; he had finished his own immediate projects and opted to retire to his homeland. In 1984 he died and was buried in Munich. There were no successors. Several members of the community at Castel Gandolfo had searched among younger Jesuits for future colleagues, who might eventually become successors of Fathers JUNKES and SALPETER; the search was constant and covered many countries where spectral studies were flourishing. It was not successful. Some candidates were trained in spectroscopy but for one reason or another could not join in the work; other possible candidates were put off by the long specialized training programme required. With the approval of the Holy See, the Vatican Observatory looked to the dismantling of the Laboratory and to the distribution of the materials (chiefly plates for the Atlases and "spectropure" elements).

Now the hallowed research workplaces of the former Astrophysical Laboratory at Castel Gandolfo are devoted to lecture halls for conferences on scientific topics. Most recently an international conference on "Physics, Philosophy and Theology" was held under the direction of RUSSELL *et al.* [20]. On alternate years these same halls are the meeting places for about 25 young aspiring graduate school candidates who come to the Vatican Observatory Summer School in Observational Astrophysics [21]. Approximately 18 nations of the world have been represented at Castel Gandolfo for an intensive month of lectures and exercises. Experienced teachers who are well known for their research have offered their services for the training of their future young colleagues in science. A special effort has been made, and succeeded in 1986 and 1988 to attract worthy candidates from the developing nations. No, things are not the same now in the halls of the Laboratory of GATTERER, JUNKES and SALPETER. However, something of the same quest for excellence and the same international flavour seems to mark the school as it did so very well the work of the Astrophysical Laboratory.

TELESCOPIC OBSERVATIONS OF SPECTRA AT THE VATICAN OBSERVATORY

Let us pick up the story of stellar spectroscopy from the time of the inauguration of the new astrophysics laboratory at Castel Gandolfo and try to see how the two units worked together but on different paths. Both had common goals but different techniques and moved *per aspera ad astra*: through "rugged ways to the stars".

A young post doctoral scholar from Germany, HERMANN BRÜCK, joined the Staff of the Vatican Observatory in the mid 1930's at the invitation of FATHER STEIN, then Director. Later BRÜCK became Director of the Dunskink Observatory in Ireland and later of the Royal Observatory Edinburgh, as well as Astronomer Royal for Scotland. BRÜCK had a new Zeiss double astrograph to work with at Castel Gandolfo and together with Fathers JUNKES and MATTHEW TIBOR SJ, a young Hungarian Jesuit, he investigated the features of the new instrument. They used the new large Zeiss spectrograph which was attached to the Cassegrain focus of the 60 cm reflector and also tested, first singly, and then in combination, the fine pair of prisms of 4° and 8°. Each was 63 cm in diameter and adaptable both to the reflector just mentioned and to its companion the Zeiss Vierlinser of refractor of 40 cm; this latter was intended for wide angle photographs of the Milky Way fields to study the spectral and spatial distribution of stars. As noted above, the skies of Castel Gandolfo were, at that time, far superior to those in downtown Rome.

The first spectral studies were successfully carried out by BRÜCK [22] and TIBOR [23–26] and published in the *Acta* of the Pontifical Academy. BRÜCK observed the 1937 eclipse of *Zeta Aurigae* and used the 12° combination prism with the 40 cm refractor. BRÜCK was later chosen as a member of the Pontifical Academy and served on its Council. The studies by Father TIBOR concerned Milky Way fields in Cepheus, Lacerta, Cassiopeia, Perseus and Taurus-Aurigae.

About the same time, Father JUNKES was making his own investigation with the 40 cm refractor plus 4° objective prism of field in Cygnus. He noted that because of the steep colour correction aimed at providing optimum focus for the blue region of the spectrum most commonly used in astronomical photometry, the spectral range achieved by the 40 cm refractor was limited. A focus for the yellow region was possible but work in the red proved unsatisfactory when surveys of different fields were planned. JUNKES next turned to tests of the spectral performance of the 60 cm reflector. Of course this telescope did not have the wide field coverage achievable with the refractor but it could go fainter and yield better resolution. When attached to the 60 cm reflector the 4° and 8° prism each worked satisfactorily and produced, under JUNKES' guidance, a fine set of spectra especially for selected standard stars. In the opinion of Academician W. W.

MORGAN of Chicago, the late Academician B. STROMGREN of Copenhagen, Dr BERTIL LINDBLAD of Stockholm and Dr WALTER BAADE of Pasadena, these were among the finest spectra they had ever seen. Unfortunately, when these two "jewels": the 4° and 8° objective prisms were combined to yield the highest possible dispersion: 80 Å mm^{-1} at H_γ and 316 Å mm^{-1} at H_α, the combined weight proved to be too heavy even for Zeiss and the effects of flexure made long exposures unsatisfactory.

Friends of the astronomers at the Vatican Observatory, including the above mentioned collegues and also Professor JASON NASSAU of Cleveland, advised that consideration be given to the purchase of a Schmidt type telescope which would combine a spherical reflector with a special correcting plate to give a fast wide angle camera which would accommodate the objective prisms both singly and in combination. This seemed the "way to the stars" and after World War II ended, this was proposed and accepted by his Holiness Pope PIUS XII. The English firm of Cox, Thompson and Hargreaves was commissioned to build the instrument. Here we had a case of constructing a telescope to fit the auxiliary equipment; that decision was sound as is shown by the many services it has given to astronomy. The story of the Vatican Schmidt is told elsewhere by O'CONNELL [27], by MCCARTHY, *et al.* [28] and by TREANOR [29]. Here I wish to point out the very important role played by Father JUNKES of the Laboratory; he designed the reflecting guider telescopes which had the great advantage of being able to "look at" the same region of the sky which the Schmidt camera, with its attached prisms, was photographing. This made for much easier guiding, especially at large hour angles [30].

In 1958, the Schmidt was installed and blessed by its donor, PIUS XII; in 1961 it went into routine service and has performed very well until the "lights came up" and the site at Castel Gandolfo became "light struck" and impossible for research astronomy at optical wavelengths. This occured in about 1975.

What was accomplished with the Vatican Schmidt in its active years at Castel Gandolfo? It was wonderful to have at one's disposal a dedicated telescope with attachable prisms. We of the Vatican team of young astronomers used it and had lots of fun and good work. We received much help and advice from Fathers JUNKES and SALPETER; Father GATTERER died in 1953 before any of the "younger fathers" (BERTIAU, TREANOR, MCCARTHY and COYNE) came to Castel Gandolfo. Our Director, Academician O'CONNELL, never observed with the Schimdt. Father O'CONNELL [31] kept very busy on the palace rooftop with the 60 cm reflector and photoelectric photometer.

Most projects were concerned with problems of the structure of the galaxy. We were fortunate in being able to choose "only the best nights" and these, at Castel Gandolfo in those years were many, especially during the summer months of no rain, fine seeing and excellent transparency. The industrialists in the Campanga Romana, some hundred meters below our telescopes, had not yet illuminated their goods and buildings and entrances to the extent that they did some 15 years later. When they did and when the tiny towns of the Castelli grew large, then our limiting magnitude shot up from 19.5 to 15.7 and this was a substantial loss of light gathering power.

Some of the major research projects in spectroscopy included the following:

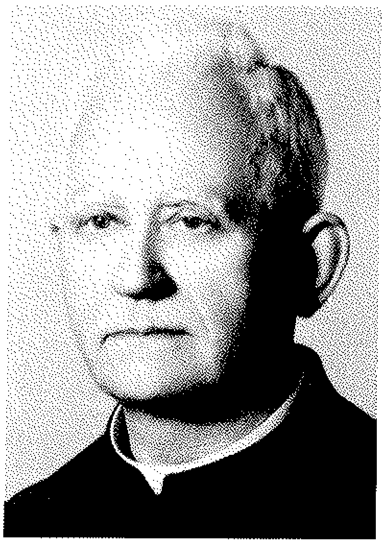
(1) Study of spectral features to serve as criteria for luminosity and metallicity in the near–u.v. region, especially for stars like our own sun [32].

(2) A spectral survey to detect the interstellar absorption band at 4430 Å. This led to the detection of regions with heavy absorption from interstellar dust. Academician TREANOR's were some of the pioneering studies [33]. These were followed up by slit spectroscopy and narrow band interference filter photometry. Now CCDs are used for this kind of research by colleagues throughout the world.

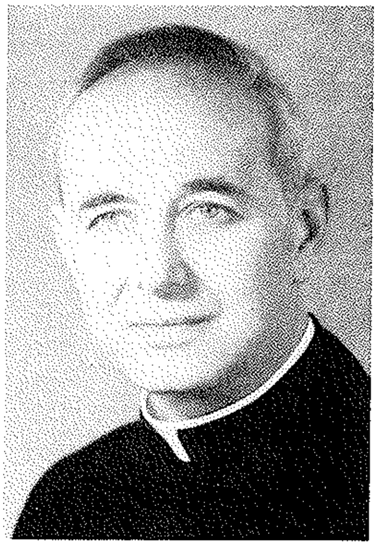
(3) To make the best use of the Vatican Schmidt, TREANOR made a classic study of plate filter combinations available; this study was prepared for the dedication symposium of the then largest Italian telescope of the Padova Observatory on Monte Ekar [29, 34].

(4) Much effort was given to the study of emission objects in various fields along the Milky Way. BERTIAU and MCCARTHY [35] made a listing of previously discovered emission stars of early type along the galactic plane in the northern hemisphere.

Father A. Gatterer SJ



Father J. Junkes SJ



Father E. Salpeter SJ

The "Three Jesuits" who led the *Specola Vaticana* during the past half-century.

TREANOR and MCCARTHY [36] discussed improvements in detecting very faint emission sources. MCCARTHY [37] tested this procedure on a field in Cygnus and discovered many new emission stars. It was noted that for the most effective detection of emission sources the highest available dispersion should be used. Thus most of our studies were made with the 12° combination prism attached. Academician COYNE [38] followed up in a full scale discovery programme which combined the use of the Vatican Schmidt and the 12° prism together with precision photoelectric photometry of the objects showing H_α in emission. The facilities of the University of Arizona in Tucson, Arizona, U.S.A., were used for the photometry. Several colleagues on both sides of the Atlantic Ocean assisted COYNE in this second largest survey programme ever undertaken at Castel Gandolfo.

(5) Selected studies of the spectra of variable stars. Among these were successful efforts made to correlate with Father O'CONNELL's observations of special eclispsing binaries as part of a world wide observing campaign. While O'CONNELL [39] was busy observing with the Zeiss reflector, recording photoelectrically the variations of Zeta Aurigae during a critical phase of its minimum, TREANOR and MCCARTHY worked simultaneously with the Schmidt making exposures of U.V., blue, yellow and red spectra on the Zeta Aurigae field. The various plate-filter combinations were changed through the night [28]. Other variable stars studied spectroscopically included Cepheids, W Ursae Majoris stars and several galactic novae. We note that many photometric studies of variable stars were carried out at the Vatican Observatory especially by Father DEKORT and by Father WALTER MILLER; since these were not spectroscopic researches, we shall not discuss them here.

(6) The search for red dwarf stars developed as a byproduct of our spectral studies of clusters in the galaxy. Colleagues with large light gathering instruments and slit spectrographs had long "harvested" the spectral data for the bluest and brightest members of the main sequences of very many of these clusters. Now MCCARTHY [40] and MCCARTHY and TREANOR [41, 42] turned to the faint red end of this sequence (to seek where it really terminated) and looked first at the Pleiades for possible faint candidates for membership in this cluster. Together with Russian colleagues, V. AMBARTSUMIAN and co-workers, and with the Asiago team under Professor L. ROSINO, we made observations with the Vatican Schmidt and looked at *M* type stars for featurs of Na, MgH and CaH. Many of these proved also to be flare stars detected photometrically in Russia or Asiago. We also compared our data with the observations with slit spectra made by GREENSTEIN and KRAFT using the large telescopes in California. Work on the Pleaides main sequence still continues at the Vatican Observatory as Father R. BOYLE works with G. and M. RIEKE of Tucson on far-i.r. studies of extremely faint stars.

(7) In 1968, the Vatican Observatory obtained on loan from the Carnegie Institution of Washington a special cascaded image tube. Around this TREANOR [43] designed a spectrograph and included a special Schmidt-type camera lens constructed by the Galileo firm in Florence. The purpose of this image tube spectrograph, which was attached to the 60 cm reflector atop the palace at Castel Gandolfo, was to provide a follow-up at higher dispersion for objects of interest detected in our objective prism surveys with the Schmidt telescope and its large prisms. Objects studied included: Cepheids at maximum phase; some of the emission objects detected in the COYNE *et al.* surveys and some of the *M* dwarf stars mentioned above.

(8) One outgrowth of work done with the Vatican Schmidt was the continuing interest in carbon stars; I have already mentioned that Father SECCHI discovered these and included them as his Type IV stars, quite different from his Type III objects we now know as the *M* type stars. Working with Dr VICTOR BLANCO, initially at Case Western Reserve in Cleveland, then with the Vatican Schmidt and later with the Curtis Schmidt in Cerro Tololo, MCCARTHY had been discovering and recording the positions of carbon stars first in the anticentre then along the galactic plane and finally in the Large and Small Magellanic Clouds, the nearest galaxies to our own Milky Way. This project turned into a much bigger one as the CTIO 4 m telescope began to be employed in reaching much fainter magnitudes than were possible even with the Curtis Schmidt. Now the prism used was a very thin one which could be cemented to a transparent grating and the whole

apparatus (called a "grism") was placed at the prime focus of a large telescope. With this combination plus hypersensitized Kodak IN plates we were able to reach *C* stars and *M* stars (all red giants) in the nearby galaxy and to separate them as distinct types. The results of these surveys by McCarthy and the Blancos have been published in *Nature* [44, 45] in the *Astrophysical Journal* [46] and the *Astronomical Journal* [47, 48]. We have intercompared the presence and distribution of *C* and *M* red giant stars in 52 regions in the Large Magellanic Cloud and in 26 regions in the Small Magellanic Cloud and in several regions in zones of minimum obscuration in the direction of the centre of the galactic nucleus in Sagittarius in our own Milky Way.

(9) When artificial light pollution became too strong at Castel Gandolfo, several initiatives were undertaken in order that optical observations of stellar spectra could continue. This sad but exciting story has been told elsewhere [49]. What we did was to "move men instead of instruments" and the observing team of the Vatican Observatory went west to Tucson, Arizona. Here we use "other people's telescopes" or better, "all people's telescopes", i.e. national or university instruments which are available through competition to applicants with successful proposals. This has worked out for all Vatican observers but we feel the need for having a dedicated telescope and so have been engaged in providing one through a fund raising campaign under the direction of Father Coyne [50]. This will give us the Vatican New Technology Telescope on top of Mt. Graham at 10 700 ft in the mountains to the east of Tucson on a site proven already to be excellent. We expect much fine spectroscopy to be accomplished with this instrument which is expected to see first light and to be operational in 1990. Corbally is serving as Project Scientist and will be able to see several of his own special observing goals initiated once the first observational testing of the new 1.8 m *f*/1 spin-cast mirror telescope is completed. Later, other staff colleagues will join Father Corbally on Mt. Graham and it is foreseen that we will be able to "give as we have long received" telescope time on an excellent modern instrument to our colleagues of the world community.

APPENDIX

Spectral Atlases of the Vatican Observatory

1. A. Gatterer und J. Junkes, *Funkenspektrum des Eisens von* 4650–2242 Å. Selbstverlag der Specola Vaticana, Castel Gandolfo (1935). *Spark Spectrum of Iron from* 4650 to 2242 Å. 1st edn., Specola Vaticana, Castel Gandolfo (1935); 2nd edn., Specola Vaticana, Città del Vaticano (1947); 2nd edn., 2nd Impression, Specola Vaticana, Città del Vaticano (1956).
2. A. Gatterer und J. Junkes, *Bogenspektrum des Eisens von* 8388–2242 *Å*. Selbstverlag der Specola Vaticana, Castel Gandolfo (1935). *Arc Spectrum of Iron from* 8388 *to* 2242 *Å*. 1st edn., Specola Vaticana, Castel Gandolfo (1935); 2nd edn., Specola Vaticana, Città del Vaticano (1947); 2nd edn., 2nd Impression, Specola Vaticana, Città del Vaticano (1956).
3. A. Gatterer und J. Junkes, *Atlas der Restlinien von* 30 *chemischen Elementen.* Specola Vaticana, Castel Gandolfo (1937). *Atlas der Restlinien, I. Band. Spektren von* 30 *chemischen Elementen.* 2. Aufl., Specola Vaticana, Città del Vaticano (1947).
4. A. Gatterer und J. Junkes unter Mitwirkung von V. Frodl, *Atlas der Restlinien, II. Band. Spektren der Seltenen Erden.* 1. Teil: Tafeln; 2. Teil: Text und Wellenlägen. Specola Vaticana, Città del Vaticano (1945); 2. Aufl. Herausgegeben von J. Junkes und E. W. Salpeter. Specola Vaticana, Città del Vaticano (1959).
5. A. Gatterer und J. Junkes, *Atlas der Restlinien,* III. *Band. Spektren seltener Metalle und einiger Metalloide.* Specola Vaticana, Città del Vaticano (1949).
6. A. Gatterer, *Grating Spectrum of Iron.* Specola Vaticana, Città del Vaticano (1951).
7. A. Gatterer, J. Junkes, E. W. Salpeter and B. Rosen, *Molecular Spectra of Metallic Oxides.* Specola Vaticana, Città del Vaticano (1957).
8. J. Junkes and E. W. Salpeter, *Spectrum of Thorium from* 9400–2000 *Å*. Specola Vaticana, Città del Vaticano (1964).
9. J. Junkes, E. W. Salpeter and G. Milazzo, *Atomic Spectra in the Vacuum Ultraviolet from* 2250–1100 *Å*. *Part One.* Specola Vaticana, Città del Vaticano (1965).

Here the author has listed the notices concerning Spectral Atlases which appeared after the listing above*. They are taken from the Annual Reports of the Vatican Observatory after 1965.

10. E. W. Salpeter with R. S. V. *Glow Discharge Spectra from* 1500 *to* 4000 Å. Part 1: Fe, Co, Cr, Mo, Nb, Ni, Ta, Ti. Introduction and 25 Photographic Tables 24 × 30 cm, Vol 1. Specola Vaticana (1971).
11. E. W. Salpeter with R. S. V. *Spectren in der Glimmentladung. Tiel 2. Edelgase von* 1500 *bis* 4000 Å. 35 photographic plates, 24 × 30 cm. Specola Vaticana (1971).
12. E. W. Salpeter with R. S. V. *Spektren in der Glimmentladung von* 1500 *bis* 4000 Å 3 Tiel: Fe, Cu–Be, Ca–Si, Hg–Zu, Pb–Bi, Sb–S, Sn–As, Mg–Cd. 25 photographic plates 24 × 30 cm. Specola Vaticana, Città del Vaticano (1972).
13. E. W. Salpeter with R. S. V. *Spektren in der Glimmentladung von* 1500 *bis* 4000 Å. Tiel 4: Fe, Ag, Au, Ir, Pd, Pt, Rh, Ru. 25 photographic plates, 24 × 30 cm. Specola Vaticana, Città del Vaticano (1972).
14. E. W. Salpeter with R. S. V. *Spektren in der Glimmentladung von* 1500 *bis* 4000 Å. Tiel 5: Fe, Al, Hf, Mn, Se–Te, V, W, Zr. Specola Vaticana, Città del Vaticano (1973).

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Molecular astrophysics

G. HERZBERG*

National Research Council of Canada, Ottawa, Canada K1A 0R6

Abstract—A brief history of Molecular Astrophysics is presented. The first molecules in space were identified in the 1920s in comets followed soon after by those in planetary atmospheres. The recent identification by MCKELLAR of the dimer of H_2, that is, $(H_2)_2$ in the atmosphere of Jupiter as well as the discovery, by DROSSART, MAILLARD, WATSON and others, of the H_3^+ ion in the auroral zone of Jupiter are described. In this laboratory there is a continuing interest in interstellar molecules. Several molecules and molecular ions were observed by collaboration of laboratory spectroscopists and astronomers. Only the most recent ones are discussed. Also a few of the molecules not yet observed but likely to be observed are mentioned.

INTRODUCTION

THE FIRST molecules in space were observed in cometary spectra; they were studied for the first time visually by DONATI [1] in 1864 (i.e. 125 years ago) in comet Tempel. The features that he saw were presumably the 4740, 5165 and 5630 Å band groups (sequences) of C_2 but at the time they were not identified as such. HUGGINS [2] in 1882 first observed (visually) the 4050 Å group, which was identified only in 1951 by DOUGLAS [3] as due to the C_3 molecule.

It may be justified to say that molecular astrophysics had its beginnings at about the same time as spectroscopy; that is, when KIRCHHOFF and BUNSEN (in 1860) recognized that every chemical element has a characteristic spectrum which can be used to detect that element in the laboratory and in space. However, it took almost the first 50 years of this period before the distinction between atomic and molecular spectra was clearly established and the molecules responsible for several important features of cometary spectra were unambiguously assigned. Many new developments in molecular astrophysics have occurred in the last 50 years, which were also the first 50 years of *Spectrochimica Acta.* I should like to discuss in this paper a few of the modern developments in this field and mention some of the problems whose solution would be of interest.

In about 1950, it was my privilege to learn to know Dr A. GATTERER, one of the founders of *Spectrochimica Acta.* His imaginative work on the spectra of the rare earth oxides, as well as his great service to the spectroscopic community by providing various carefully prepared atlases of atomic and molecular spectra, has helped me and many others greatly in our work. I am glad to have this opportunity to join in honouring his memory.

COMETARY SPECTRA

The molecules identified as being present in comets on the basis of their spectra are listed in Table 1, both for the coma and the tail. Most of them were easy to identify, given the knowledge of laboratory spectra but a few were fairly difficult to identify. I shall mention only two with whose identification I was, in one way or other, connected; namely C_3 in the coma and H_2O^+ in the tail.

In 1941 at the time when I was writing Volume II of the series, *Molecular Spectra and Molecular Structure*, I received a letter from the late P. SWINGS (even then well known for his work on cometary spectra) asking me whether I had any ideas on the origin of the

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[*] Member, Pontifical Academy of Sciences.

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Table 1. Molecules identified in comets

Coma	Tail
CH, NH, OH, C_2, CN, CS, S_2, NH_2, H_2O, HCN, C_3	CH^+, OH^+, N_2^+, CO^+, H_2O^+, CO_2^+

4050 Å group, which was first observed in cometary spectra in 1881 by HUGGINS [2]. SWINGS' letter had a remarkable influence on my subsequent work in molecular spectroscopy. Having just written about the spectra of symmetric top (or nearly symmetric top) molecules in the manuscript of my book, it occurred to me that the 4050 Å group as published by SWINGS would fit the expected structure of a perpendicular band of a symmetric top molecule (seen under low resolution), especially if one assumed that it belonged to CH_2. Subsequent experiments on interrupted discharges through CH_4 did indeed produce the 4050 Å group in the laboratory [4] and thus appeared to confirm the identification as CH_2. However, after a few years it was found by MONFILS and ROSEN [5] that the spectrum is unchanged when CH_4 is replaced by CD_4, thus eliminating CH_2 as the carrier of the spectrum. It was soon found to be due to C_3 by the experiments of CLUSIUS and DOUGLAS with $^{13}CH_4$ [3, 6]. The question then arose, what is the true spectrum of CH_2? It was solved only after another 10 years. The full analysis of the 4050 Å group was accomplished only in 1965 (GAUSSET *et al.* [7]) when it was shown that the bending frequency of C_3 is very small, viz. 63 cm^{-1}, which accounts for the apparent wide "rotational" structure which was in the early work taken as evidence for CH_2. This short history illustrates the strong interplay of molecular spectroscopy and astronomy.

The so-called α bands of ammonia observed in discharges through NH_3 or oxy-ammonia flames were assigned to the NH_2 radical. They were observed in cometary spectra at a fairly early stage, but a definitive identification could only be made after the detailed fine structure analysis by DRESSLER and RAMSAY [8] in 1956 in this laboratory.

The spectrum of Comet Kohoutek was obtained soon after the comet was discovered in 1973. BENVENUTI and WURM [9] sent me one of their spectra showing two fairly strong doublets in the yellow and red and asking for their possible identification. At that time Dr H. LEW with a summer student, I. HEIBER [10], had just obtained extensive laboratory spectra of H_2O^+: the four lines of BENVENUTI and WURM and a number of other lines observed by HERBIG and co-workers [11] agreed precisely with the strong lines in the laboratory spectrum of H_2O^+. Moreover, the strongest lines were those assigned to the lowest rotational quantum numbers showing a low temperature of cometary emission and leaving no doubt that H_2O^+ was present in the tail. It has, indeed, been found since then in many other comets. The observation of H_2O^+ in the tails of comets was the first conclusive evidence that neutral H_2O must be ejected from the cometary nucleus.

The same spectrum of H_2O^+ has been observed more recently in the twilight glow in the earth's atmosphere by KRASSOVSKY and VINIUKOV [12] as interpreted by the author [13].

PLANETARY SPECTRA

The spectroscopic study of planetary atmospheres started nearly 60 years ago with the discovery of large amounts of CO_2 in the atmosphere of Venus by ADAMS and DUNHAM [14] in 1932 and the identification of large amounts of CH_4 in the atmospheres of the outer planets by WILDT [15] in 1932. Much later CO_2 was found in Mars by KUIPER [16].

It must be realized that some obvious molecules are very difficult to detect spectroscopically because they have no normal i.r. spectrum (since they have no dipole moment) and no electronic transitions in the visible or near–u.v. Such molecules are H_2 and N_2. On theoretical grounds it seemed very probable that there are large amounts of H_2 in the atmospheres of the outer planets. In 1938, I pointed out [17] that H_2 might be detected with the help of the quadrupole rotation–vibration spectrum whose wavelengths were predicted from the known far–u.v. spectrum of this molecule. I proceeded to look for this spectrum in the laboratory by means of a long absorbing path set up at the Yerkes Observatory in 1947 and did indeed find several lines of the 2–0 and 3–0 bands of the quadrupole spectrum [18]. Much later the 4–0 band was observed in the laboratory by BERGSTRALH *et al.* [19] and TRAUGER *et al.* [20]. Twenty-two years after the first prediction, some of these lines were indeed found in the spectrum of Jupiter (first by KIESS *et al.* [21] and later by GIVER and SPINRAD [22], OWEN and MASON [23], FINK and BELTON [24], OWEN [25] and TRAFTON [26]). Thus, the presence of large amounts of H_2 was established in the atmosphere of Jupiter and later in Uranus.

This is by now a very old story. I mention it here because the quadrupole spectrum has again become of importance in some recent work in this field (see below).

The quadrupole rotation–vibration spectrum of N_2 is of course predictable from the vacuum u.v. spectrum of the molecule. The 1–0 band was first observed in absorption in the solar spectrum in 1981, independently by GOLDMAN *et al.* [28] and CAMY-PEYRET *et al.* [27]*. In the laboratory, this spectrum was first observed with a long absorbing path (434 m) by REUTER *et al.* [30] in 1986. Up until now, this spectrum has not led to the discovery of the presence of N_2 in any other planetary atmosphere. However, there is good indirect evidence obtained with *Voyager II* of the presence of large amounts of N_2 in the atmosphere of Titan, the largest of Saturn's satellites, which also shows substantial amounts of CH_4.

The i.r. spectra taken from the *Voyager I* and *II* spacecraft have given a lot of information about the minor constituents of the atmospheres of Jupiter, Saturn and Uranus, like C_2H_2, C_2H_4, C_2H_6, PH_3 and others, but we shall not pursue this subject further.

There are, however, two further interesting points about hydrogen which have recently come up and which I would like to describe briefly.

The i.r. spectra obtained by means of the IRIS spectrometer on the two *Voyager* spacecraft show very clearly the collision-induced broad $S_0(0)$ and $S_0(1)$ features first observed by BIRNBAUM [31]; but in addition, they show one or two sharp peaks near the maximum of each of the collision induced features. In this laboratory, McKELLAR [32] first suggested that these peaks are due to the hydrogen dimer $(H_2)_2$. Quite recently, by careful laboratory studies of the absorption spectrum of hydrogen at 20 K, he conclusively proved this identification [33(a)]. Figure 1 shows the comparison of Jupiter and laboratory spectra from McKellar's paper. There can be no question that $(H_2)_2$ is present in the atmospheres of both Jupiter and Saturn.

Still more recent and not yet fully published are observations of the auroral displays in the Jupiter atmosphere made in the same spectral region by DROSSART *et al.* [34] with the Fourier transform interferometer attached to the Canada–France–Hawaii telescope. These astronomers were looking for, and observed, the $S(1)$ line of the quadrupole rotation–vibration spectrum in emission during auroral displays on Jupiter, in itself a remarkable result. But in addition they observed some 36 lines of comparable intensity in the region 4600–4800 cm^{-1}. Figure 2 shows one of their spectra. The quadrupole line is marked near the centre. The nature of the additional emission lines was under lively discussion in this laboratory for several weeks until WATSON showed, on the basis of the unpublished laboratory spectra of MAJEWSKI, that they fitted very closely with the predicted $2\nu_2$ band of the H_3^+ ion [35]. There may be a few lines due to the higher electronic states of H_2 but the majority of the lines observed in this region are due to H_3^+. This represents the first observation of H_3^+ outside the laboratory. The question of why H_3^+ is so strongly excited in the Jovian atmosphere in auroral displays is not easy to answer. The fact that MAJEWSKI's spectra were produced at a substantially higher

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* The same authors also observed the magnetic dipole and quadrupole rotation–vibration spectrum of O_2 but this is astronomically less interesting since O_2 is more easily detected by the well known atmospheric oxygen bands in the visible region.

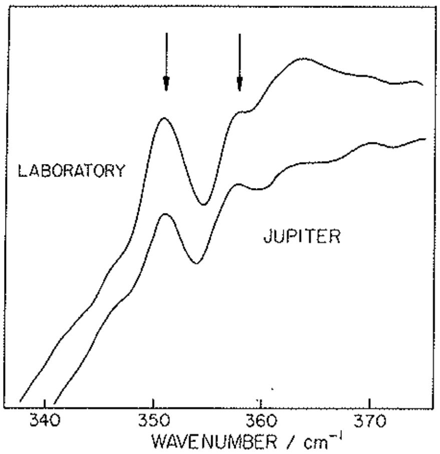


Fig. 1. Comparison of the far i.r. spectrum of Jupiter with a laboratory spectrum at 77 K after McKELLAR [33(a)] showing absorption features of $(H_2)_2$. The Jupiter spectrum is from GAUTIER *et al.* [33(b)] obtained by the *Voyager* spacecraft. The two peaks at 351.3 and 355.45 cm^{-1} correspond to the transitions $l=1\leftarrow2$ and $l=1\leftarrow0$ in $(H_2)_2$.

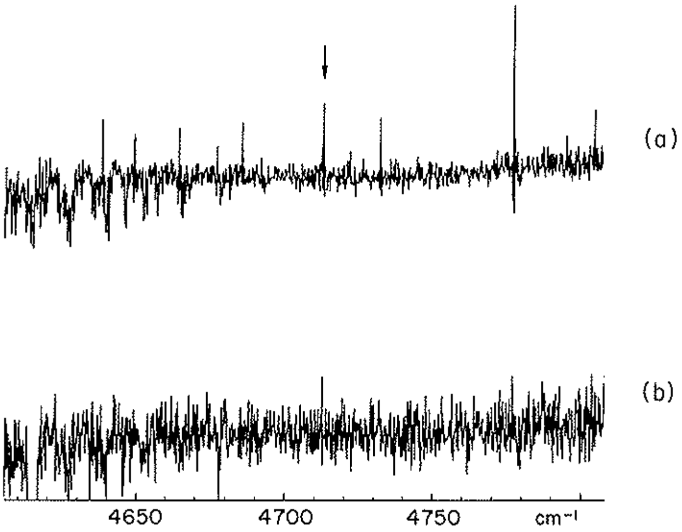


Fig. 2. Infrared spectra of Jupiter at 60° latitude (a) at an auroral spot (mean longitude 60°) and (b) at a non-auroral spot (longitude 284°) after DROSSART *et al.* [35]. The arrow in (a) marks the quadrupole $S(1)$ line of the 1–0 rotation–vibration band. All other emission lines in (a) are due to H_3^+. The absorption lines in (b) are due to CH_4.

pressure than used in our earlier work with hollow cathodes suggests that the high pressure in the Jovian atmosphere may be the main cause for the preferential excitation of H_3^+. Certainly, the well known reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ is favoured by higher pressure.

THE INTERSTELLAR MEDIUM

It is 52 years since the first molecule was discovered in the interstellar medium. At that time (1937), DUNHAM and ADAMS [36] took the first high resolution spectra of O type stars which showed, in addition to the interstellar atomic lines of Ti, Fe, Na and others, a few fairly strong sharp absorption lines, clearly interstellar in character, which they could not identify. It was SWINGS and ROSENFELD [37] at Liège who noticed in the same year that one of these unidentified lines at 4300.3 Å coincided closely with a line in the well known CH band at 4315 Å. This could have been a chance coincidence, but they found that the coincidence occured for the only line in the band which had the lowest rotational level of CH in the ground state as lower state. Since DUNHAM and ADAMS had already established that in atomic multiplets only the lines from the lowest component level of the lower state appeared in interstellar absorption, the observation of the coincidence with the very line that had the lowest rotational level of CH as lower state made the identification of the carrier of the interstellar line as CH practically certain, a conclusion that was fully confirmed by later evidence from other transitions of CH found three years later by McKELLAR [38] in Victoria. I think, therefore, that we must consider SWINGS and ROSENFELD as the discoverers of the first interstellar molecule. Five of the remaining unidentified interstellar lines listed by DUNHAM and ADAMS were identified in 1941 by McKELLAR [39] as being due to a second transition of CH and to the $R(0)$, $R(1)$ and P(1) lines of the 0–0 band of the violet system of CN. Finally, in 1942, the last remaining lines were identified by the laboratory discovery of a new band system due to CH^+ by DOUGLAS and HERZBERG [40]. CH^+ was the first molecular ion observed in the interstellar medium and indeed the first molecular ion to be observed in absorption.

It took 22 years after the discovery of CH, CN and CH^+ before a further molecule was discovered, namely OH, the first molecule to be found by radio-astronomical methods (WEINREB *et al.* [41]). It was another five years before TOWNES *et al.* [42] found NH_3 and H_2O, the first polyatomic molecules. After that, almost every year two or more new molecules were added, so that now more than 70 interstellar molecules are known, most of them discovered by radio-astronomers in the microwave and radio-frequency regions. In the last few years the enormous development of i.r. detectors has made possible the detection of a few interstellar molecules by their i.r. spectra.

I shall not attempt to give a comprehensive survey of this field but rather concentrate on a few molecules in which members of this Institute have been specially interested.

One of the striking observations initiated in our Institute by OKA [43] was the first observation of cyano-diacetylene in interstellar clouds following the laboratory observation of its microwave spectrum by KROTO and his associates [44] at the University of Sussex. Shortly after, the latter group also observed the spectrum of cyano-triacetylene in the laboratory and it was soon observed in Heiles's cloud 2 [45]. Subsequently, cyano-tetraacetylene and cyano-pentaacetylene were also found; these are the largest interstellar molecules observed so far.

There could never have been any doubt that a substantial fraction of the interstellar medium (i.e. of interstellar clouds) consists of molecular hydrogen. However, it took until 1973 before a definite proof for this statement was obtained. H_2, of course, has no dipole moment and therefore does not have an ordinary i.r. spectrum, that is, a rotation or rotation–vibration spectrum. It does, however, have a strong electronic absorption spectrum in the vacuum u.v. region from 1100 Å to shorter wavelengths and as soon as it became possible to operate u.v. spectrometers from rockets or artificial satellites, extremely strong absorption bands of H_2 (viz. the Lyman bands and Werner bands) were observed (CARRUTHERS [47] and SPITZER *et al.* [48]). Figure 3 shows, as an example, a section of the spectrum of ξ Persei between 1086 and 1098 Å. The absorption is so strong that even the HD spectrum can be observed (MORTON [49]). Table 2 shows a comparison of the wavelengths of fairly weak lines in ζ Oph and laboratory measurements of HD.

Surprisingly, a few years later, upon observing the i.r. spectrum of the Orion nebula, lines of the quadrupole rotation–vibration spectrum of H_2 were found to appear prominently *in emission* (GAUTIER *et al.* [50], CONNES *et al.* [51]). At somewhat longer wavelengths even the pure rotation spectrum was observed (GEBALLE [52]) for high J values. New laboratory measurements of the vacuum–u.v. emission spectrum made by DABROWSKI [53] in this laboratory, allowed us to establish the exact wave numbers of high J lines necessary for the prediction of the wave numbers of the i.r. quadrupole lines. The mechanism by which the quadrupole lines are excited in emission is generally agreed to be the presence of shock waves in these clouds, which in turn are produced by the star formation processes.

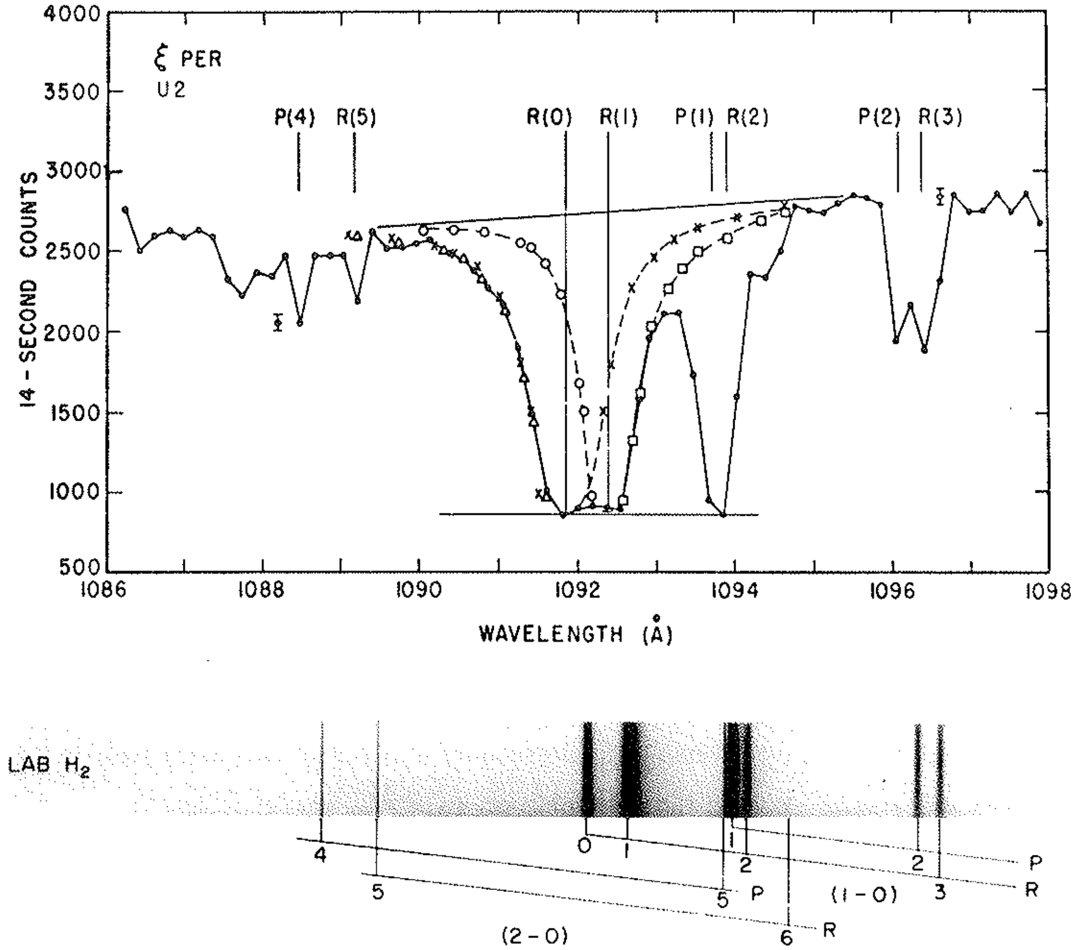


Fig. 3. H_2 interstellar absorption lines near 1190 Å after SPITZER *et al.* [48] compared with a laboratory spectrum reduced to the same scale.

The N_2 molecule, like the H_2 molecule, has no ordinary i.r. spectrum. Its quadrupole spectrum would occur near 2300 cm^{-1} but could not be observed by ground based instruments because of the strong absorption of the ν_3 fundamental of CO_2. N_2 has strong vacuum–u.v. absorption in the region below 1100 Å. But the Copernicus spectra of SPITZER *et al.* [48] do not show any sign of N_2 absorption even though CO bands of similar laboratory intensity have been found. As far as I am aware, no N_2 has been spectroscopically identified in any astronomical object.

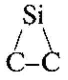
The atmospheres of most carbon stars show strong absorption bands of C_2 (the Swan bands) and of SiC_2 (the Merrill–Sanford bands). It was first shown by BALLIK and RAMSAY [54] in this laboratory that the lower state of the Swan Bands ($^3\Pi_u$) is not the

Table 2. HD in the interstellar medium

Band	$\lambda_{\text{int. }(\zeta \text{ Oph})}$ (Å)	$\lambda_{\text{lab.}}$ (Å)
3–0	1066.272	1066.2712
4–0	1054.288	1054.2855
5–0	1043.845	1042.8471
6–0	1031.920	1031.9091
7–0	1021.452	1021.4534

ground state of C_2 but rather that the lower state $^1\Sigma_g^+$ of the Phillips bands is the ground state. Indeed a few lines of the 1–0 and 2–0 Phillips bands have been found by Souza, Chaffee and Lutz [55, 56] in the near-i.r. in interstellar absorption: C_2 has an abundance similar to CN.

The ν_3 fundamental of the C_3 molecule has recently been observed in emission in the extended atmosphere of the i.r. star IRC+10216 by Bernath *et al.* [57], a noteworthy observation followed closely by the laboratory observation of this band [58]. Weltner *et al.* [59] have recently observed the i.r. spectrum of the C_5 molecule in an argon matrix and shown that the molecule is linear. The main observed band is the fundamental ν_3; in a 50:50 mixture of ^{12}C and ^{13}C it shows a beautiful pattern of 20 isotopomer bands which establishes the identification of C_5 and its linearity beyond any doubt. Very soon afterwards, two laboratories reported the observation of the same band at high resolution in the gas phase [60, 61]. This work confirmed the linear structure and enabled an accurate determination of the rotational constant B_0. At the same time Bernath *et al.* [62] observed this band in emission in the circumstellar atmosphere of the star IRC+10216.

Many years ago, in this laboratory, Kleman [63] observed a spectrum that had earlier been observed by Merrill and Sanford in N-type stars (see especially McKellar [64]). Kleman confirmed the suggestion made by McKellar that this band system is due to the SiC_2 molecule. But it was only a few years ago that Smalley *et al.* [65] showed that this molecule is not linear but has the form  and subsequently it was found by Thaddeus *et al.* [66] in the atmosphere of the molecular cloud in Orion. Naturally, the question arose whether diatomic SiC is also present, but until very recently no spectrum of SiC was known. Indeed on various occasions during the last 60 years I tried to find such a spectrum but failed. It was only a few months ago that Thaddeus and his associates [67] succeeded to find a microwave spectrum, both in the laboratory and again in the atmosphere of the Orion cloud. An i.r., visible or u.v. spectrum of this molecule still has to be found. The ground state of SiC is found to be a $^3\Pi$ state like the lower (and low-lying) $^3\Pi_u$ state of the C_2 Swan bands.

In the last 10 years the study of molecular ions in the interstellar medium has become more and more important. The early identification of CH^+ as an important constituent, comparable in abundance to CH or CN, was for many years the only case of a molecular ion. However, in 1970, on the basis of a suggestion of Klemperer [68] (at the IAU meeting in Brighton) the HCO^+ ion was established as the carrier of a strong microwave line at 89190 MHz (until then unidentified) and was later observed in the laboratory by Woods *et al.* [69]. Soon after, a similar development arose for N_2H^+ [70].

On the basis of these results it soon became clear, in view of the presumed large abundance of H_2, that H_3^+ must be an important ion in interstellar clouds since it could be the starting point of many ion–molecule reactions that are going on in the clouds. From laboratory experiments, it is well known that H_3^+ is readily formed from H_2^+ by the reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H,$$

where H_2^+ is either formed by photoionization of H_2 or by ionization by cosmic rays. H_3^+ which is a very stable ion $[D(H_3^+ \rightarrow H_2 + H^+) = 4.3\,\text{eV}]$ could be destroyed by the reaction;

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

or

$$H_3^+ + N_2 \rightarrow HN_2^+ + H_2.$$

Neutral CO is the most abundant molecule next to H_2 but nothing is known about the abundance of N_2. An alternative path to HCO^+ or HN_2^+ could be the ionization by u.v. or cosmic radiation of CO and N_2 followed by

$$CO^+ + H_2 \rightarrow HCO^+ + H \tag{1}$$

and

$$N_2^+ + H_2 \rightarrow HN_2^+ + H. \tag{2}$$

The failure to observe the well known electronic transitions of CO^+ [71] and N_2^+ in the visible or near-u.v. regions may be due to reactions (1) and (2) which are exothermic and which, because of the high abundance of H_2, occur fairly fast, thus accounting for the low concentration of CO^+ and N_2^+. Actually, one microwave line of CO^+ has recently been observed in the Orion molecular cloud (ERIKSON *et al.* [71]). It is interesting to note, as mentioned earlier, that vacuum–u.v. absorption of CO has been observed by the Princeton group [72] but N_2 has not been seen.

In spite of considerable effort, the presence of H_3^+ has not yet been directly established by its i.r. absorption spectrum known precisely from the laboratory work of OKA [73] and others. While H_3^+ because of its symmetry has no microwave spectrum, the unsymmetrical H_2D^+ has, but the tentative observation [74] of one of its absorption lines has so far not been confirmed. In spite of these negative results, there is little question that H_3^+ plays an important role in the chemistry of the interstellar medium.

One could also establish the presence of H_3^+ indirectly by observing the visible emission spectrum of H_3, well known from laboratory work. However, a tentative identification by PRITCHET and GRILLMAIR [75] in the planetary nebula NGC 7027 has later been withdrawn (GUSSIE and PRITCHET [76]).

One other ion that has been identified, first by THADDEUS [77] in the cloud Saggitarius *B2* is protonated CO_2, that is HCO_2^+, later observed in the laboratory by BOGEY *et al.* [78] in the microwave region and by AMANO and TANAKA [79] in the i.r. This observation establishes the presence of CO_2 in fairly high concentration in interstellar clouds. Again the failure to observe the well known visible and near–u.v. bands of CO_2^+ must be caused by its prompt reaction with H_2 forming HCO_2^+.

There are a number of other molecular ions which one might expect to find in interstellar clouds but which have, as yet, not been observed. The C_2^- ion has a strong characteristic discrete absorption spectrum [80] near 5416 Å (similar to the 3914 Å band of N_2^+). Very recently, MAIER and RÖSSLEIN [81] have observed a ${}^4\Sigma_u^- - {}^4\Sigma_g^-$ transition of C_2^+ at 5071 Å which involves the ground state, as they have shown by a very elegant technique. Neither of these spectra have been observed in interstellar clouds. The reason for this negative result may be similar to that for the non-observation of N_2^+.

A molecular ion that must almost certainly be present in the interstellar medium is CH_2^+. According to BLACK and DALGARNO [82], the two-body recombination reaction

$$C^+ + H_2 \rightarrow CH_2^+,$$

on the basis of *ab initio* calculations, is sufficiently fast to make a dominant contribution to the formation of CH_2^+ which in turn is required to account for the formation of the more complicated organic molecules which have been observed in interstellar clouds. However, up until now a spectrum of CH_2^+ has not been observed, either in the laboratory or in space. CH_2^+ is iso-electronic with BH_2 for which an electronic spectrum has been observed in the red region [83]. In the lower state BH_2 is bent with an angle of 130°, while in the upper state it is linear. We have tried to find the analogue of this spectrum for CH_2^+ in the laboratory but up until now without success. Even the presence of the neutral CH_2 molecule has not been definitely established in space although there is a suggestion of an absorption in Copernicus spectra, near 1416 Å found by SNOW *et al.* [84(a)] which may correspond to the transition from the ground state to the first Rydberg state (by means of which the first spectrum of CH_2 was obtained in the laboratory 30 years ago)[*].

If an electronic spectrum of CH_2^+ could be found in the laboratory it would be possible to predict microwave and i.r. spectra which might eventually lead to the observation of CH_2^+ in interstellar clouds. This problem seems to me sufficiently important that further effort would be justified.

Another group of ions which might have a good chance of being discovered in space are H_2O^+, H_3O^+, NH_2^+ and NH_3^+. For all four of these, laboratory i.r. spectra are known and can be used for searches in interstellar spectra. For H_2O^+ an extensive electronic spectrum is known, which as mentioned earlier has been used to detect H_2O^+ in comets and in the upper atmosphere, but because of its appearance in the upper atmosphere it blocks observation of weak absorption or emission in molecular clouds. We have rudimentary laboratory spectra of NH_2^+ and NH_3^+ in the u.v. but unfortunately have so far not been able to improve them to the point where they might be of real use for the study of these ions in molecular clouds. Another related ion is CH_3^+ which has been observed in the laboratory by OKA [85]. Neither it nor neutral CH_3 have been observed in the i.r. spectra of molecular clouds (they have no permanent dipole moment and therefore no microwave spectrum).

There are two other molecular ions which deserve some attention. One is HeH^+, for which now a fairly complete i.r. (1–0) band is known (BERNATH and AMANO [86]) but no conclusive evidence for its presence in space has yet been obtained. Finally, $HeNe^+$ must be mentioned. An extensive electronic spectrum has been observed in the region 4000–4300 Å and has been fairly completely analysed (DABROWSKI and HERZBERG [87]). Instead of giving the constants obtained in this analysis, the potential functions of the observed electronic states are presented in Fig. 4. The two excited states are very weakly bound (van der Waals binding) while the ground state is moderately strongly bound with a dissociation energy of $5580\,\mathrm{cm}^{-1}$. According to the Franck–Condon principle, transitions from both the $B\,^2\Sigma^+$ and $A_2\,^2\Pi_{1/2}$ states reach the ground state $X\,^2\Sigma^+$ in the upper part of the potential function at $v = 6, 7, 8$ and 9 for $^4HeNe^+$ (and $v = 5, 6, 7$ and 8 for $^3HeNe^+$). The numbering is unambiguously established by the isotope effect. In order to predict the microwave spectrum or the fundamental in the i.r., a fairly long extrapolation

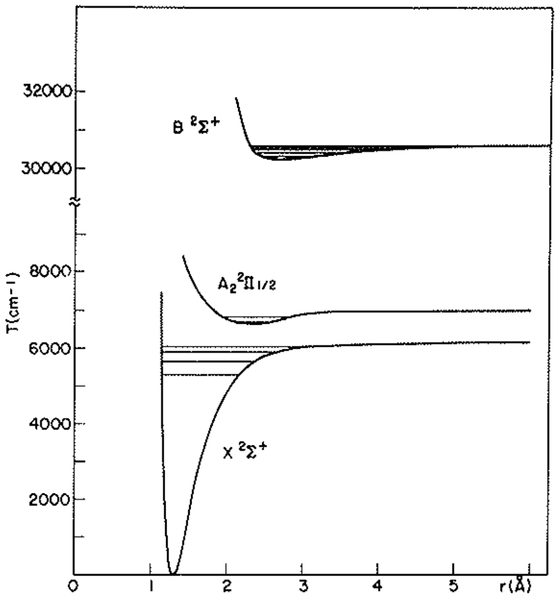


Fig. 4. Potential functions of the three observed states of $HeNe^+$. The observed vibrational levels are indicated.

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[*] Later much lower resolution spectra with the IUE satellite did not show this absorption (SEAB and SNOW [84(b)]).

Table 3. HeNe$^+$: $X^2\Sigma^+$ ground state observed and *ab initio* constants

	Observed (cm^{-1})	Theoretical (cm^{-1}) ref. [88]	Theoretical (cm^{-1}) ref. [89]
B_e	(2.991)	2.472	2.404
B_0	(2.984)	2.450	
B_6	1.5898	1.610	
B_7	1.3576	1.361	
B_8	1.0904	1.083	
B_9	0.8431	0.814	
$\Delta G(\frac{1}{2})$	(1144)	902	
$\Delta G(6.5)$	341.59	349	
$\Delta G(7.5)$	233.42	229	
$\Delta G(8.5)$	146.27	135	
r_e(Å)	(1.30)	1.43	1.45

* The numbers in parentheses refer to extrapolations.

is necessary and therefore these predictions are not very accurate, particularly since the B_v and ΔG curves are fairly strongly curved. There have been two fairly elaborate *ab initio* calculations of the ground state [88, 89]. In Table 3 the theoretical values for B_v and $\Delta G_{v+1/2}$ are compared with the observed values and with the extrapolated B_0 and $\Delta G_{1/2}$ values. Considering the uncertainty of the extrapolation, the agreement is really quite reasonable. With the help of Dr MOAZZEN-AHMADI we have recently tried using a diode laser spectrometer to obtain absorption of the fundamental but have had no success so far.

I believe that this problem should be further pursued, both from an astronomical and purely spectroscopic point of view.

CONCLUSIONS

The preceding discussion shows that a great deal has been accomplished in the identification of many molecules and molecular ions in comets, in planetary atmospheres and in interstellar clouds. Much remains to be done, but even now a good deal of information has been accumulated for detailed discussions of the physical and chemical processes in interstellar clouds and their eventual condensation to new stars.

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Spectroscopy beyond molecular constants

ROBERT W. FIELD, DAVID P. BALDWIN, ERNEST J. HILL, MINGGUANG LI* and MICHAEL C. MCCARTHY

Department of Chemistry and the George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

Abstract—The spectra of diatomic molecules containing an atom with a partially filled *d* or *f* shell are exceedingly complex. Nonetheless, simple bonding arguments and a simple, predictive zero-order electronic structure model can be used to organize and understand the unavoidably dense and confusing manifold of molecular states. The correspondence between molecular constants and a global periodicity-based structural model is only possible when large quantities of spectral information have been acquired and deciphered. This paper discusses how a variety of new and powerful, single and multiple resonance spectroscopies can be used to efficiently and rapidly generate the large amounts of high quality spectral information required to reveal what appears to be an elegant underlying electronic simplicity.

INTRODUCTION

FOR MANY spectroscopists, FATHER GATTERER's photographic atlas, *Molecular Spectra of Metallic Oxides* [1], provided the first glimpse of the incredible congestion and complexity of diatomic electronic spectra. These spectra are so complex that, aside from some herioc studies by BARROW, LAGERQVIST and MERER, their successful analysis had to await the advent of tunable laser techniques and matrix, rather than algebraic, effective Hamiltonian models. The electronic structure of many of these seemingly simple *diatomic* molecules is so profoundly different from that of molecules from the second and third rows of the periodic table, that even the most powerful *ab initio* electronic structure calculations are unable to *go beyond molecular constants* to a simple, predictive, zero-order electronic structure model. Quantitative relationships between the electronic structures of isoelectronic as well as non-isoelectronic atoms, based on semi-empirical reduction of spectroscopic observables to one- and two-electron orbital integrals [e.g. spin–orbit $\zeta(nl)$, Coulomb $F^k(nl, n'l')$ and exchange $G^k(nl, n'l')$], which illustrate so beautifully the predictive and interpretive power of *periodicity*, are altogether unavailable for the electronic structures of gas phase diatomic molecules. In contrast, the power of periodicity-based ideas (e.g. crystal and ligand field theory) is universally acknowledged in the interpretation of spectra of ionic crystals and inorganic metal–ligand complexes.

The purpose of this paper is to provide a summary of the powerful new experimental techniques that will be required to collect the huge quantity of high quality spectroscopic information from spectra of unprecedented complexity in order to begin to look beyond molecular constants for a periodicity-based, zero-order global electronic structure model for diatomic molecules with partially filled or low-lying *d* and *f* subshells.

In their introduction to *Molecular Spectra of Metallic Oxides*, FATHER JUNKES and FATHER SALPETER discussed the difficulty of finding suitable sources for generating all of the molecules on FATHER GATTERER's original list of target species. The required operating characteristics (path length, number density, temperature and temporal stability) of molecule sources differ enormously between classical, photographic grating spectrographs on the one hand and laser-based techniques on the other. One of

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* Dalian Institute of Chemical Physics, 129 Street, Dalian, Liaoning, China.

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us (R.W.F.), as a postdoctoral associate in the research group of BROIDA, became acquainted with the remarkably versatile "Broida oven" [2] and along with his students and collaborators, used this cw Broida oven source in laser spectroscopic studies of 13 of the 42 molecules in the original atlas! Many molecule sources well suited to laser spectroscopy have been designed and exploited. One of these, a cw, magnetically confined, multipass, sputter source [3], appears to be at least as versatile as the Broida oven, but has been shown to produce a molecular number density times pathlength more than 10^5 times larger than that achievable with the usual Broida oven. This sputter source is therefore valuable for absorption-based laser and non-laser spectroscopies, whereas the Broida oven was limited to laser excited fluorescence-based techniques. A variety of ingenious pulsed sources, typically used in a pulsed molecular beam apparatus, based on laser vaporization or photo-ablation have been invented by SMALLEY and co-workers [4] and FRIICHTENICHT [5]. In addition, the cw discharge and pyrolysis sources developed by ENGELKING [6] and CLOUTHIER [7] and co-workers have been successful in generating unstable and refractory molecules.

The extreme congestion of metal oxide spectra can be understood as arising from two factors: the high degeneracy associated with a partly filled d or f subshell and the importance of both $M^{2+}O^{2-}$ and $M^{+}O^{-}$ zero-order structures. For example, the degeneracy of an f^5 configuration is

$$\frac{14 \cdot 13 \cdot 12 \cdot 11 \cdot 10}{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1} = 2002$$

which will give rise to 1001 Ω-doubled molecular case (c) sub-states, each with nearly identical B_e and ω_e constants! Since the $4f$ orbitals in the rare earth oxides are too small to participate significantly in bonding, the open-core f^n structure is a spectator much like a nuclear spin, and the molecular states arising from f^n are distributed over the same energy range as the corresponding free-atom L–S–J states. Thus an f^5 open-core will split *each* of the usual dozen or so s, p-derived valence states into 1001 sub-states spread over a $\sim$30 000 cm^{-1} energy region. The resultant electronic density of *valence* states, $\rho_{\text{elect.}} \sim 1$ per 10 cm^{-1}, is staggering. Prior experience with second and third row diatomic molecules leaves us utterly unprepared for such a high ρ_{elect}. However, the situation is enormously simplified by the perfect nesting of the potential curves (resulting in strong $\Delta v = 0$ propensity rules for electronic transitions and spectroscopic perturbations) and the existence of many almost good electronic quantum numbers (open-core atomic J_c, L_c, S_c, Ω_c) which place stringent restrictions on observably strong transitions and perturbations.

The CaO orange and green bands illustrate the contrasting spectral complexity and electronic simplicity of the $M^{+}O^{-}$ structure. Except for the $X^1\Sigma^+$ and $A^1\Sigma^+$ states, all of the known electronic states of CaO are, to an excellent approximation, understandable as resulting from a weakly interacting electron-hole pair. The electron is well localized on the Ca and resides in an orbital derived from Ca$^+$ $4s$, $3d$, $4p$ orbitals shifted, split and mixed by the "crystal field" of a -1 point change at a distance, r_e, from the Ca nucleus [8–10].

Since the electronic states of CaF and CaO have similar r_e values, the Ca-centered orbitals in CaO are expected and observed to be identical to corresponding orbitals in CaF. The hole is well localized on O$^-$ $2p$ (i.e. p^{-1}) and may be oriented either π^{-1} or σ^{-1}. The O-centered hole orbital in CaO is well represented by the corresponding hole state in NaO, which has an r_e similar to that of CaO. Thus CaO is modelled by the Ca-centered $B\sigma$, $A\pi$, $X\sigma$ electron orbitals and the O-centered π^{-1}, σ^{-1} hole orbitals taken, respectively, from the single-electron and single-hole model molecule with the most similar r_e. The key evidence in support of this localized e$^-$/hole pair picture is the extremely small direct Coulomb and exchange Coulomb splittings among, for example, the $A\pi\pi^{-1}$ states of CaO [11].

TECHNIQUES FOR SIMPLIFYING COMPLEX AND CONGESTED SPECTRA

Examples will be taken from systematic studies of the spectra of CaO and NiH.

The CaO *orange and green systems*

The electronic structure of CaO, with a single hole localized on O^- and a single valence electron localized on Ca^+ (except in the divalent $X^1\Sigma^+$ state), gives rise to extremely congested spectra due to the simplicity of the structure. The localization of the two charges on separate centers necessarily leads to very small exchange and direct Coulomb integrals, and is reflected in the degeneracy of electronic states within each doubly localized Ca^+O^- electronic configuration. Also complicating the spectra is the fact that changing the electronic orbital of the electron centered on Ca^+ does not significantly affect the molecular constants, giving spectra in which many strong $\Delta v = 0$ band heads will be located very near one another. To make experimental studies more difficult, the Broida oven [2] source of CaO ($Ca + N_2O$) produces a sizable steady-state population in the two excited electronic states >1 eV above the ground state. These are the $A'^1\Pi$ and $a^3\Pi$ electronic states, the lower states in both the green and orange band systems of CaO. It is only through the use of the four laser-induced fluorescence excitation techniques described below that the analysis of the complex, congested and perturbed green and orange band systems of CaO has been made possible.

The first technique is laser induced intermodulated fluorescence excitation (IMF) [12]. The density of rovibronic transitions in almost the entire visible spectrum of CaO is ~10 lines cm^{-1} and increases dramatically near band heads. In order to resolve these features in our thermal source (~1 torr and 300°C), it is necessary to use this one-laser, sub-Doppler technique. By splitting the output of a single-mode, frequency stabilized, cw dye laser, amplitude modulating both beams at different frequencies, counterpropagating and crossing the two beams in the detection region and phase-sensitively detecting the fluorescence signal at the sum of the amplitude modulation frequencies, we obtain linewidths of approximately 100 MHz (power broadened) instead of the Doppler limited linewidth of ~1.5 GHz. This type of sub-Doppler resolution is critical for obtaining line positions accurate to the limit of the accuracy of our wavelength standard (I_2 molecular spectra [13]).

The second technique, dispersed fluorescence, involves laser excitation of a single rovibronically selected transition. Fluorescence from the excitation feature is dispersed by a 1-m monochromator at a typical resolution of ~1 cm^{-1}. Scanning the monochromator around the wavelength of the laser excitation gives several pieces of information important to assigning transitions in CaO. First, resolution of P, Q and R branch fluorescence gives both branch assignment and approximate (±1) J assignment for the transition, since rotational constants are known for both the $A'^1\Pi$ and $a^3\Pi$ states. It also gives $\Delta\Lambda = 0$ or ± 1 (parallel or perpendicular) electronic transition types as deduced from the relative strengths of $P(J+1)$, $Q(J)$ and $R(J-1)$ lines. Second, the spin-orbit mixing between $A'^1\Pi$ and $a^3\Pi_1$ generally allows fluorescence excited via any transition originating from one of these two lower states to be observed into the other lower state as well. The well characterized spin–orbit splittings of $a^3\Pi$, along with the well known $\Delta E_0(^1\Pi - {}^3\Pi_1) = 308\ cm^{-1}$, allows assignment of the lower electronic state from the resolved fluorescence spectra. Third, the lambda doubling in both the lower electronic states is well known, so that observation of the sign of an asymmetry in the P, Q and R triplet spacing in resolved fluorescence, typical of lambda doubled electronic states, allows assignment of e/f symmetry for both the upper and lower electronic states. Finally, fluorescence into other vibrational levels of the lower state may give an assignment of v''.

The third technique, selectively detected fluorescence excitation, simplifies fluorescence excitation spectra by detecting only transitions which result in fluorescence into a well-defined spectral detection bandwidth. This may be done by filtering the laser excited fluorescence with a colored glass filter or a monochromator. In the case of CaO, this technique was used in two different ways. First, upon locating a well-defined branch and identifying the P, Q and R nature of the branch using resolved fluorescence, we would center the monochromator bandwidth on one or more transitions in that branch, then scan the dye laser in the region of branches which share a common upper rotational level with the detected transition. This form of selective detection gives essentially the same information as resolved fluorescence spectroscopy, but at much higher resolution (0.005 cm^{-1} if used in conjunction with IMF). If the bandwidth is selected to be large enough to include several rotational levels in a branch, this allows assignment of a whole series of transitions within a branch. The second type of selective detection employed in the analysis of CaO takes advantage of the fact that some of the orange and green band transitions, excited out of the $a^3\Pi$ and $A'^1\Pi$ electronic states, >1 eV above the $X^1\Sigma^+$ state, may result in fluorescence back into the ground electronic state. This fluorescence, up to 8600 cm^{-1} to the blue of the laser frequency, is possible only for $^1\Pi$ and $^1\Sigma^+$ upper electronic states due to dipole selection rules for fluorescence into $X^1\Sigma^+$. Therefore, by detecting fluorescence through a blue pass colored glass filter, it was possible to selectively detect only $^1\Pi$ and $^1\Sigma^+$ states.

The fourth technique employed is modulated population spectroscopy (MPS) [14], a two-laser, lower level linked, optical-optical double resonance technique [15]. In this technique, one amplitude modulated laser is fixed on a well-characterized transition, thereby labelling the lower level of that transition. When the second laser is scanned through a transition originating in the same lower rotational level, fluorescence from this transition will be modulated at the amplitude modulation frequency of the fixed laser. This technique has three major applications in these studies. First, by labelling some well known lower state, it is possible to identify unambiguously the lower state in an unknown transition. Second, once a branch has been identified, MPS may be used to locate all other branches originating from the same lower rotationally, vibrationally and e/f-symmetry selected state. Third, in the case of a perturbation in the upper electronic state of a transition, a common occurrence in the congested CaO spectrum, the pump or fixed laser may be used to label the main line in the perturbation, selectively labelling the extra line originating from the common lower state and terminating in the perturbing state. The selectivity of MPS [14, 15] for labelling these usually weak extra lines makes this technique invaluable in analysing upper state perturbations.

Magnetic rotation spectroscopy and sideband optical–optical double resonance Zeeman spectroscopy

Single and multiple resonance spectroscopies are essential in locating and unambiguously determining the absolute rotational and electronic assignments of individual eigenstates in many molecular systems. Single resonance schemes, such as laser-induced fluorescence (LIF), are experimentally simple to perform and can rapidly generate a large quantity of spectral information. Unfortunately, for diatomic systems containing a transition metal, single resonance methods often lack sufficient selectivity to facilitate meaningful analysis. Traditional methods of spectral analysis and interpretation can be prohibitively tedious for single resonance schemes because of the congestion of the spectrum and the apparent complexity of a multiply perturbed energy level diagram. Multiple laser, multiple color, multiple resonance schemes, such as Zeeman optical–optical double resonance (OODR) spectroscopy, although experimentally more difficult to perform and more time-consuming than LIF, generate a relatively small amount of well-resolved and easily interpretable spectral information. The development of new types of survey spectroscopies which are experimentally simple to perform and which are simultaneously capable of significant spectral simplification and rapid generation of diagnostically important spectral information is of primary interest.

We have used two spectroscopic techniques; magnetic rotation spectroscopy (MRS) and sideband OODR–Zeeman spectroscopy (SOODRZ) [16], to simplify the rotational and electronic assignment of complicated diatomic spectra. MRS is generally selective to low-J lines, can unambiguously distinguish between P, Q and R branches and can presort $\Delta\Omega = 0, \pm 1$ sub-bands. Using SOODRZ, definitive information about the electronic character (g values) of the upper and lower states and absolute rotational assignments (J' and J'') for the diagnostically important low-J lines can also be determined.

Magnetic rotation spectroscopy is a simple, diagnostically powerful, one-laser, one-color absorption-based technique. Historically, MRS has been used as a method for detecting perturbations in the spectra of diatomic and small polyatomic molecules [17]. Recently, the sensitivity enhancement [18] and selectivity [19] of MRS has been recognized and documented. Unfortunately, its usefulness as a selective survey spectroscopy, potentially its most important feature, has gone largely unnoticed. An MRS experiment is performed by passing the output of a frequency-stabilized ring dye laser through a linear polarizer, a multipass sputter source and through a second, crossed polarizer. Only $\Delta M = \pm 1$ transitions are observed since a fixed, externally applied longitudinal magnetic field is used.

The MRS signal (its strength, phase and lineshape), detected through crossed polarizers, is very sensitive to the Zeeman pattern of the magnetically sensitive rovibronic transition being probed. In order to understand the usefulness of the Zeeman effect in providing meaningful information to electronic and rotational assignment and analysis, consider the classical expression of the Zeeman energies in Hund's coupling case (a):

$$E = -\mu_0 g_e H \frac{M\Omega}{J(J+1)}, \tag{1}$$

where $\mu_0 = 1.400$ MHz/Gauss is the Bohr magneton, H is the magnetic field strength and g_e is the electronic g-factor which contains information about the coupling of the total electronic spin and orbital angular momentum and is given by $g_e = \Lambda + 2.002\Sigma$ at the case (a) limit. Although the electronic states of transition metal-containing diatomic molecules, due to the large number of nearly degenerate and strongly interacting electronic multiplet components, can rarely be described by case (a) quantum labels ($^{2S+1}\Lambda\Omega$), the usefulness of Eqn. (1) can be retained by replacing g_e and Ω by $(g\Omega)_{\rm eff}$ for case (c) or intermediate case (a)–(b) situations. The Zeeman transition frequencies are:

$$\nu_{J',M''\pm1\leftarrow J'',M''} = \nu^0_{J'\leftarrow J''} \mp \mu_0 H \frac{(g\Omega)'_{\rm eff}}{J'(J'+1)} + \mu_0 H M'' \left[\frac{(g\Omega)'_{\rm eff}}{J'(J'+1)} - \frac{(g\Omega)''_{\rm eff}}{J''(J''+1)}\right]. \tag{2}$$

The strength of the MRS signal depends on the degree to which the M-dependent term is minimized in Eqn. (2). Equivalently, the signal strength is proportional to the frequency separation between the centroids of the $\Delta M = +1$ and $\Delta M = -1$ transitions. The phase depends on the relative position of the $\Delta M = +1$ and $\Delta M = -1$ centroids. For an arbitrary J', $\Omega' \leftarrow J''$, Ω'' electronic transition, strong MRS signals occur when $\Delta J = \Delta\Lambda = \Delta\Omega$ (or more precisely when $\Delta J = \Delta(g\Omega)_{\rm eff}$), because this type of transition minimizes the M-dependent term. Finally, the ability to discriminate low-J lines from high-J lines is a result of the $[J(J+1)]^{-1}$ dependence of the Zeeman effect. Initial experiments on the NiH $B^2\Delta_{5/2} - X^2\Delta_{5/2}(1, 0)$ ($\Delta\Omega = 0$ transition) sub-band demonstrate the potential power of this method. Figure 1 and Table 1 illustrate the selectivity and presorting achievable with MRS as compared to LIF. Unlike the LIF spectrum, where many relatively strong features are observed, in the magnetic rotation spectrum the lowest Q lines, $Q(2.5)$ and $Q(3.5)$, are 10 times stronger than any other P, R or higher-J Q branch feature. Also, the P branch is discriminated from the Q and R branches by relative phase.

Sideband OODR Zeeman Spectroscopy is a *one-laser, two-color* absorption-based technique where sub-Doppler Zeeman splittings are presented in a uniquely simple and diagnostically powerful format [16]. Unlike other Zeeman spectroscopies (such as IMF, see Fig. 2) where complex Zeeman resonance patterns [20, 21] obscure the *M-independent* $\Delta M = 2$, $(J, M+1) - (J, M-1)$ Zeeman interval

$$\Delta_J \equiv E_{J,M+1} - E_{J,M-1} = -\frac{2\mu_0 (g\Omega)_{\rm eff} H_J}{J(J+1)} \tag{3}$$

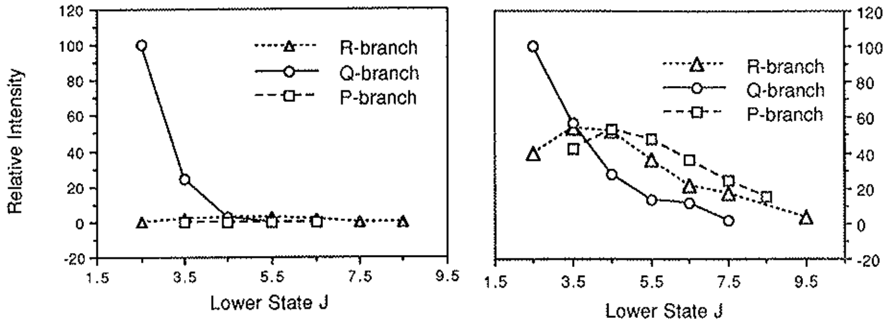

Fig. 1. MRS and LIF spectra of the NiH $B^2\Delta_{5/2}(v=1)-X^2\Delta_{5/2}(v=0)$ sub-band. Unlike the LIF spectrum, where many strong features are observed, in the MRS spectrum only two lines, the $Q(2.5)$ and $Q(3.5)$ lines, are strong. Since this is a $\Delta\Omega=0$ transition, the Q branch is, as expected, very strong relative to any other feature. Both the R and Q branches have the same relative phase. The P branch, like the R branch, is weak, but is of opposite phase. Despite the apparent weakness of the MRS signals for the R and P branches, they are observed without difficulty.

in *either* the upper state or lower state of an individual rovibronic transition, in SOODRZ [16] only two Zeeman resonance features corresponding to the *two* crucial Zeeman intervals are observed (H_J is the magnetic field strength at which the SOODRZ resonance occurs in the J level). The SOODRZ experiment is performed by passing the output of a frequency-stabilized ring dye laser through an acousto-optic modulator. The undiffracted laser beam at ω_l and the spatially separated, acousto-optically shifted first-order diffracted sideband beam at $\omega_l+\omega_{ao}$ are recombined and copropagated through the multipass sputter source. SOODRZ resonances, detected in the magnetic

Table 1. Experimental MRS and LIF relative intensities for the NiH B–X (1–0) $^2\Delta_{5/2}-{}^2\Delta_{5/2}$ sub-band

Line	Relative phase	Normalized relative intensities	
		MRS*	LIF†
$R(2.5)$	+	0.18	40.0
$R(3.5)$	+	1.60	54.0
$R(4.5)$	+	2.20	52.0
$R(5.5)$	+	2.40	36.0
$R(6.5)$	+	1.60	22.0
$R(7.5)$	+	0.24	17.0
$R(8.5)$	+	0.20	—
$R(9.5)$	+	—	3.7
$Q(2.5)$	+	100.00	100.0
$Q(3.5)$	+	24.00	57.0
$Q(4.5)$	+	2.50	28.0
$Q(5.5)$	+	0.31	13.0
$Q(6.5)$	+	—	12.0
$P(3.5)$	−	0.04	42.0
$P(4.5)$	−	0.31	53.0
$P(5.5)$	−	0.53	48.0
$P(6.5)$	−	0.58	36.0
$P(7.5)$		—	25.0
$P(8.5)$		—	15.0

* MRS line strengths were determined from peak heights and normalized relative to the strongest MRS feature, the $Q(2.5)$.

† Line strengths for the LIF data were determined by calculating the total integrated area for each line, correcting for laser power and normalizing relative to the most intense line, the $Q(2.5)$

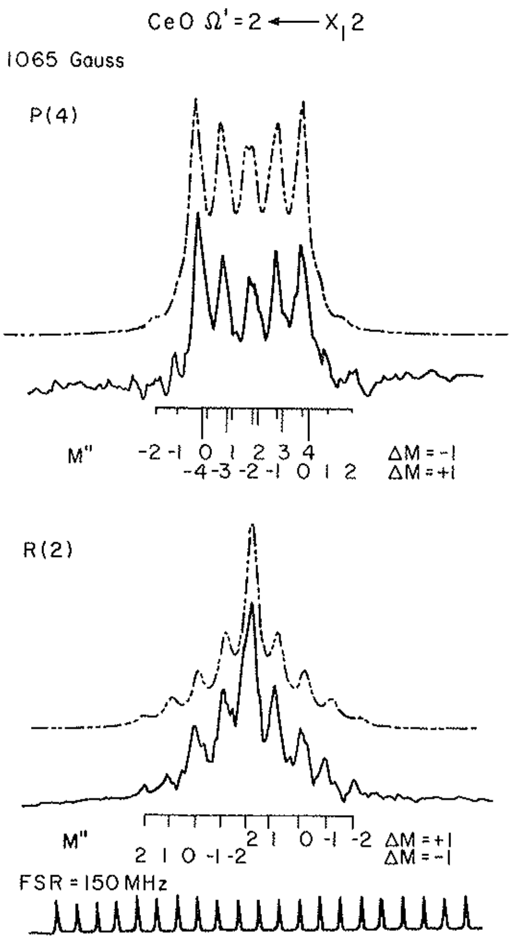

Fig. 2. Intermodulated fluorescence Zeeman spectra for the $P(4)$ and $R(2)$ lines of the $[16.5]\Omega' = 2 \leftarrow X_1 2(0,0)$ band of CeO. After assigning the experimental spectrum (solid line), combination differences between Zeeman components can be used to obtain upper state and lower state g_e values. Using g_e values obtained from the combination differences and intensity factors for the transition under question, the simulated Zeeman pattern can be calculated (dashed line) to check the original assignment.

rotation configuration, occur when the Zeeman interval $(J, M+1)-(J, M-1)$ tuned with an applied, longitudinal, magnetic field equals the acousto-optic modulation frequency ω_{ao}. A two-resonance SOODRZ spectrum (see Fig. 3), corresponding to one lower level linked and one upper level linked resonance, is observed.

Absolute rotational assignments can be determined from SOODRZ data. Since a fixed acousto-optic frequency is used, all resonances occur at the same frequency, ω_{ao}. From adjacent lines in a partial rotational branch fragment we have the following SOODRZ correspondences

$$\Delta_{J+1} \equiv E_{J+1,M+1} - E_{J+1,M-1} = \frac{2\mu_0 (g\Omega)_{\mathrm{eff}} H_{J+1}}{(J+1)(J+2)} \tag{4}$$

$$\Delta_J = \Delta_{J+1} = \omega_{ao}$$

$$J = \frac{2H_J}{H_{J+1} - H_J} \tag{5}$$

assuming that $(g\Omega)_{J,\mathrm{eff}} = (g\Omega)_{J+1,\mathrm{eff}}$ which is usually valid at low J. Once J has been assigned, information about the electronic state can be determined from $(g\Omega)_{\mathrm{eff}}$.

Zero-order electronic structure models

Figure 4 shows how the 16 lowest lying states of CeO can be easily understood in terms of the free Ce^{2+} (*fs*) atomic states [22, 23]. At the left of the figure is the CeO level diagram as it is determined from the analysis and absolute energy linkages of many electronic transitions [22]. Each level is labelled, through unambiguous identification of the lowest-J lines in the P, Q and R branches, with only an Ω quantum number. No pattern is evident in such a vertical stack of Ω-labelled levels. When the vertical stack is rearranged as five separate groups of states according to $(J_a-\Omega)=0$, 1, 2, 3, 4, the multiply replicated free Ce^{2+} (*fs*) energy level pattern immediately becomes evident. J_a is the atomic total angular momentum quantum number that results from the coupling of the open-core (f'') J_c with the Ce-centered valence $6s$, $j=1/2$ to yield $J_a=J_c+j$. The utility of this ligand field atomic-ion-in-molecule model (and the associated L_c, S_c, J_c, J_a, Ω_a quantum numbers) [23] is further illustrated by the successful *a priori* calculation of

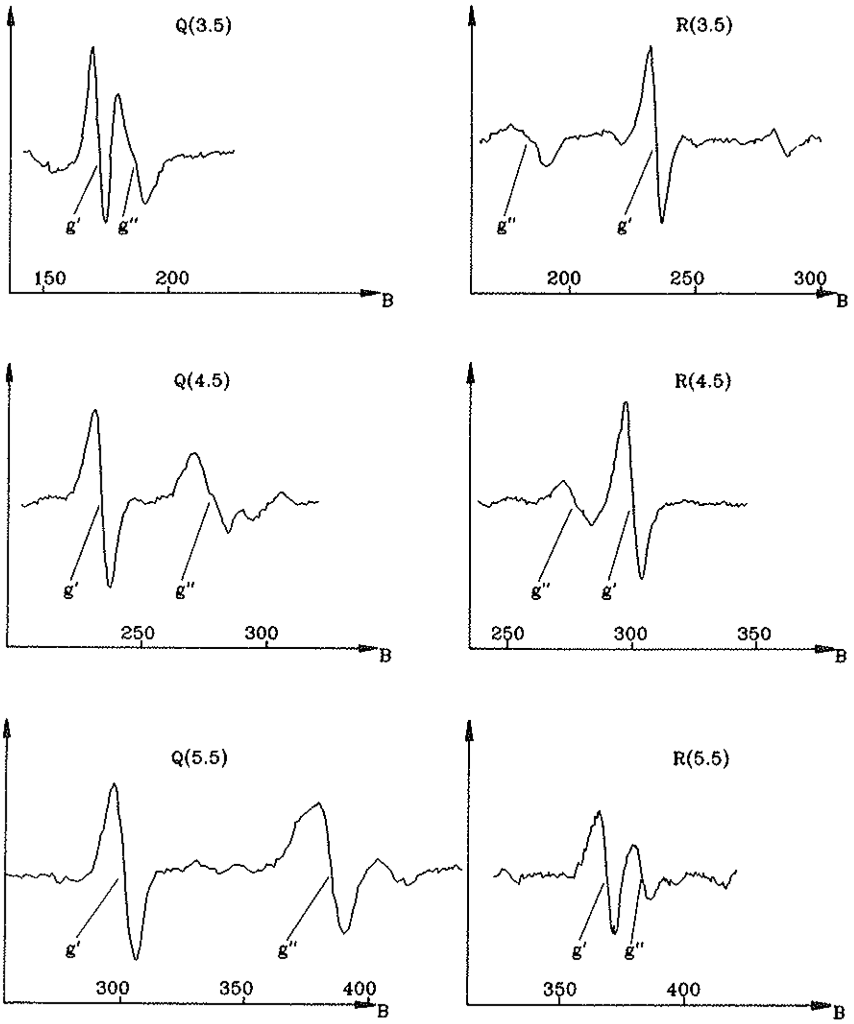

Fig. 3. SOODRZ resonances for the three lowest J, Q and R branch lines of the NiH $B^2\Delta_{5/2}(v=1)-X^2\Delta_{5/2}(v=0)$ sub-band (arbitrary intensity vs H, the magnetic field strength in gauss). Each spectrum contains two resonance features, which have been labelled g' and g'' according to whether the $(J, M+1)-(J, M-1)$ Zeeman interval probed was in the upper state (g') or lower state (g''). Adjacent, horizontally placed pairs of spectra have common lower state (g'') SOODRZ resonances, as indicated by identical H fields for one of the two resonance features. In the Q branch the upper state resonance always occurs at a lower magnetic field than the lower state resonance, implying that the upper state g value is larger and increases more rapidly with J than in the lower state. Similarly, in the R branch, the g' resonance overtakes g'' as J increases. Analysis is nearly instantaneous since typical scans times are approximately 2 min.

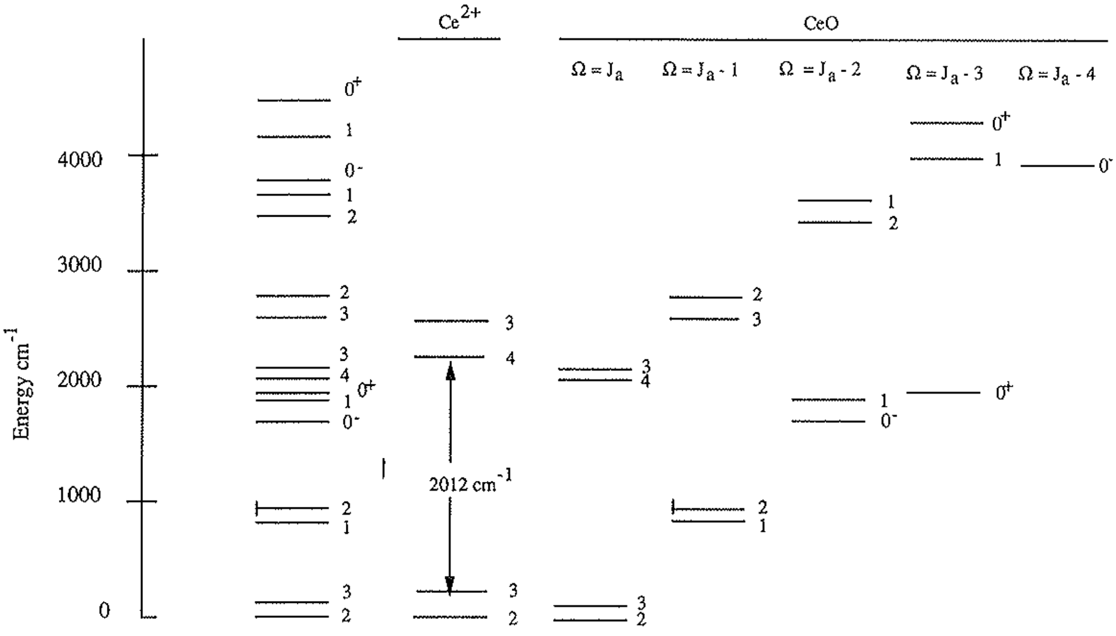

Fig. 4. The lower electronic states of CeO, arranged according to energy, J_a, and Ω.

magnetic g values for the fs states of CeO using the eigenvectors of the crystal field effective Hamiltonian [21].

Figure 5 shows how the energy level diagram for CaO resembles that of CaF [11]. Again we see the zero-order structure of a simpler system (CaF) multiply replicated in the electronic structure of a more complex system (CaO). The extremely small exchange splittings within the various $Ca^+O^-(p^{-1})$ electron/hole pair configuration is a dramatic illustration of the extreme localization of open shell electronic structures onto two separate atomic ions. Localization implies that one-electron orbital properties, such as spin–orbit and BL^+ orbit–rotation matrix elements, can be quantitatively transferred from CaF or NaO model systems to CaO. More significantly, an electron localized on Ca^+ and a hole on O^- implies that the electronic structure of CaO will be represented by zero-order integer valence Ca^+O^- and $Ca^{2+}O^{2-}$ structures. The recovery of such integer valence zero-order structures from real mixed-valence spectra can be viewed as a

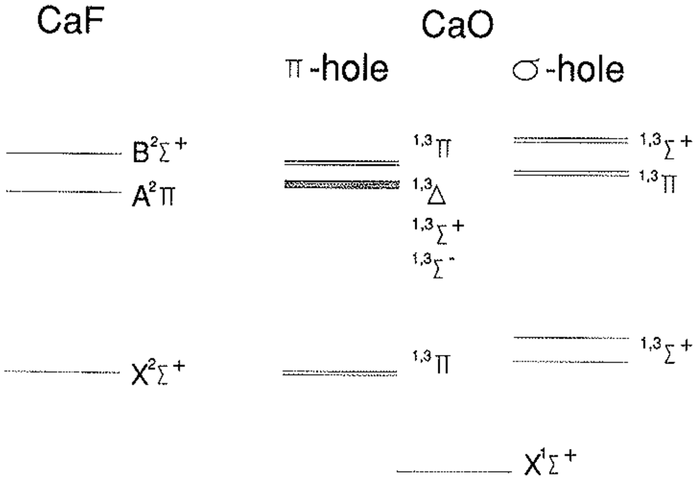

Fig. 5. Energy level diagram for CaF (left) and CaO. The CaO diagram has been divided, with the exception of the divalent $X^1\Sigma^+$ state, into O^- $2p\pi^{-1}$ and σ^{-1} manifolds of states. For each Ca^+ centered state in CaF, two mononvalent configurations appear in CaO, based on that Ca^+ orbital combined with either an O^- π^{-1} or σ^{-1} hole.

generalization of the deperturbation procedure whereby state-mixing effects resulting from accidental degeneracies are "removed" by fitting the observed energy levels against the eigenvalues of a suitable effective Hamiltonian matrix [24].

Monovalent/divalent deperturbation of CaO $^1\Sigma^+$ *states*

The ligand field, atomic-ion-in-molecule model presents some unique opportunities in a case such as CaO, in which most of the low-lying electronic states (14 of 17 predicted electronic states below 29 000 cm^{-1}) are observed and analysed [11, 25]. In this model, the low lying states are all understood within an integer-valence monovalent structure (Ca^+O^-) with extreme charge localization preserving the atomic-ion character on the two separate centres. The only exception to this model is the $X^1\Sigma^+$ ground state, which is predominantly divalent in character ($Ca^{2+}O^{2-}$). The monovalent electronic character of CaO may be understood as a combination of two isolated monovalent structures with the same structural characteristics as the model monovalent molecules with similar internuclear distances: CaF and NaO. The CaF structure is modelled as a single electron outside of a closed shell Ca^{2+} core [8–10]. The Ca^+ atomic-ion orbitals are perturbed by the F^- point-charge and induced dipole, lifting the l degeneracy of the atomic-ion orbitals. A similar effect is seen in NaO where the p^{-1} hole on the O^- centre is split into π^{-1} and σ^{-1} orientations, with the π^{-1} being more stable by about 2000 cm^{-1} at this internuclear separation [26, 27]. Electronic configurations in CaO are therefore composed of a Ca^+ part (named $X\sigma$, $A\pi$ and $B\sigma$ from analogy with the CaF $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ electronic states) and an O^- part (either π^{-1} or σ^{-1}): for example, $X\sigma\pi^{-1}$, giving rise to the $a^3\Pi$ and $A'^1\Pi$ electronic states (see Fig. 5).

It is a further consequence of the extreme localization of the electron/hole structures, on Ca^+ and O^- respectively, that direct and exchange Coulomb integrals, which are responsible for the observed splittings within a configuration, are very small compared to separations between different electronic configurations. It is therefore possible to determine accurate deperturbed potential curves for unknown or strongly perturbed electronic states based upon data from an analysed state of the same electronic configuration. The key to the M^+O^- and $M^{2+}O^{2-}$ deperturbation is that only states of $^1\Sigma^+$ symmetry can be of mixed-valence character because (i) the only symmetry possible for the double closed shell $Ca^{2+}O^{2-}$ structure is $^1\Sigma^+$ and (ii) the $1/r_{ij}$ electronic perturbation term has $\Delta\Lambda=0$, $\Delta\Sigma=0$ selection rules.

The $X^1\Sigma^+$ ground state of CaO is predominantly divalent at the equilibrium internuclear distance; however, the extrapolation to separated ions is four times faster ($4e^2/r$ vs $1e^2/r$) for the divalent $X^1\Sigma^+$ state than for the monovalent $A^1\Sigma^+$ state, just 11 550 cm^{-1} (1.4 eV) higher in energy [28]. It is therefore reasonable to expect these two potentials to cross at relatively short internuclear distance in the diabatic limit. Indeed, the $A^1\Sigma^+$ state, arising from the $X\sigma\sigma^{-1}$ configuration, has molecular constants considerably larger than the $b^3\Sigma^+$ state of the same configuration [25] and lies ~1500 cm^{-1} above that state compared to an expected exchange splitting of only 60 cm^{-1} [25], indicating considerable configuration interaction with the divalent ground state.

There are four $^1\Sigma^+$ states at $T_0 \leqslant 29\,000$ cm^{-1}: the X state (divalent), A state ($X\sigma\sigma^{-1}$, $T_0=11\,550$ cm^{-1}), C' state ($A\pi\pi^{-1}$, $T_0=24\,640$ cm^{-1}) and C state ($B\sigma\sigma^{-1}$, $T_0=28\,770$ cm^{-1}). In order to deperturb these interacting states, we must either locate another state from the same configuration which will provide a deperturbed reference potential curve, or predict the deperturbed potential curve using the ligand field model [8–10]. Recent work has located $v=1$ of the $b^3\Sigma^+(X\sigma\sigma^{-1})$ state [25], which, combined with rotational constants obtained from this study, a predicted exchange splitting for this configuration of ~60 cm^{-1} [25], and vibrational constants based on the $a^3\Pi(X\sigma\pi^{-1})$ state constants corrected by the NaO π^{-1}/σ^{-1} ($X^2\Pi$: $A^2\Sigma^+$) ratio of vibrational constants [26], yields a deperturbed location for the $A^1\Sigma^+$ state. The $C'^1\Sigma^+$ state has five states of the same configuration fully rotationally and vibrationally analysed, and its molecular constants fall well within the range of the other $A\pi\pi^{-1}$ states [11]. Any deperturbed curve we might construct for this state would be negligibly different from the observed $C'^1\Sigma^+$ state. We therefore conclude that this state does not measurably interact with the divalent potential curve at internuclear distances near equilibrium. The $C^1\Sigma^+$ state has been observed and analysed [29]; however, its $^3\Sigma^+$ configurational partner has not yet been observed. It is therefore necessary to construct a model deperturbed $C^1\Sigma^+$ state potential and energy location based on the ligand field model [8–10, 25]. The potential curve for this state may be constructed from the vibrational and rotational constants of the $B^1\Pi\,(A\pi\sigma^{-1})$ state [29] corrected by the ratios of constants for the CaF $B^2\Sigma^+$ and $A^2\Pi$ states [30]. We can then set the energy separation of this deperturbed curve, above the $A^1\Sigma^+$ deperturbed curve, equal to the $B^2\Sigma^+ - X^2\Sigma^+$ energy interval of CaF. The deperturbed reference potential curve thus produced lies less than 100 cm^{-1} below the observed potential curve over most of the outer wall of the potential. So, this shift is negligible in the region of interest for this CaO monovalent–divalent deperturbation.

Thus, we have only a two-state interaction between the CaO $A^1\Sigma^+$ and $X^1\Sigma^+$ states. We may therefore assume that the $X^1\Sigma^+$ potential curve has been shifted down by the amount that the $A^1\Sigma^+$ state has been shifted above its deperturbed potential. Plotting these two deperturbed potentials (X^* and A^*) corresponding to the integer–valence divalent and monovalent diabatic potentials, we observe a crossing at $r_c = 2.16$ Å (Fig. 6). If we include the shifts in $C^1\Sigma^+$ in the $X^1\Sigma^+$ deperturbation, the r_c value changes by less than 0.01 Å. We may therefore estimate the error in this internuclear distance to be ~0.5%.

The significance of this empirically determined $Ca^+O^- \sim Ca^{2+}O^{2-}$ monovalent–divalent curve crossing internuclear distance, $r_{1\sim2}$, is that the negative (and unmeasurable) electron affinity of O^-, corresponding to the endothermic process

$$O^- + e^- \Rightarrow O^{2-}$$

can be derived from the ionization potentials of Ca and Ca$^+$, the electron affinity of O, $r_{1\sim2}$ and the long-range $-1e^2/r$ and $-4e^2/r$ Coulomb attractions. The value of EA (O^-) $= -8.13 \pm 0.04$ eV derived from this integer valence deperturbation of gas phase CaO spectra is in satisfactory agreement with the value derived from alkaline earth oxide crystals, -8.08 ± 0.08 eV [31].

Now that EA(O^-) is known, the relative energies of the covalent (M^0O^0), monovalent (M^+O^-) and divalent ($M^{2+}O^{2-}$) $r \rightarrow \infty$ asymptotes for all MO diatomic molecules are

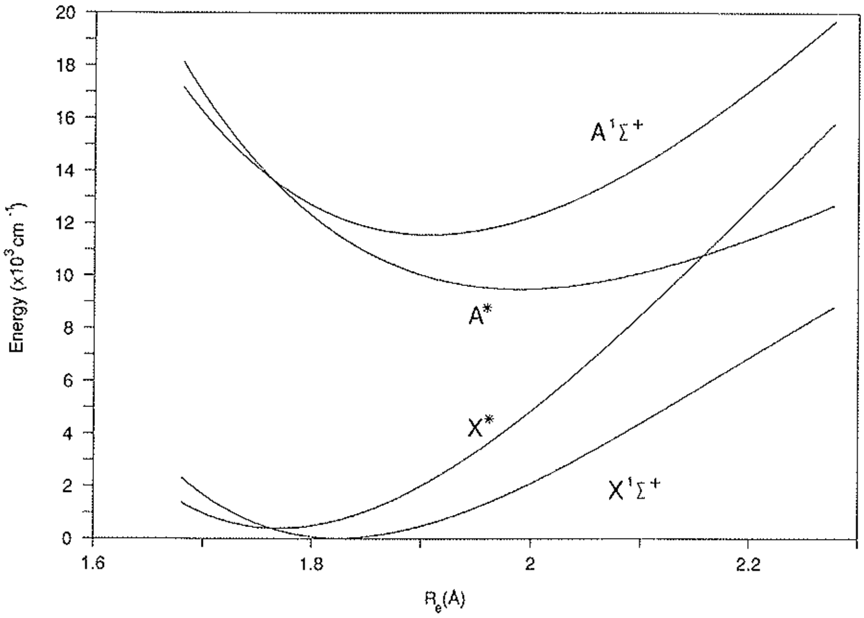

Fig. 6. RKR potential curves for the $A^1\Sigma^+$ and $X^1\Sigma^+$ electronic states of CaO. The two curves are deperturbed to their diabatic, integer valence potentials. This deperturbation yields a monovalent (A^*)/divalent (X^*) crossing distance of 2.16(1) Å and an electrostatic interaction matrix element of 5000(25) cm^{-1}.

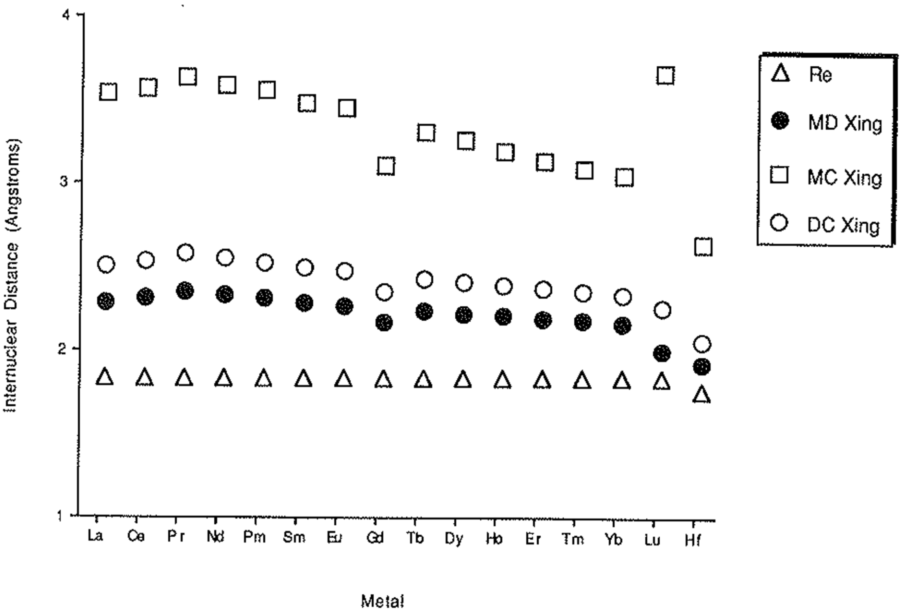

Fig. 7. The internuclear separations at which zero-order integer-valence potential curves calculated for the lanthanide oxides cross. DC: divalent/covalent; MC: monovalent/covalent; MD: monovalent/divalent. The ground state equilibrium bond lengths are included.

known. Figures 7 and 8 display the values of r_e (open triangle), $r_{1\sim2}$ (solid circle), $r_{1\sim0}$ (open square), and $r_{2\sim0}$ (open circle) for all of the 3*d* transition metal and 4*f* rare earth monoxide diatomic molecules. Figure 9 summarises the zero-order energies at r_e of the electronic ground state for covalent, monovalent and divalent transition metal oxides. Near r_e, the lowest lying electronic states of La⇒Yb and Ca⇒V monoxides are predicted to be predominantly divalent. (This zero-order $M^{2+}O^{2-}$ structure should not be confused with charge separations derived from Mulliken populations or electric dipole moments.) CuO is predicted to have a monovalent rather than divalent ground state.

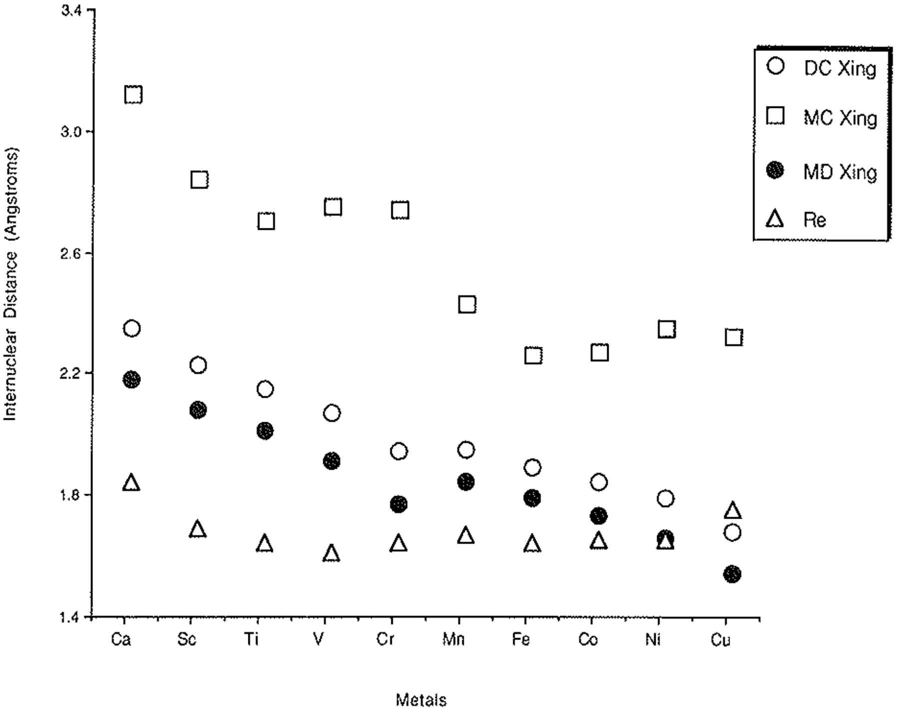

Fig. 8. The same quantities as in Fig. 7 are plotted for the 3*d* transition metal oxides.

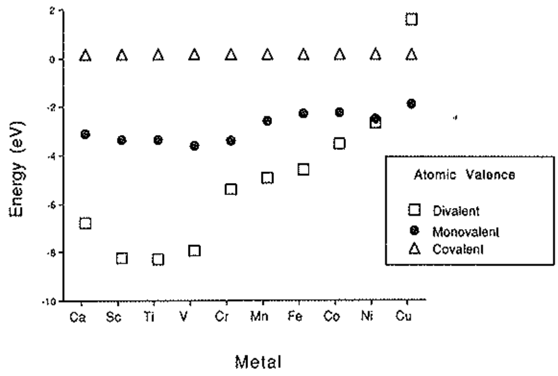

Fig. 9. The potential energy of each of the zero-order integer–valence configurations is shown at the ground-state equilibrium internuclear separation for the 3*d* transition metal oxides. As described in the text, these simple calculations accurately predict observed periodicities in the electronic structures of these molecules. The calculations of Figs 7–9 are made possible by the spectroscopic measurement of the electron affinity of O^- in CaO.

The small energy gap between M^+O^- and $M^{2+}O^{2-}$ structures for Co and Ni monoxides implies an extraordinarily complex, mixed-valence structure for these late 3*d* monoxide molecules.

SUMMARY

Remarkable progress has been made in recording, analysing, and understanding the "Molecular Spectra of Metallic Oxides" that were the subject of the photographic atlas initiated by FATHER GATTERER [1]. It now begins to appear that, although these spectra are pathologically complex by standards evolved from the analysis of second row diatomic molecules, the electronic structure that lies behind the molecular constants is elegantly simple. When one puts aside traditional molecular orbital, covalent bonding ideas and replaces then with integer valence, atomic-ion-in-molecule, ionic bonding ideas, periodicity is revealed with much of the quantitative predictive power so familiar in the spectra of many-electron atoms.

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DISCUSSION

PROFESSOR A. SCHEELINE: How can the spectral data be codified in a way that can easily be transmitted to someone else who wishes to reproduce the spectrum, without having to generate massive books or entire CD–ROMs filled with tables of line frequencies and assignments? Is there a smaller set of constants that can reproduce the actual line positions to spectroscopic accuracy, or are the perturbations simply too extensive?

PROFESSOR FIELD replied that while there is no zero-order model capable of reproducing the thousands of observed lines to measurement accuracy, i.e. eight significant figures, there are models based on known atomic Slater–Condon and spin–orbit parameters which can explain the energy level diagrams at the tens of wavenumbers level. The global structure of the levels can be reduced to a much smaller number of atomic-like parameters that are interpretable in terms of "Freshman Chemistry" concepts about orbital sizes and contractions. In order to provide a higher level of accuracy, the model must be expressed in terms of a larger and more elaborate Hamiltonian matrix. Such matrices are difficult to reproduce in print media, but perhaps could be distributed in computer-readable form.

PROFESSOR D. MILLEN: Can different molecular states have "exactly" the same constants, or are there differences beyond the limit of resolution? Also, have isotopes been deliberately chosen to avoid the effects of nuclear spin hyperfine structure?

PROFESSOR FIELD replied that rotational constants for different electronic states may differ in the fifth significant figure, but are frequently compromised by perturbations. The nuclear hyperfine structure, which is present for many of the transition-metal nuclei studied, and the Zeeman effect can be used to establish a unique identification.

PROFESSOR L. DE GALAN: For some of these molecules, there are about 24,000 low-lying electronic states. How does the molecule know which one of these is the lowest-energy state?

PROFESSOR FIELD replied that crystal field theory can be used in a way analogous to Hund's Rules in molecular orbital theory to determine the lowest-energy configuration and angular momentum states of these molecules. The ordering of the atomic configurations can be calculated without recourse to adjustable molecular parameters; predictable crystal-field, Slater and spin–orbit parameters then give the ordering of states within those configurations.

PROFESSOR R. BACIS: Is the model limited to ionic states, and can it be extended to the higher electronically excited states?

Professor Field replied that the model works well for homonuclear diatomic molecules, such as diatomic nickel, as well as for molecules such as calcium fluoride in which the bonding is clearly ionic. The situation becomes much more complicated for states arising from other than the lowest super-configuration, or for states in which there are two- or three-electron excitations; there are many more interactions present, and it is not yet possible to describe such systems in complete detail.

Theoretical considerations on the optogalvanic detection of laser induced fluorescence in atmospheric pressure atomizers*

N. OMENETTO,† B. W. SMITH and J. D. WINEFORDNER
Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

Abstract—Several theoretical considerations are given on the potential and practical capabilities of a detector of fluorescence radiation whose operating principle is based on a multi-step excitation–ionization scheme involving the fluorescence photons as the first excitation step. This detection technique, which was first proposed by MATVEEV *et al.* [*Zh. Anal. Khim.* **34**, 846 (1979)], combines two independent atomizers, one analytical cell for the excitation of the sample fluorescence and one cell, filled with pure analyte atomic vapor, acting as the ionization detector. One laser beam excites the analyte fluorescence in the analytical cell and one (or two) laser beams are used to ionize the excited atoms in the detector. Several different causes of signal and noise are evaluated, together with a discussion on possible analytical atom reservoirs (flames, furnaces) and laser sources which could be used with this approach. For properly devised conditions, i.e. optical saturation of the fluorescence and unity ionization efficiency, detection limits well below pg/ml in solution and well below femtograms as absolute amounts in furnaces can be predicted. However, scattering problems, which are absent in a conventional laser-enhanced ionization set-up, may be important in this approach.

INTRODUCTION

IN THE continuous search of new analytical methodologies, capable of detection sensitivities for trace metals down to 1 part in 10^{12} or less, Laser Induced Fluorescence (LIF) and Laser Enhanced Ionization (LEI) have emerged as useful approaches during recent years, especially when coupled to electrothermal atomizers. LEI in an air–acetylene flame is characterized by pg/ml detection limits [1, 2] and LIF with graphite furnace atomization currently achieves absolute detection limits of the order of femtograms [3–5]. These two techniques can therefore be important tools in many fields (e.g. the nuclear, electronic and biomedical industries) for ultratrace analysis of metals which can be present at concentration levels inaccessible even to highly sensitive techniques, such as graphite furnace atomic absorption or inductively coupled plasma emission or even plasma – mass spectrometry.

When attempting, however, the direct analysis of such low concentrations in real matrices, some problems exist. In LIF, the efficiency of detecting the fluorescence photons needs to be improved, for example by decreasing the transmission losses of the dispersion device used and by increasing the quantum efficiency of the photomultiplier. LEI suffers from the so-called "electrical interferences" which occurs in the presence of high concentrations of easily ionizable elements (e.g. alkalis) which severely modify the electric field distribution in the atomizer (and consequently the signal collection efficiency) while in addition increasing the noise level due to the increased fluctuations in the background current [2].

One possible way of overcoming both problems would be to detect the fluorescence photons via a resonance ionization detector, i.e. by the "resonance monochromator" technique. Such an approach for detecting radiation in atomic spectroscopy has been known for many years and has been advantageously exploited in absorption, emission and fluorescence spectroscopy. As pointed out by MATVEEV [6] in his recent review of this field, atomic resonance monochromators have been not only used for analytical applications but also for a variety of other applications, including frequency standards, conversion of i.r. into visible radiation and recording of dynamic holograms. Several typical applications of resonance detection of the radiation emitted by useful analytical sources such as glow

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† Present address: Commission of the European Communities, Environmental Institute, Chemistry Division, I-21020 Ispra (VA), Italy.

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discharges [7] or inductively coupled plasmas [8] have been reported in the literature, emphasizing the high spectral selectivity achieved.

The use of the ionization technique to detect fluorescence radiation was first proposed by MATVEEV *et al.* [9] and subsequently discussed by MATVEEV [10]. In this approach, the fluorescence from the sample to be analyzed is excited in one analytical cell, referred to here as the Sample Atomizer (SA), and subsequently conveyed by an optical system into another cell, filled with pure analyte vapor, referred to here as the Ionization Detector (ID). The analytical signal is the electrical current measured in the ionization detector. One laser beam is used to excite the fluorescence in the SA and one (or two) lasers are used to ionize the excited atoms in the ID. Therefore, the fluorescence photons emitted from the SA (and transferred to the ID) accomplish the first excitation step of the multi-step ionization scheme taking place in the detector. Such an excitation–ionization scheme is schematically depicted in Fig. 1. Two obvious advantages of such an approach are the elimination of the electrical interferences and increased noise in the ionization detector (since the sample and the ionizing cell are now separated) and the improvement in the quantum efficiency of the detector, which can be made close to unity, once the fluorescence photons are absorbed.

Apart from an attempt to monitor atomic absorption of pulsed dye laser radiation in a flame cell with an hollow cathode lamp acting as an optogalvanic detector [11], there seems to have been no other efforts made with conventional atom reservoirs used in LIF and LEI. The purpose of this paper is to present a detailed evaluation of the analytical capabilities of the proposed detection approach, in which both SA and ID are atmospheric pressure atomizers such as flames and graphite furnaces. One dye laser excites the analyte fluorescence while ionization is accomplished by one (or two) laser beam(s) (see Fig. 1). Scattering in the SA as well as its intrinsic radiative background are also considered as possible causes of signal (and noise) in the ID. Finally, a numerical evaluation of the possible signal-to-noise ratio attainable will be given for a typical element, a conventional two-flame (or flame and furnace) arrangement, and for typical laser systems such as excimer- or Nd–YAG–pumped tunable dye lasers.

2. THEORETICAL CONSIDERATIONS

In order to evaluate the feasibility of the ionization detection approach, we consider the simple atomic level scheme shown in Fig. 1. In this scheme, one laser is tuned to λ_{12}, i.e. to a strong resonance absorption wavelength of analyte atoms in the sample atomizer and

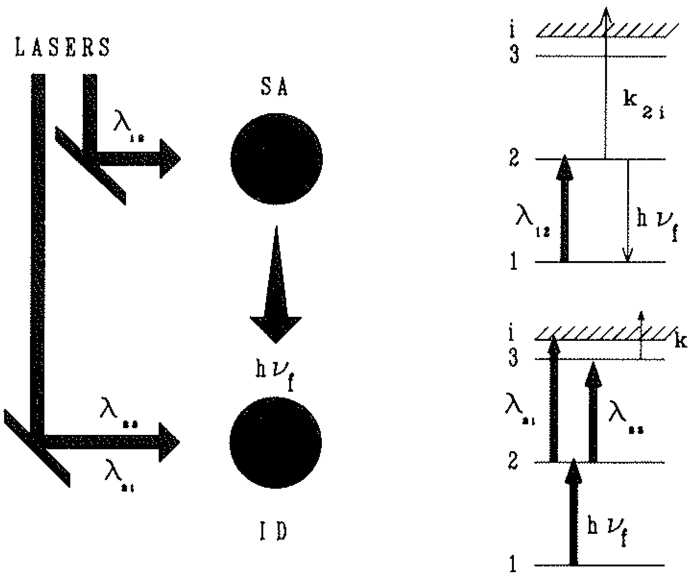

Fig. 1. Schematic principle of operation of the ionization detector. SA: sample atomizer; ID: ionization detector. Large arrows indicate laser and fluorescence excitation (at frequency $\nu_f = \nu_{12}$), while narrow arrows indicate collisional ionization, with rate coefficients k_{2i} and k_{3i}. Direct photoionization in the continuum (λ_{2i}) is also shown.

another laser, simultaneously sent into the ionization detector, is tuned either to a bound–bound transition (λ_{23}) or to a bound–unbound transition directly into the ionization continuum (λ_{2i}). The resonance fluorescence signal, plus any scattered radiation, thermal emission from the analyte and background emission from the atomizer are also collected into the detector and are possible sources of signal. Because of the different interaction times involved in these processes (since fluorescence and scattering will be pulsed while thermal and background radiation will be continuous), it was felt useful to separate here the discussion of the fluorescence process from the other processes.

2.1. *Ion production in the ID due to fluorescence in the SA*

In order to keep the treatment simple, use will be made of the rate equations approach by considering the lasers to be broad-band with regard to the absorption profile of atoms both in the SA and ID. In addition, because of pulsed laser excitation, recombination of ions and electrons is neglected. Also, in the sample atomizer, ionization losses from level 2 during the laser pulse are considered to be negligible compared to the fluorescence de-excitation process. This assumption will be more justified if the exciting laser pulse is short and if level 2 lies several eV below the ionization potential of the atom.

$$\dot{N}_f = (n_2)_{\text{SA}} A_{21} V_F = \left(\frac{g_2}{g_1 + g_2}\right)(n_T)_{\text{SA}}\left(\frac{\xi^s}{1 + \xi^s}\right) A_{21} V_F. \tag{1}$$

Here, $\dot{N}_f$ represents the number of fluorescence photons emitted per unit time over the entire fluorescence spectral profile and over 4π steradians, g_1 and g_2 are the statistical weights of levels 1 and 2, $(n_2)_{\text{SA}}$ and $(n_T)_{\text{SA}}$ are the number densities of excited atoms and the total number densities of atoms in the SA (cm^{-3}), $A_{21}(\text{s}^{-1})$ is the Einstein coefficient of spontaneous emission, $V_F(\text{cm}^3)$ is the fluorescence volume and ξ^s is a parameter describing the degree of saturation of the transition, and is given by

$$\xi^s \equiv \frac{I_l(\lambda)}{I_a^s(\lambda)} \tag{2}$$

where $I_l(\lambda)$ is the laser spectral photon irradiance ($\text{s}^{-1}\text{cm}^{-2}\text{cm}^{-1}$) at the transition $1 \rightarrow 2$ and $I^s(\lambda)$ represents the saturation spectral photon irradiance for a 2-level system, which can be expressed as [12, 13]

$$I_a^s(\lambda) = \frac{(2\tau)^{-1}}{\int\sigma(\lambda)\mathrm{d}\lambda}, \tag{3}$$

where τ is the actual lifetime(s) of level 2 and $\sigma(\lambda)$ is the spectral absorption cross section (cm^2) at wavelength λ of analyte atoms for the transition $1 \rightarrow 2$.

The effective photon irradiance (photons $\text{s}^{-1}\text{cm}^{-2}$), for excitation of the atoms in the ionization detector, will be governed by the efficiency of transferring the fluorescence radiation into the ID, i.e.

$$\dot{N}_{f,\text{exc}} = \dot{N}_f\left(\frac{\Omega_{\text{exc}}}{4\pi}\right)\left(\frac{1}{S_{\text{exc}}}\right), \tag{4}$$

where Ω_{exc} is the solid angle of excitation and S_{exc} is the excitation cross section in the ID.

From the foregoing considerations, it is clear that in order to maximize the fluorescence radiation into the detector, one should make ξ^s and V_F as large as possible. However, V_F and ξ^s go in opposite direction, since saturation is usually achieved with focussed laser beams. The solid angle of collection (Ω_{exc}) of the fluorescence should be large and S_{exc} should be made so to maximize its overlapping with the ionizing laser beam in the detector.

The number of electrons (and ions) formed in the ionization detector can be found by solving a system of differential equations, following the level scheme of Fig. 1. The ideal situation, however, is clearly that in which the ionization process is saturated, i.e. once the atoms are excited into level 2, they are ionized with 100% efficiency. With pulsed laser excitation, where the pulse duration does not exceed ~1 μs, it is the pulse width which dictates the interaction time. Therefore, in order to have unity ionization efficiency for the photoionization scheme of Fig. 1, the product of the ionization cross section (σ_{2i}) times the laser *fluence* ($I_l \Delta t_l$) must be (much) greater than unity. Likewise, in a collision-dominated atom reservoir (e.g. atmospheric pressure flame), when the laser is tuned to transition 2 → 3, the product of the collisional ionization coefficient (k_{3i}) and the interaction time (Δt_i) must be greater than unity. If these conditions are met, then the overall production of electrons during one probing time will be governed by the linear interaction between the fluorescence radiation and the atoms in the detector, leading to the following expression [14].

$$N_e \equiv n_e V_i = (n_T)_{\mathrm{ID}} V_i \{1 - \exp - \sigma_{\max} \dot{N}_{f,\mathrm{exc}} \Delta t_i\}. \tag{5}$$

Here, n_e and $(n_T)_{\mathrm{ID}}$ are the number density (cm^{-3}) of electrons and total number density of atoms in the ionization detector, V_i(cm^3) is the ionization volume, $\sigma_{\max}$(cm^2) is the peak absorption cross section for the transition 1 → 2 (see below) and $\Delta t_i(s)$ is the interaction time. It is worth noting that, the longer the interaction time Δt_i, the larger will be the ion yield. In this respect, therefore, longer laser pulses should be preferred or, ideally, the interaction time should coincide with the residence time of the atoms in the interaction volume. This requirement is not the same as that put forward for the sample atomizer, where long pulses are not advocated since they might favor atom losses due to ion production and enhanced chemistry within the SA.

Since the concentration of atoms in the SA is bound to be low for the technique to be analytically useful, the spectral profile of the fluorescence radiation can be assumed to be narrower than the absorption profile of the atoms in the ionization detector, at least for similar atom cells (e.g. flames and graphite furnaces). In this case, the absorption cross section at the line center can be expressed as [12]

$$\sigma_{\max}(\lambda_{12}) = 8.83 \times 10^{-13} \lambda_{12}^2 f_{\mathrm{abs}} \left(\frac{1}{\delta\lambda_{\mathrm{abs}}}\right) \tag{6}$$

where f_{abs} is the absorption oscillator strength (dimens) of the transition, $\delta\lambda_{\mathrm{abs}}$(cm) is the effective absorption linewidth and λ_{12} is the excitation wavelength (cm).

From Eqns (1) through (5), we then arrive at the following expression for N_e, after substituting $(N_T)_{\mathrm{ID}}$ for $(n_T)_{\mathrm{ID}} V_i$,

$$N_e = (N_T)_{\mathrm{ID}} \left\{1 - \exp - \left(\frac{g_2}{g_1 + g_2}\right) \sigma_{\max} (n_T)_{\mathrm{SA}} \left(\frac{\xi^s}{1 + \xi^s}\right) A_{21} V_F \left(\frac{\Omega_{\mathrm{exc}}}{4\pi}\right) \left(\frac{1}{S_{\mathrm{exc}}}\right) \Delta t_i \right\}. \tag{7}$$

This expression indicates the parameters involved in the interaction and their relative importance. It is seen that the total number of electrons will increase directly with $(N_T)_{\mathrm{ID}}$. However, it is clear that there will be a maximum value for n_T in the ionization detector, dictated by the shape of the *absorption* curve of growth for the fluorescence line. This curve will show a logarithmic slope of one at low values of n_T and a slope of zero at high n_T [12].

2.2. *Ion production in the ID due to other radiation processes in the SA*

As alluded to earlier, fluorescence is not the only radiation collected from the SA into the ID which can cause a pulsed ionization signal. In fact, scattering can arise in the SA from unvaporized particles due to the matrix, as well as thermal emission from the analyte atoms and background radiation. We evaluate here the relative importance of these contributions to the total signal in the ionization detector.

For the *scattering* photon irradiance, we can derive the following expression, with the assumption of isotropic scattering,

$$\dot{N}_{\mathrm{sc,exc}} = (n_{\mathrm{sc}})_{\mathrm{SA}} \mathrm{I}_l \sigma_{\mathrm{opt,sc}} \left(\frac{\Omega_{\mathrm{exc}}}{4\pi}\right) V_{\mathrm{sc}} \left(\frac{1}{S'_{\mathrm{exc}}}\right) \left(\frac{\delta\lambda_{\mathrm{abs}}}{\delta\lambda_l}\right). \tag{8}$$

Here, $(n_{\mathrm{sc}})_{\mathrm{SA}}$ is the number density (cm^{-3}) of scattering particles in the SA, I_l is the laser photon irradiance (s^{-1}cm^{-2}) integrated over its spectral profile, $\delta\lambda_l$, $\sigma_{\mathrm{opt,sc}}$(cm^2) is the optical cross section for scattering of particles, V_{sc} is the scattering volume (cm^3), and the other parameters have already been defined. The ratio between the spectral absorption profile half-width and the laser profile half-width takes into account that a broad-band laser was assumed; as a consequence, the scattered radiation will reproduce the spectral profile of the laser.

In the case of *thermal emission* of the analyte, we have

$$\dot{N}_{\mathrm{em,exc}} = (n_T)_{\mathrm{SA}}\left(\frac{g_2}{g_1}\right)\exp\left(-\frac{E_2-E_1}{kT}\right)A_{21}\left(\frac{\Omega_{\mathrm{exc}}}{4\pi}\right)V_{\mathrm{em}}\left(\frac{1}{S_{\mathrm{exc}}}\right), \tag{9}$$

where V_{em} is the thermal emission volume from the SA and S_{exc} is considered to be the same as that for the fluorescence and scattering signal.

In the case of *background radiation*, we have

$$\dot{N}_{\mathrm{bk,exc}} = \left(\frac{B(\lambda)}{h\nu_{12}}\right)S_{\mathrm{bk}}\,\Omega_{\mathrm{exc}}\left(\frac{1}{S_{\mathrm{exc}}}\right)\delta\lambda_{\mathrm{abs}}, \tag{10}$$

where $B(\lambda)$ is the spectral radiance (W cm^{-2}sr^{-1}cm^{-1}) of the atomizer, S_{bk} is the emitting area (cm^2) and Ω_{exc} and S_{exc} are assumed to be the same as in the other equations.

By taking into account that all these signal sources from the SA can excite atoms in the ID from level 1 to level 2 (disregarding any possibility of further excitation into level 3 or ionization into the continuum), Eqn (7) needs to be modified to include these possibilities, and the expression for N_e can be obtained as follows:

$$\begin{aligned} N_e = (N_T)_{\mathrm{ID}}\{1 - \exp[&-\sigma_{\max}\Delta t_l(\dot{N}_{f,\mathrm{exc}} + \dot{N}_{\mathrm{sc,exc}})] \\ &\exp[-\sigma_{\max}\tau_{\mathrm{res}}(\dot{N}_{\mathrm{em,exc}} + \dot{N}_{\mathrm{bk,exc}})]\}. \end{aligned} \tag{11}$$

Eqn (11) has been written so as to emphasize the different interaction times between the different radiations emitted from the SA and the atoms in the ID, i.e. the laser pulse, Δt_l, for the fluorescence and scattering processes and the residence time, τ_{res}, for the other processes. However, it is clear that, in an experimental set-up such as that schematized in Fig. 1, the interaction times for the fluorescence and ionization processes will be the same and will be given by the duration of the laser pulses, which can be considered to be equal, and for a gated detection system, τ_{res} should be replaced by the boxcar gate width.

2.3. *Numerical evaluation of the ion yield*

The results of the calculation of N_e for the different processes described above are collected in Table 2. These data were obtained by using for the parameters appearing in Eqns (1)–(11) the numerical values listed in Table 1.

By inspecting the data reported in these tables, several considerations can be pointed out:

(i) an atomic density in the SA (flame or graphite furnace) of 10^{11} cm^{-3}. This corresponds to about 1 μg/ml of a typical element (e.g. Na or Mg) in an air–acetylene flame and to several tens of picograms as an absolute amount deposited in a graphite furnace;

(ii) optically saturated conditions are assumed in the SA ($\xi^s \geqslant 10$);

(iii) the fractional solid angle available for excitation is 10^{-3}, which assumes a conventional *f*/2 lens collection system;

(iv) any signal induced in the ID by the background radiation emitted from the SA should be negligible during the short interaction time of the processes; and

(v) the parameters of the scattering process are calculated by assuming that a solution containing ~0.1% matrix is nebulized into the flame and that the diameter of the droplets formed is ~5 μm [17].

As one could have easily anticipated, scattered photons in the SA can cause an ID signal whose magnitude is comparable to that of the fluorescence signal. It seems therefore worthy to discuss how the scattering signal could be avoided. First of all, the fluorescence excited in the SA might well be of the non-resonance type, as schematized in Fig. 2. If level 1′ is thermally populated in the SA, then the first laser can be tuned to 1′ → 2 and the resulting scattered signal at the same frequency prevented from reaching the ID by an appropriate cut-off filter. The fluorescence radiation can still be effective, provided that the wavelength separation between the fluorescence and the excitation transition is sufficiently large. In fact, this scheme would allow the use of several fluorescence transitions reaching the same (or

Table 1. Numerical values for the parameters necessary for the evaluation of the number of electrons created in the detector

$V_F = V_{sc} = V_{cm} = 0.5\ \text{cm}^3$	$\delta\lambda_{abs} = 5 \times 10^{-10}\ \text{cm}$
$\frac{\Omega_{exc}}{4\pi} = 10^{-3}$	$\delta\lambda_l = 3 \times 10^{-9}\ \text{cm}$
$S_{exc} = 0.5\ \text{cm}^2$	$A_{21} = 10^8\ \text{s}^{-1}$
$(n_T)_{SA} = 10^{11}\ \text{cm}^{-2}$	$I_l(\equiv \int_{\Delta\lambda_l} I_l(\lambda)\text{d}\lambda) =$
$\xi^s = 10$	$= 10^{24}\ \text{s}^{-1}\text{cm}^{-2} (0.5\ \text{MWcm}^{-2})$
$g_1 = g_2$	$\sigma_{opt,sc} = 10^{-9}\ \text{cm}^{2\ddagger}$
$\exp\left(\frac{E_2 - E_1}{kT}\right) = 10^{-6}$	$n_{sc} = 10^4\ \text{cm}^{-3\ddagger}$
$(T = 2000\ \text{K}, \Delta E = 3\ \text{eV})$ $B(\lambda) = 1.7$ $\times 10^{-4}\ \text{Wcm}^{-2}\text{sr}^{-1}\text{cm}^{-1}$ (Air–C_2H_2 flame at 400 nm)	$h\nu_f = 5 \times 10^{-19}\ \text{J}$ (400 nm)
$B(\lambda) = 1.7$ $\times 10^3\ \text{Wcm}^{-2}\text{sr}^{-1}\text{cm}^{-1}$ (graphite furnace at 2000°C and at 400 nm)†	$\sigma_{max} = 6.8 \times 10^{-13}\ \text{cm}^2$
$\dot{N}_{f,exc} = 4.5 \times 10^{15}\ \text{s}^{-1}\text{cm}^{-2}$	$\Delta t_l = 10^{-8}\ \text{s}$
$\dot{N}_{cm,exc} = 10^{10}\ \text{s}^{-1}\ \text{cm}^{-2}$	$\tau_{res} = 10^{-3}\ \text{s}$
$\dot{N}_{bk,exc} = 2.2 \times 10^{10}\ \text{s}^{-1}\ \text{cm}^{-2}$	$S_{bk} = 0.5\ \text{cm}^2$
	$\Omega_{exc} = 1.3 \times 10^{-2}\ \text{sr}$
	$\dot{N}_{sc,exc} = 1.7 \times 10^{15}\ \text{s}^{-1}\ \text{cm}^{-2}$
	$N_{bk,exc} = 2.2 \times 10^3\ \text{s}^{-1}\ \text{cm}^{-2}$ (flame)

*From Ref. [15].
†From Ref. [16].
‡From Ref. [17].

Table 2. Total number of electrons (N_e) created in the ionization detector during one interaction time by the different radiation processes occurring in the sample atomizer

Process in the sample atomizer	$N_e(\equiv n_e V_i)$
Fluorescence ($\Delta t_i = \Delta t_l$)	$3.1 \times 10^{-5} (N_T)_{ID}$
Scattering ($\Delta t_i = \Delta t_l$)	$1.2 \times 10^{-5} (N_T)_{ID}$
Thermal emission ($\Delta t_i = \tau_{res}$)	$6.8 \times 10^{-6} (N_T)_{ID}$
Thermal emission ($\Delta t_i = \Delta t_l$)	$6.8 \times 10^{-11} (N_T)_{ID}$
Flame background emission ($\Delta t_i = \tau_{res}$)	$1.5 \times 10^{-12} (N_T)_{ID}$
Flame background emission ($\Delta t_i = \Delta t_l$)	$1.5 \times 10^{-17} (N_T)_{ID}$
Furnace emission ($\Delta t_i = \tau_{res}$)	$1.5 \times 10^{-5} (N_T)_{ID}$
Furnace emission ($\Delta t_i = \Delta t_l$)	$1.5 \times 10^{-10} (N_T)_{ID}$

nearby) levels in the ionization detector (see Fig. 2). Secondly, since the laser is polarized, it might be advantageous to use a crossed linear polarizer in front of the ID. Third, in principle, since the laser is pulsed, the fluorescence pulse in the SA might be longer than the scattering pulse, if the quantum efficiency of the transition is high. One could then delay the ionizing pulse until the scattering is decreased to zero. However, this would be difficult to realize in conventional atomizers, where the collision frequency is very high. Finally, if the fluorescence signal in the SA is saturated, one should decrease the laser intensity (e.g. with neutral

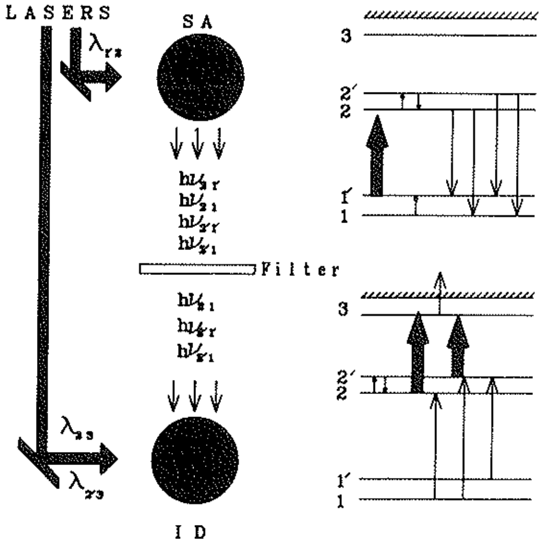

Fig. 2. Schematic illustration of the use of non-resonance fluorescence emitted in the SA to prevent the resonantly scattered signal from reaching the ID. The meaning of the arrow is the same as that of Fig. 1.

density filters in front of the SA) to take advantage of the linear decrease of the scattering signal with minimal loss of fluorescence intensity. This procedure has been advantageously used in analytical fluorescence studies in a graphite furnace [18].

As pointed out before, there will also be an optimum value for $(n_T)_{\mathrm{ID}}$, i.e. for the total number of atoms in the ionization detector. This value depends upon the shape of the absorption curve of growth for the fluorescence photons emitted in the SA.

2.4. *Considerations on noise, signal-to-noise ratio and detection limits*

If we assume that the limiting noise of the system is that commonly reported for optogalvanic detection, i.e. statistical shot noise fluctuations in the current accompanying the signal [2], it can be seen from the data reported in Table 2 what will be the relative importance of the different contributions to the overall noise level. Clearly, any instrumental noise, such as radiofrequency pick-up noise, which is particularly troublesome in many systems, is assumed here to be negligible. In addition to the noises in the signals of Table 2, there will be, of course, the noise due to the fluctuations in the background ionization current, characteristic of the detector itself. If this detector is a flame, then it is easy to convert the data of Table 2 into attainable signal-to-noise ratios.

An air–acetylene flame has an average background current, I, of about 10 μA while for a hydrogen-fuel flame this value decreases to about 0.04 μA. Therefore, the noise associated with the numbers of electrons collected during one interaction time will be given by $(2I\Delta t_i/q_e)^{1/2}$, or 1.1×10^3 and 71 in the case of acetylene and hydrogen flames, respectively, for $\Delta t_i = 10^{-8}$ s. As seen from the data of Table 2, this noise is much greater than those due to background radiation or thermal emission, for $(N_T)_{\mathrm{ID}} \sim 10^{13}$. A more realistic calculation takes into account the measuring time, which for pulsed laser excitation is the duration of the gate, and the averaging time, which dictates the number of interactions and is related to the repetition rate of the laser. For a 100 ns gate width, a 10 Hz repetition rate and 1 s averaging time, the above noise figures have to be multiplied by a factor of 10, i.e. 1.1×10^4 for the acetylene flame and 7.1×10^2 for the hydrogen flame. If one aspirates in the ionization detector a solution of 100 μg/ml of analyte, then $(n_T)_{\mathrm{ID}}$ will be approximately 10^{13} cm^{-3} and could be equal to $(N_T)_{\mathrm{ID}}$, if $V_i = 1$ cm^3. By considering the fluorescence in the SA as the only source of signal and background flame current as the limiting noise in the ID (i.e. by neglecting any increase in the noise due to thermal ionization of atoms in the detector), a signal-to-noise ratio of 3×10^4 and 4.4×10^5 for the acetylene and hydrogen detector flames, respectively, can be calculated. In the most favorable case, a concentrational detection limit, for a S/N ratio of 3, of 7×10^5 cm^{-3} ($\sim$70 pg/ml) or an absolute amount below femtograms would be achievable. It is certainly worth noting that a fluorescence transfer efficiency of 10^{-3} was assumed (see Table 1) since this is what can be easily realized in practice. With specially devised optics, once could realize a transfer efficiency of at least 10%, which would push the concentrational detection limit down to about 0.7 pg/ml, and the absolute amount in a graphite furnace to spectacular values, i.e. close to attograms.

3. Conclusions

As pointed out by Matveev [10], the optogalvanic detection of resonance radiation is indeed, in principle, characterized by extremely high detection sensitivities. The advantage of high detection efficiency, which is an inherent characteristic of the laser enhanced ionization technique, is coupled here with that of separating the excitation and detection processes in two independent atomizers.

Contrary to the case of conventional ionization measurements, this technique, however, may suffer from scattering problems, like the single-resonance excitation fluorescence method. In addition, the achievement of high detection sensitivity is contingent upon reaching unity ionization efficiency. As pointed out in the theoretical considerations, this strictly implies that the product of the laser fluence times the ionization cross section must be (much) greater than unity. In the case of direct photoionization, high laser powers are then needed. If, on the other hand, one relies upon collisional ionization, the requirement on the laser power might be in principle relaxed, since the laser is now tuned to a strong bound–bound transition. However, in such a collision-dominated system, the excitation process in the ionization detector has also to compete with *downward* collisional rates, which might severely impair the efficiency of the ionization process. *If these conditions are not met, then the technique will lose its attractiveness.*

The ideal sample atomizer should be characterized by the following features:

(i) it should have a high quantum efficiency for the fluorescence process;

(ii) it should be capable of complete vaporization of the sample matrix as well as complete atomization of the analyte; and

(iii) it should have a low-to-moderate thermal emission background.

The ideal ionization detector should be characterized by the following features:

(i) it should have a large acceptance solid angle for the incoming radiation and a practical geometry for the ionization detection;

(ii) it should provide a minimal ionization background current, i.e. it should not be itself the cause of limiting noise;

(iii) it should provide a maximum uniform density of absorbing atoms in the ground state and in a volume which matches perfectly the irradiation volume transferred from the SA; and

(iv) it should provide a long residence time of the atoms in the interaction volume.

The ideal laser for the excitation of the fluorescence in the SA should have a short pulse width capable of saturating the fluorescence transition with minimal losses of excited atoms due to enhanced ionization or chemical reactions. For the ID, the laser should provide an interaction time equal to the residence time of the atoms in the detector.

It is easy to conclude that these requirements will hardly be met simultaneously. A good compromise, at least for several easily atomized elements, might be realized by using a graphite furnace as a sample atomizer and a narrow, penciled argon–oxygen–hydrogen flame as the ionization detector.

It seems fair to anticipate that this technique will not be simple to implement from the practical standpoint when compared to the individual techniques from which it is composed, i.e. LEI and LIF. On the other hand, the concept of resonance ionization detection can certainly be extended to other techniques as well, for example, to conventional *emission* measurements. In this case, only the ionizing laser (or lasers) would then be needed. An experiment is now in progress in our laboratory using a 2-flames and a flame-and-furnace arrangement to evaluate the practical feasibility of the proposed approach.

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A new, sensitive, high resolution Raman detector based on ionization

B. W. SMITH, N. OMENETTO* and J. D. WINEFORDNER†
Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

Abstract—A novel detection method for weak pulsed or cw Raman fluxes is described. The detector is based upon the production of Raman scatter with a tunable pulsed or cw dye laser, collecting a large fraction of the Raman scatter and transferring it efficiently into an ionization detector containing a metal (M) vapor, such as Li. The resonance ionization detector (RID) is simultaneously illuminated by a second dye laser. When the second laser is tuned to an excited state transition of the metal vapor M and when the first laser is at such a wavelength that the Raman scatter appears at the ground state absorption transition of the metal, then a current will be produced in the RID which is proportional to the Raman scatter intensity. Both the production and collection of this current can be made very efficient (approaching 100%) and should result in improved sensitivity compared to conventional dispersive or FT Raman techniques. The new approach should be much less sensitive to scatter, should have a spectral resolution better than 0.1 cm^{-1} and should allow Raman scatter measurements to be made at wavenumbers below 100 cm^{-1} and under certain conditions to 0.01 cm^{-1}. The approach should be especially useful in highly scattering environments like Ag-sols in surface enhanced Raman and should be useful for detection of ultratrace levels of drugs and metabolites in biological fluids. The Raman–RID approach should also be useful for resonance Raman since laser scatter and molecular fluorescence should have minimal effects.

INTRODUCTION

THE DETECTION of one spectroscopic process by observing its effect upon another spectroscopic process is termed resonance detection. Such detectors have been called resonance monochromators, especially when used to detect atomic fluorescence [1, 2]. The use of resonance monochromators for atomic fluorescence has been based primarily upon the generation and detection of fluorescence in a separate cell [1, 2] although MATVEEV [3] has recently proposed and evaluated an ionization detector for laser excited atomic fluorescence. OMENETTO *et al.* [4] have also theoretically evaluated this detector. The principles of resonance detectors (RD) for line spectra detection are shown in schematic form in Fig. 1. Resonance detectors can be based on either ionization (RID) or on fluorescence (RFD). In the case of the RID, the signal is measured optogalvanically, and in the case of the RFD, the signal is measured photoelectrically.

Because of the rather small cross-sections for Raman scatter and because of the presence of stray light, the requirements for Raman detection are unusually stringent [5, 6]. In the conventional approach, the laser induced Raman scatter is collected by suitable optics, transferred to a double or triple monochromator and detected by a photomultiplier tube. In a more recent approach, the laser induced scatter is made to occur in the near i.r., is collected and transferred via suitable optics (including a source line rejection filter) to a Michelson interferometer, detected by a photodiode and the interferogram is treated by Fourier transformation to give the Raman spectrum. In both cases, stray laser light scatter is rejected to a large degree but with loss of signal (and thus signal to noise ratio) which results in rather poor detection limits even when resonance enhancement and/or surface enhancement techniques are used. These systems are characterized by a restricted spectral range which is limited at the low energy end by the laser profile, laser intensity, spectral rejection of the system and by a nominal resolution which is often limited by the need for reasonable spectral bandpass in the dispersive

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* Present address: Commission of the European Communities, Environmental Institute, Chemistry Division, I-21020 Ispra (VA), Italy.

† Author to whom correspondence should be addressed.

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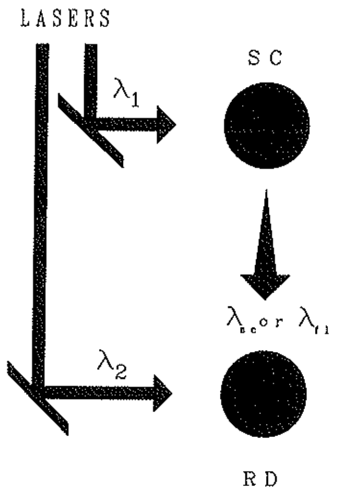

Fig. 1. The sample in the sample cell (SC) is excited by λ_1 to produce line emission, fluorescence or line scatter (Raman), and the resulting fluorescence (fl) or scatter (sc) produced in the SC is collected and impinges on the resonance detector (RD) where λ_{fl} or λ_{sc} excites an atom M in RD to an excited level. The laser at λ_2 present only in RD excites the same M atom onto a level near the ionization limit where collisional ionization occurs. λ_2 can also directly ionize M. The optogalvanic signal is an ionization current. The RD could also be based on fluorescence where the two excitation processes occur but then fluorescence in the u.v. ($\lambda_{fl} < \lambda_1$ and $\lambda_{fl} < \lambda_2$) is measured.

system or short mirror travel in the interferometer. In this manuscript, a new approach to detection of spontaneous Raman scatter as well as resonance Raman [7], surface enhanced Raman [8] and surface enhanced resonance Raman [9] is evaluated theoretically. The new approach involves the use of a resonance ionization detector which overcomes many of the difficulties occurring with the currently used Raman detection techniques.

BASIS OF RAMAN RESONANCE–IONIZATION DETECTOR

In the laser excited Raman–RID detector, Raman scatter in a gas, liquid or solid will be produced using a tunable dye laser, with a wavenumber designated as $\tilde{\nu}_{l1} = 1/\lambda_{l1}$. The Raman scatter (plus all other forms of scatter, emission, and fluorescence background) will be efficiently collected and transferred to an RID containing atomic species, M, which has a first resonance transition of λ_1 (process $1 \rightarrow 2$). Simultaneously, the RID is illuminated with a second dye laser at λ_2 to excite atom M to the ionization limit ($2 \rightarrow i$) or to an excited state ($2 \rightarrow 3$) near the ionization limit. When the first laser, $\tilde{\nu}_{l1}$, is adjusted so that $\tilde{\nu}_{l1} - \tilde{\nu}_1$ equals the energy of a vibrational transition, $\Delta\tilde{\nu}_v$, then ionization of M will occur in the RID via the collisionally assisted two color excitation or directly via two color photoionization. This process is depicted in Fig. 2. The RID cell must be capable of producing M atoms with minimal production of M^+; a simple RID cell would be an atmospheric pressure H_2–air flame containing Li (nebulization of $100\,\mu g\ ml^{-1}$ at ~ 1 ml min^{-1}). The energy level diagram of Li is shown in Fig. 3 with a possible transition scheme. The upper state is within 0.85 eV of the ionization limit. Once a Li atom is excited to 4.5 eV, it will be efficiently collisionally ionized. Therefore, Raman scatter which occurs at 670.8 nm ($\tilde{\nu}_1 = 1/\lambda_1$) will produce a signal as long as 460.3 nm laser radiation is also illuminating the RID. The dye lasers can be cw (Ar^+, Kr^+ or Nd–YAG pumped) or pulsed (Excimer, Nd–YAG or Cu-vapor pumped). In the case of the pulsed lasers, it is essential that there is proper temporal and spatial overlap of the Raman pulse ($\tilde{\nu}_1$) and the pulse of the second laser ($\tilde{\nu}_2$) within the RID.

The resulting Raman–RID system should be immune to scatter, emission and fluorescence, except that which spectrally overlaps the absorption line profile (FWHM of

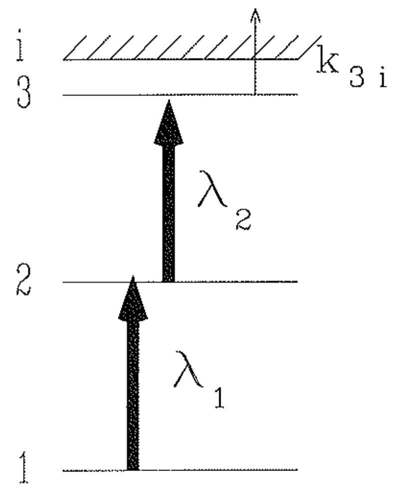

Fig. 2. Energy level diagram of metal M in RID. Dye laser at λ_2 is fixed and dye laser (number 1) scans until $1/\lambda_{l1} - 1/\lambda_1 = \Delta\tilde{\nu}$, resulting in Raman scatter at λ_1.

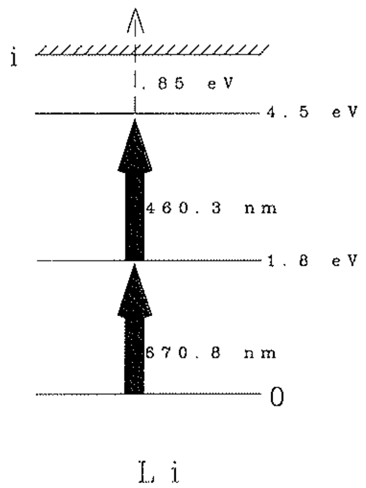

Fig. 3. Energy level diagram of Li showing two transitions.

$\delta\tilde{\nu}_{\text{abs}}$) of the metal M in the RID. In addition, the Raman–RID should allow a much larger throughput ($L = A \cdot \Omega \cdot \Pi T_i$; where A is the limiting aperture (cm^2), Ω is the limiting solid angle and ΠT_i is the product of the transmittance or reflectance of all optical components) than conventional Raman systems and therefore much larger Raman signals. Since the RID should have extremely low noise levels, the Raman limits of detection should be excellent. Finally, because of the narrow dye laser lines ($\tilde{\nu}_{l1}$ and $\tilde{\nu}_2$) and the narrow $\delta\tilde{\nu}_{\text{abs}}$ of M in the RID, the Raman–RID system should be capable of measuring Raman spectra over a range starting from less than 100 cm^{-1} (depending upon the absorption profile of M in RID) to an upper limit depending on the dye used in the first laser.

ESTIMATION OF SIGNALS AND SIGNAL TO NOISE RATIOS WITH THE RAMAN–RID APPROACH

The Raman photon flux impinging on the RID (photons cm^{-2} s^{-1}) can be estimated [4] using

$$\dot{N}_R = (n_A)_{SC}\phi_l\left(\frac{\delta\sigma_R}{\delta\Omega}\right)Gl_{SC}\left(\frac{\Omega_{exc}}{S_{exc}}\right)\left(\frac{\delta\tilde{\nu}_A}{\delta\tilde{\nu}_R}\right), \tag{1}$$

where

$(n_A)_{SC}$ = number density of analyte, A, in the sample cell, SC (cm^{-3}),
$(n_A)_{SC}$ = $(C_A)_{SC}N_A\rho/MW_A \times 10^6 = (C_A)_{SC}\left(\frac{6\times10^{17}\rho}{MW_A}\right)$ (cm^{-3}),
$(C_A)_{SC}$ = concentration of analyte, A, in SC ($\mu g\ g^{-1}$ or ppm),
ρ = density of solvent ($g\ ml^{-1}$),
MW_A = molecular weight of analyte, A ($g\ mol^{-1}$),
N_A = Avogadro's number $= 6\times10^{23}$ (molecules mol^{-1}),
ϕ_l = source (laser) photon flux (photons s^{-1}),
ϕ_l = $E_l(\lambda_1)\cdot S_l$,
S_l = area of laser beam, λ_1, which results in analyte Raman scatter (cm^2),
$E_l(\lambda_1)$ = laser photon irradiance at λ_1 ($cm^{-2}\ s^{-1}$),
S_{exc} = area over which Raman scatter occurs (cm^2),
$\frac{\delta\sigma_R}{\delta\Omega}$ = differential Raman cross-section ($cm^2\ sr^{-1}$),
G = multiplication or gain due to surface enhancement effect (electrodynamic or chemical) (dimensionless),
l_{SC} = path length over which Raman scatter in SC is collected and transferred to RID (cm),
Ω_{exc} = solid angle of Raman scatter collected and transferred to RID (sr),
$\delta\tilde{\nu}_R$ = Raman line width (cm^{-1}),
$\delta\tilde{\nu}_A$ = absorption line width of metal, M, in RID (cm^{-1}).

In Eqn (1), it is assumed that $\delta\tilde{\nu}_A/\delta\tilde{\nu}_R \leqslant 1$. If the ionization efficiency of M from level 3 is unity, the number of electrons, N_e, produced in the RID [4] as a result of Raman scatter is given by

$$N_{e(R)} = (n_T)_{RID}V_i[1-\exp(-\sigma_{abs_1}\dot{N}_R\Delta t_i)]\cdot ft_m, \tag{2a}$$

if the transition of λ_2 is optically saturated. The number of electrons will be

$$N_e(R) = (n_T)_{RID}V_i[1-\exp(-\sigma_{abs_1}\dot{N}_R\sigma_{23}E_l(\lambda_{23})\tau_2)\Delta t_i]\cdot ft_m, \tag{2b}$$

if the transition at λ_2 is not optically saturated, which may occur for cw lasers when a quenching flame is used as the ionization detector. In Eqns (2a) and (2b) the symbols are as follows:

$(n_T)_{RID}$ = number density of metal, M, in RID (cm^{-3}),
V_i = volume of interaction region in RID (cm^3),
σ_{abs_1} = absorption cross-section for M (transition 1→2) at λ_1 in RID (cm^2),
$\dot{N}_R$ = Raman photon flux impinging on RID [given by Eqn. (1)] ($cm^{-2}\ s^{-1}$),
Δt_i = interaction time for Raman scatter (s). This time is given by the laser pulse duration in case of pulsed excitation and by the residence time of the atoms in the laser beam, τ_{res}, in the case of cw excitation,
f = repetition rate of pulsed laser (s^{-1}). This parameter can be identified with $(\tau_{res})^{-1}$ in the cw case,
t_m = total measurement time (s),
σ_{abs_2} = absorption cross-section for M at λ_2 in RID (cm^2),
$E_l(\lambda_2)$ = laser photon irradiance at λ_2 ($cm^{-2}\ s^{-1}$),
τ_2 = effective lifetime of level 2 of M in RID (s).

By expansion of the exponentials, one can see that the lack of saturation results in a large loss in the number of electrons produced, i.e. by the factor of $\sigma_{\mathrm{abs}_2} E_l(\lambda_2)\tau_2$ (which is usually much less than unity).

The only source of SC background in the case of Raman spectroscopy of molecules in the condensed phase is background fluorescence from concomitants and possibly the analyte itself. Of course, as long as the first laser wavelength, λ_{l1}, is sufficiently long (say $\geqslant 650\,\mathrm{nm}$), fluorescence should be minimal or non-existent. In the case of RRS (resonance Raman spectroscopy), however, fluorescence is possible from the analyte or interferents. In this case, an estimate of the fluorescence flux from SC, $\dot{N}_\mathrm{F}$, can be found from

$$\dot{N}_\mathrm{F} = (n_\mathrm{A})_\mathrm{SC} \phi_l Y_\mathrm{F} S_\mathrm{F}(\lambda) \left(\frac{\delta\sigma_\mathrm{A}}{\delta\Omega}\right) l_F \Omega_\mathrm{exc} \left(\frac{\delta\tilde{\nu}_\mathrm{A}}{\delta\tilde{\nu}_\mathrm{F}}\right) \tag{3}$$

and

$$N_{\mathrm{e(F)}} = (n_\mathrm{T})_\mathrm{RID} V_\mathrm{i}[1 - \exp(-\dot{N}_\mathrm{F}\sigma_{\mathrm{abs}_1}\Delta t_\mathrm{i})] \cdot f t_\mathrm{m}, \tag{4}$$

where all terms have been defined above except for

$\dfrac{\delta\sigma_\mathrm{A}}{\delta\Omega}$ = differential absorption cross-section of concomitant or analyte in SC ($\mathrm{cm}^2\,\mathrm{sr}^{-1}$),

l_F = path length over which fluorescence in SC is collected and transferred to RID ($l_\mathrm{SC} \approx l_\mathrm{f}$), (cm),

Y_F = quantum efficiency for the fluorescence process (dimensionless),

$S_\mathrm{F}(\lambda)$ = fraction of fluorescence at λ_1 compared to the peak fluorescence (dimensionless),

$\dfrac{\delta\tilde{\nu}_\mathrm{A}}{\delta\tilde{\nu}_\mathrm{F}}$ = ratio of absorption line width of M in RID to fluorescence band of analyte (or concomitant) in SC (dimensionless).

The differential absorption cross-section is given by

$$\frac{\delta\sigma_\mathrm{A}}{\delta\Omega} = \frac{B_{ij} h\nu_0 S_\nu}{\mathrm{c}\Omega_\mathrm{exc}} = \frac{A_{ji} g_j \lambda_0^2 S_\nu}{8\pi g_i \Omega_\mathrm{exc}}, \tag{5}$$

where

B_{ij} = Einstein coefficient of stimulated absorption, $i \rightarrow j$ ($\mathrm{cm}^3\,\mathrm{Hz/J \cdot s}$),

λ_0 = peak absorption wavelength (cm),

S_ν = spectral profile of the band or line (Hz^{-1})

g_i, g_j = statistical weights of lower, i and upper, j, states (dimensionless).

In the gas phase, additional noise sources may arise from thermal emission, such as in combustion flames or plasmas, and coincidental line emission at λ_1. However, both of these noise sources will seldom produce RID shot noise currents approaching the inherent shot noise in the background current of the RID and so will not be evaluated here. For example, if a H_2–air flame is used as the RID with optogalvanic detection, the electron number shot noise in the interaction time Δt_i is given by

$$\Delta N_{\mathrm{e(b)}} = \left(\frac{2\bar{i}_\mathrm{b}\Delta t_\mathrm{m}}{e}\right)^{1/2} \tag{6}$$

where

$\bar{i}_\mathrm{b}$ = average background current in the RID with no laser excitation at $\tilde{\nu}_{l1}$ ($\mathrm{C\,s}^{-1}$),

e = charge of the electron ($1.6 \times 10^{-19}\,\mathrm{C}$),

Δt_m = $\Delta t_\mathrm{g} f t_\mathrm{m}$ (s), for the pulsed case and t_m (s), for the cw case,

Δt_g = boxcar gate width (s),
f = laser repetition rate (s^{-1}),
t_m = total measurement time (s).

It should be noted that any process in the SC, including Raman scatter, fluorescence and thermal emission which increases $\bar{i}_b$ will increase the electron number shot noise as shown in Eqn. (6).

In Table 1, approximate numerical values for parameters are given to evaluate the Raman signal, $N_{c(R)}$, the Raman signal to noise ratio and the detection limit for several SC cells and for a H_2–air flame as the RID. It is assumed that λ_{l_1} (and λ_1) are sufficiently long and/or the concentration of impurity species (or analyte) is sufficiently low and/or $S_F(\lambda)Y_F(\delta\nu_A/\delta\tilde{\nu}_F)$ is sufficiently low so that there is no measurable fluorescence background in SC and thus no fluorescence induced shot noise in the RID. It is also assumed that only the RID background current shot noise in the RID is significant, which should be realistic for spontaneous Raman (SR), and surface enhanced Raman (SER) (and possibly for RR and SERR). As one can see from the data of Table 2, for the SR process, the pulsed case gives the best signal to noise ratio and correspondingly, the best detection

Table 1. Estimated numerical values for parameters necessary for evaluation of N_e for Raman scatter

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SA and RID

$V_i = 1\ cm^3$; $l_{SC} = 1$ cm, $S_{exc} = 1\ cm^2$, $\Omega_{exc} = 1$ sr.

$(n_A)_{SC} = 10^{16}\ cm^{-3}$; $\delta\tilde{\nu}_A/\delta\tilde{\nu}_R = 0.1$ (for molecules in condensed phase).

Solution ($MW = 60$ for analyte); $(C_A)_{SC} = 1\ \mu g\ ml^{-1}$; $\rho = 1\ g\ ml^{-1}$
Gas ($MW = 60$ for analyte); $(C_A)_{SC} = 1\ \mu g\ cm^{-3}$ gas.

$\sigma_{abs_1} = \sigma_{abs_2} = 10^{-12}\ cm^2$ (1→2 of M in RID). The value for Li (670 nm) is a little higher and for Pb(283 nm) is a little lower.
$(n_T)_{RID} = 10^{13}\ cm^{-3}$ (~100 $\mu g\ ml^{-1}$ nebulized into H_2–air flame).

$\tau_2 = 1$ ns.

$\bar{i}_b = 4 \times 10^{-8}$ A (H_2–air flame). For the case of Li, the background current is not influenced by the Li until the Li concentration exceeds 100 $\mu g\ ml^{-1}$ which is already on the plateau region of the calibration plot of Li–RID vs Li concentration introduced into the RID.

Lasers

Pulsed dye laser (λ_{l1}): $\phi_l = 10^{24}$ photons s^{-1}; λ_2 saturates.

cw Dye laser (λ_{l1}): $\phi_l = 10^{18}$ photons s^{-1}; $E_l(\lambda_2) = 10^{18}\ s^{-1}\ cm^{-2}$; λ_2 saturates or is linear.

Raman (non-resonance) [10]

$$\frac{\delta\sigma_R}{\delta\Omega} = 10^{-30}\ cm^2\ sr^{-1}$$

Raman (resonance) [10]

$$\frac{\delta\sigma_R}{\delta\Omega} = 10^{-26}\ cm^2\ sr^{-1}$$

Multiplication due to surface enhancement [10–12]: $G = 10^6$

Interaction times

Pulsed laser $\Delta t_l = 10$ ns, $\Delta t_g = 100$ ns, $f = 10$ Hz, $t_m = 1$ s

cw Laser $\tau_{res} = 1$ ms (H_2–air flame)

Shot noise due to thermal ionization background current in RID

Pulsed-gated $\Delta N_e \sim 10^3$ in 1 s

cw System $\Delta N_e \sim 10^6$ in 1 s

Table 2. Estimation of signals (S), signal to noise ratios (SNR) and detection limits (LOD) (S/N = 3) for several cases (see Table 1) assuming thermal background current shot noise†

	SR	RR	SER	SERR
S‡§				
cw (linear)	10	10^5	10^7	10^{11}
cw (saturated)	10^4	10^8	10^{10}	10^{14}
pulsed	10^3	10^7	10^9	10^{13}
SNR‡§				
cw (linear)	10^{-5}	10^{-1}	10	10^5
cw (saturated)	10^{-2}	10^2	10^4	10^8
pulsed	1	10^4	10^6	10^{10}
LOD*§				
cw (linear)	$3\times10^{21}(3\times10^8)$	$3\times10^{17}(3\times10^4)$	$3\times10^{15}(3\times10^2)$	$3\times10^{11}(3\times10^{-2})$
cw (saturated)	$3\times10^{18}(3\times10^5)$	$3\times10^{14}(3\times10)$	$3\times10^{12}(0.3)$	$3\times10^8(23\times10^{-5})$
pulsed	$3\times10^{16}(3\times10^3)$	$3\times10^{12}(3\times10^{-1})$	$3\times10^{10}(3\times10^{-3})$	$3\times10^6(3\times10^{-7})$

SR = spontaneous Raman, RR = resonance Raman, SER = surface enhanced Raman, SERR = surface enhanced resonance Raman (SER and SERR only apply to solids or liquids), S = signal level or N_e (counts), SNR = signal to noise ratio.

* A H_2–air flame is used as the RID (see Table 1).

† All values in terms of species cm^3 are for gases and liquids. LOD values in (ng ml)$^{-1}$ are only for liquids.

‡ S and SNR refer to 1 μg ml^{-1} (see Table 1).

§ For cw case, there are two subcases, namely, the laser at λ_2 interacts with M atoms *linearly* [Eqn. (2b)] or results in optical saturation [Eqn. (2a)].

limit. As anticipated in our earlier discussion, if saturation of the second transition is not reached in the ionization detector, the technique would be practically useless. Where the proposed approach appears to be very attractive is in the pulsed RR, SER and SERR cases. It is worth stressing, however, that we have assumed here that the overall gain for the SERR case (10^{10}) can be obtained by multiplying each individual gain (for the RR and SER cases) together, while maintaining the same number density of scatterers, $(n_A)_{SC}$. In addition, we have assumed that the resonance Raman cases do not optically saturate. Obviously, the detection limits reported in Table 2 are calculated, not measured values and in real experimental systems, other noises such as radio-frequency interference from the pulsed laser or scattered amplified stimulated emission (ASE) from the dye laser producing λ_1 may contribute. In addition, we may have overestimated several parameters such as the differential Raman cross-section, $\delta\sigma_R/\delta\Omega$, the ratio $\delta\bar{\nu}/\delta\bar{\nu}_R$, the laser flux, ϕ_l and the solid angle of collection of Raman from the SC, Ω_{exc}. However, we feel the overestimation of the product of these values will not exceed a factor of 10, assuming a reasonably optimized experimental set-up. Also, if an RID with an even lower background current and electron number shot noise is used, such as a pulsed glow discharge then the signal to noise ratio should be even better. For a glow discharge, RID, photoionization may be required. It should also be stressed that the signal to noise ratio of the pulsed Raman–RID surpasses the signal to noise ratio of the cw Raman–RID.

COMPARISON OF RAMAN–RID WITH CONVENTIONAL RAMAN SYSTEMS

In Table 3, a comparison is made between the instrumental figures of merit and the types of components for typical dispersive, FT systems and a hypothetical Raman–RID system. It should be noted that the Raman–RID system (with atmospheric pressure H_2–air flame) should achieve a poorer resolution and lower energy limit than a good dispersive Raman and an equivalent resolution and lower energy limit to FT–Raman. However, with a narrower (Gaussian profile) laser ($\bar{\nu}_{\mathit{l}1}$), such as a tunable single mode diode laser or a ring dye laser, an intense second laser at $\bar{\nu}_2$ and a low pressure glow discharge detector (effective stray light level at 1 cm^{-1} for a Doppler broadened absorption line is less than 10^{-10} and at 10 cm^{-1} is less than 10^{-44}), it should be possible to

Table 3. Comparison of Raman–ID with conventional dispersive Raman and FT Raman spectrometry

	Dispersive*	FT*	RID
Spectral range (cm^{-1})			
Top of line	5–3000	200–3000	0.1–1800‡
Low cost	50–3000	300–3000	100–1800§
Spectral resolution (cm^{-1})			
Top of line	0.2	0.2	<0.1‡
Low cost	2–4	2–4	~2§
Throughput (cm^2 sr)†			
Top of line	6×10^{-9}	3×10^{-4}	0.1
Low cost	6×10^{-8}	1×10^{-3}	
Stray light			
100 cm^{-1}	$<10^{-14}$	*N*‡	$\ll 10^{-50}$ (GD–RID)‡ $\sim 10^{-8}$ (flame-RID)§
1 cm^{-1}	$\sim 10^{-3}$	*N*‡	$\sim 10^{-44}$ (GD–RID)‡ $\sim 10^{-3}$ (flame-RID)§
Instrumentation source	cw Ar$^+$ laser (514.5 nm)	cw Nd–YAG laser (1064 nm)	Ring dye laser,‡ cw Ar$^+$ laser pumping,§ 2-dye lasers or pulsed dual dye lasers§
Spectrometer	Double or triple grating	Michelson	Low pressure RID,‡ H_2–air flame§
Detector	Photomultiplier	Photodiode	Optogalvanic

* Top of line models for dispersive and FT represent average of the best commercial models and low cost models are the lowest cost versions available.

† $A\Omega\Pi T_i$ where A = limiting aperture area (cm^2), Ω = limiting solid angle of Raman collected (sr) and ΠT_i is the product of the transmittances and/or reflectances of all optical components.

‡ N = not available

§ First value is for best system involving narrow tunable first laser and low pressure RID; second value is for simpler system involving conventional tunable first laser and atmosphere pressure H_2–air RID.

cover the spectral range of 0.01–2 cm^{-1} with a resolution of <0.01 cm^{-1}. The high throughput (see Table 3) and near immunity to scatter and various background sources in the SC should result in extremely high signal to noise ratios and extremely low limits of detection as shown in Table 2.

EXPERIMENTAL REALIZATION OF RAMAN–RID SYSTEM

A possible Raman–RID experimental system is shown in Fig. 4. The pump laser is a pulsed laser, such as a Nd–YAG, an excimer or a Cu-vapor pumped dye laser. The RID

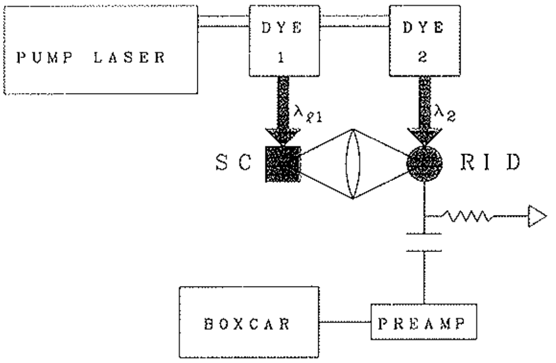

Fig. 4. Possible experimental realization of Raman–RID system.

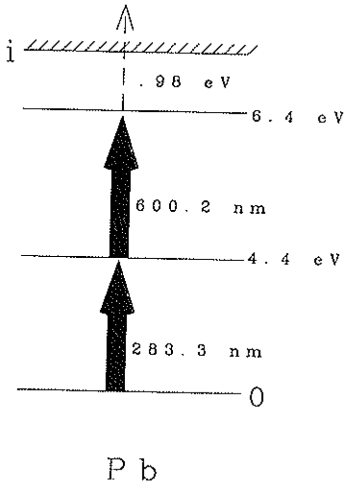

Fig. 5. Energy level diagram of lead showing two transitions.

could be a H_2–air flame with a water-cooled positive biased electode and a negative burner base. Although a variety of metals could be used in the RID, two possibilities include Li for spontaneous (SR) and surface enhanced spontaneous (SER) and Pb for resonance (RR) or surface enhanced resonance (SERR) Raman. The energy level diagram of Li is given in Fig. 2 and that of Pb in Fig. 5; both figures contain possible λ_1 and λ_2 transitions. As can be seen in Fig. 4, the experimental system is extremely simple.

The sample cell, SC, can be either a solution, a solid or a gas. In the latter case, the gas can be a non-emitting gas, a combustion flame or even a plasma. The high spectral selectivity and freedom from scatter interference should allow measurements even within a luminous background media. To scan a Raman spectrum, the second dye laser is adjusted to $\tilde{\nu}_2$ and the first dye laser, ν_{l1}, is scanned while recording the RID signal. The spectral range at the low wavenumber end and the spectral resolution will be determined by the convolution of the Raman scatter spectral profile due to natural Raman broadening processes, $\delta\tilde{\nu}_R$, the first laser spectral profile, $\delta\tilde{\nu}$, and by the absorption half width, $\delta\tilde{\nu}_{abs}$, of M in the RID. The spectral range at the high end will be determined by the dye used in the first dye laser. As noted previously, the signal to noise ratio will increase with the square root of the total measurement time assuming the shot noise limit, which should be valid as long as t_m does not exceed 10 s or so.

The capability of the RID to reject stray light is mainly a function of the spectral profiles of the Raman scatter line and the absorption line of the metal (Li, for example) in the RID. Figure 6 shows the relative absorption coefficient for the Li 670.7 nm line in a H_2–air flame for purely Gaussian and Lorentzian broadening. Assuming a Gaussian or Lorentzian shaped Raman profile and a Lorentzian shaped absorption line of M in the RID, the stray light response at a Raman shift of 100 cm^{-1} will be $\approx 10^{-8}$. If a low pressure RID is used, such as a glow discharge, the stray light response at 1 cm^{-1} will be $\approx 10^{-10}$ and at 10 $cm^{-1} \approx 10^{-44}$ assuming the Raman scatter line profile is Gaussian. Obviously, to obtain the highest spectral resolution and lowest Raman shift, a narrow band tunable laser of $\leqslant 0.01$ cm^{-1}, such as a single mode diode laser or a ring dye laser, a glow discharge RID and photoionization (rather than collisional ionization) must be used. Photoionization from level 2 of M in the RID will require an intense dye laser ($\geqslant 10^{25}$ photons cm^{-2} s^{-1}).

Finally, the Raman–RID detector should be ideally suited to the detection of Raman scatter in highly scattering media, such as from silver substrates, silver electrodes and silver sols used in SER and to the detection of RR scatter in the presence of a fluorescence background. In the case of scatter and fluorescence, only radiation within several $\delta\tilde{\nu}_{abs}$ of the absorption line of M in the RID will result in an appreciable signal and thus in appreciable noise. In the case of fluorescence, the detected fluorescence signal depends upon $\delta\tilde{\nu}_A/\delta\tilde{\nu}_F$ which can be quite small (say 10^{-3}–10^{-4}) and $S_F(\lambda)$ which

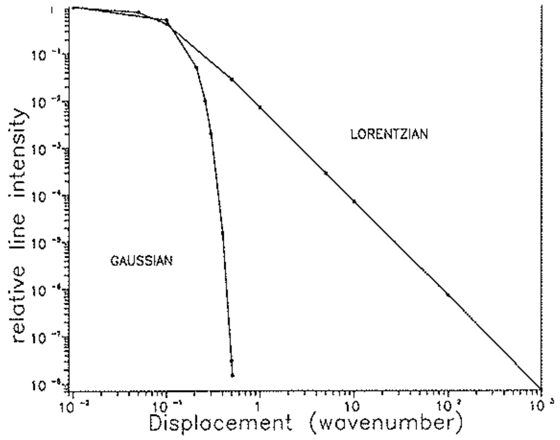

Fig. 6. Absorption line profile for the Li 670.7 nm transition in a H_2–air flame assuming pure Doppler (Gaussian) or Lorentzian broadening.

will be unity only if the peak fluorescence also occurs at λ_1. In the case of scatter, the interferent signal will be small since the scatter appears at a wavelength other than λ_1 and so the only contribution is a result of overlap of the scatter spectral profile and the absorption spectral profile of M. Finally, the contribution of RFI can be made small by appropriate laser shielding. The contribution of ASE is difficult to predict and must be evaluated experimentally. We are currently evaluating both pulsed and cw Raman–RID (H_2–air flame and glow discharge) detection systems for solutions using SR and SER with the Li–H_2–air RID and for solutions using RR and SERR with the Pb–H_2–air RID, even though we expect the pulsed Raman–RID system to be vastly superior to the cw Raman–RID system.

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DISCUSSION

HEINZ FALK, Central Institute for Optics and Spectroscopy, Berlin, D.D.R.: For single atom detection, the atomizer used needs to fulfil certain conditions for efficiency and residence time. Using tube furnaces for atomization, single atom detection may be achieved if the system is operated at atmospheric pressure and the transition under consideration may be saturated using a c.w. laser. I would like to stress that atomization with the help of atomic beam techniques would improve the detection capability of atomic spectroscopy because extremely high spectral resolution may be achieved in this way, and gas phase reactions are avoided.

When carrying out single atom detection using an atomic beam, it is necessary to reduce the kinetic temperature of the atoms under consideration into the mK range and to keep them in an atom trap. Such a trap may be realized by optical resonance cooling and localization using crossed laser beams. Such a system will be able to detect single atoms with spectral resolution better than 1 MHz. This low atomic line width enables one to use relatively inexpensive low power (mW range) lasers to saturate the transition.

Further discussion of DR WINEFORDNER's paper focused on the statistical limitations inherent in the detection of very small numbers of atoms and ultimately single-atom detection. For example, with a sample of 100 atoms per unit volume one would expect density fluctuations of the order of the square root of the number of atoms, i.e. 10% from one sample to another. There are also fluctuations inherent in the sampling process itself, viz. atomization and vaporization. The question was also raised by several participants of how the increasing levels of sensitivity which can be achieved by these new techniques relate to practical analytical problems. For instance, it may not be possible to prepare a blank or background sample in which one or a few atoms or molecules of the analyte are not present. This has further implications, which need to be explored, with regard to legally mandated requirements of "no detectable concentrations" of a particular contaminant, such as a carcinogen, in materials intended for public consumption.

Toward improved understanding and control in analytical atomic spectrometry

GARY M. HIEFTJE
Department of Chemistry, Indiana University, Bloomington, Indiana, U.S.A.

Abstract—As with most papers which attempt to predict the future, this treatment will begin with a coverage of past events. It will be shown that progress in the field of analytical atomic spectrometry has occurred through a series of steps which involve the addition of new techniques and the occasional displacement of established ones. Because it is difficult or impossible to presage true breakthroughs, this manuscript will focus on how such existing methods can be modified or improved to greatest advantage. The thesis will be that rational improvement can be accomplished most effectively by understanding fundamentally the nature of an instrumental system, a measurement process, and a spectrometric technique. In turn, this enhanced understanding can lead to closer control, from which can spring improved performance. Areas where understanding is now lacking and where control is most greatly needed will be identified and a possible scheme for implementing control procedures will be outlined. As we draw toward the new millennium, these novel procedures seem particularly appealing; new high-speed computers, the availability of expert systems, and our enhanced understanding of atomic spectrometric events combine to make future prospects extremely bright.

1. INTRODUCTION

IT IS a privilege to be able to contribute to this special volume of *Spectrochimica Acta*, dedicated to the 50th anniversary of its founding. It is appropriate at this time to recognize the succession of outstanding editors who have made the current two-part embodiment of the journal the premier vehicle in the world for communicating new findings about spectrometry and, in the particular case of *Spectrochimica Acta, Part B*, about atomic spectrometric analysis.

This treatment will be divided into three sections. First, a historical perspective will be offered in which past trends will be used in an effort to predict future events. Next, existing methods for atomic spectrometric analysis will be examined and their shortcomings recognized. It will be argued that these shortcomings can probably best be overcome by understanding better the nature of an atomic spectrometric instrument, how its signals are generated, and what experimental parameters are critical. From this knowledge, improved control strategies can be developed which will enhance the overall performance of the techniques. Finally, a scenario will be offered for improved control strategies for the future. It will be shown that instrumental modifications are possible which are more compatible with computer-based control and which lend themselves more readily to optimization and recalibration procedures.

2. HISTORICAL PERSPECTIVE

It is not uncommon for attempted projections into the future to degenerate into a discussion of past events. Even Thomas Jefferson once said "I know naught to judge the future save by the past." It is therefore not inappropriate for us to examine trends in analytical atomic spectrometry that have taken place over the 50-year period during which *Spectrochimica Acta* has been published. In this discussion, the thesis will be developed that the most significant improvements in atomic spectrometry arise through either innovation or improved control. Of course, truly innovative breakthroughs are impossible to predict since they do not depend in a straightforward way on present-day techniques, technologies, or concepts. On the other hand, closer control of instruments and procedures can be effective, can be foreseen, and can be implemented in a straightforward way. However, they

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will be enhanced by improved understanding of the fundamental behavior of instrumental systems and spectrometric procedures.

It is interesting to trace the introduction and decline of atomic spectrometric methods over the past 50 years. In the 1940s, arc and spark emission spectrography was developed to a fine art. When these sources are coupled with modern multichannel spectrometers (i.e. direct-reading spectrometers), they remain useful tools even today. In the 1950s, it was recognized that flame emission spectrometry offered a simpler and lower-cost solution to the determination of a substantial number of metallic elements. Single-channel filter-based or monochromator-based instruments became widely available and were used heavily until the late 1960s. Today, however, the method is used widely only in clinical assays, where a limited number of strongly emitting elements must be determined.

Although flame atomic absorption spectrometry (AAS) was introduced in 1955 as an analytical method, it did not gain prominence until the 1960s, when laminar-flow, long-path flames and stable nebulizer/spray-chamber combinations became available. However, like flame-emission spectrometry, flame AAS declined slowly while its burdens were assumed by furnace-atomization AAS. Furnace-atomization techniques for AAS rose in use dramatically in the 1970s because of their microsampling capability and the unusually low detection limits they provided. At the same time, the advantages of the inductively coupled plasma (ICP) as an emission source were realized. Throughout the 1970s and into the 1980s, ICP optical emission spectrometry (ICP-OES) gained in prominence as more and more instruments were offered which provided truly multielement capability, high precision, rapid sample throughput, minimal interferences, and a broad linear working range.

During the current decade, ICP-mass spectrometry (ICP-MS) has achieved prominence, because it offers many of the same attributes as its OES counterpart, but adds to them the ability to perform rapid isotopic analysis, spectral simplicity, and detection limits comparable to those of furnace AAS.

It is interesting in this perspective that the earliest methods, based on arc and high-voltage spark emission, remain in active use today in the metals industries and compete in some quarters with furnace AAS, ICP-OES, and plasma-source mass spectrometry. Yet, flame emission and flame AAS have declined in popularity. Not surprisingly, the overall pattern is to discard those techniques which are completely replaced by others but to retain those which offer unique capabilities. The clear trends, in terms of technique performance, are generally along the following lines: lower detection limits, better precision, fewer matrix interferences, a greater degree of automation, entrenchment of established techniques within particular applications areas, and the introduction of previously unforeseen instrumental approaches.

In view of these developments, it might be appropriate to modify somewhat the seven stages of an analytical method that were first set down by LAITINEN [1] and later applied to atomic spectrometry by BARNES [2] and FASSEL [3]. In the latter descriptions, the seven stages were applied specifically to inductively coupled plasma spectrometry, and included:

1. conception of an idea;
2. design and construction of the first operating apparatus;
3. successful demonstration of the idea and the appearance of initial publications;
4. improvement in the instrumentation and the establishment of reliable figures of merit;
5. maturity of the technique, general acceptance of its capabilities, and automation;
6. improved understanding of fundamental principles which underlie the method; and
7. old age and senescence.

However, from the earlier discussion, it appears that, like old soldiers, some analytical methods never die. Instead, their unique capabilities in some operational areas make it appropriate for them to be examined more closely, improved, and preserved. Accordingly, a possibly better description of the seven stages of such methods can be found in Table 1. The major difference in this new listing is that improvements in the spectrochemical instrumentation and in figures of merit, the resulting maturity, general acceptance, and automation, are often followed by a better understanding of fundamental principles which repeats the sequence. That is, the improved understanding leads to a further evolution of instrumentation and figures of merit, which are later accepted more widely and benefit from advanced

Table 1. Seven stages of an analytical method

1. Conception of idea
2. Successful demonstration and publication of idea
3. Improvement of instrumentation; figures of merit
4. Maturity; general acceptance; automation
5. Improved understanding of fundamental principles
6. Iteration of steps 3–5
7. Old age and senescence

automation. It is only when this cycle ceases to be competitive with newly introduced technology does a technique ever reach its period of "old age and senescence".

This improvement through understanding and control is a concept which has been advanced before [4]. In brief, when an application, an analytical method, or a concept is sufficiently important, its significance drives the development of theoretical frameworks and models that describe its features. In turn, this developing body of knowledge is exploited to improve the method or application itself. The result is a two-way symbiosis, diagrammed in Fig. 1, which also illustrates more clearly the relationship between the importance of a fundamental understanding and the effectiveness of functional control. In particular, the advancing body of knowledge concerning a technique improves our understanding of it. In turn, this understanding enables the intelligent control of variables that improve the application. In the absence of novel concepts or unforeseen discoveries, this approach is among the most effective for improving an analytical method.

3. Achieving Improved Understanding and Control

In our attempt to identify the pathways by which improved understanding and control can be realized, let us first define our objective and targets. Ultimately, what would be desired is an "ideal" multielement method. Such an ideal might not be practically attainable but provides an absolute standard against which all techniques can be compared. Because an ideal is a fixed standard, such comparisons remain valid forever. Even more importantly, the degree to which a real method departs from the ideal indicates where deficiencies are greatest and where attention is most sorely needed. The attributes of the ideal multielement analytical technique listed in Table 2 are not the only ones which might be cited but are certainly among the most significant.

Next, let us examine the components of a typical instrumental system for producing an atomic spectrometric signal. From this diagram, we might be able to deduce where the weaknesses of the system lie. From a conceptual standpoint, an atomic spectrometric instrument appears as in Fig. 2a. Here, the instrument is viewed as a system for producing information about a chemical problem. Information about the chemical problem itself is extracted in the form of a *sample* which hopefully has contained within it information of the sort which can solve the problem. The sample is then directed into a *source*, which has the task of encoding the chemical information in the form of a spectrum incorporated within a beam of electromagnetic radiation. Physically, the source will consist of an atom reservoir and auxiliary lamps and other units necessary for the encoding process.

For a scientist to utilize the spectral information, the information must be sorted by, for example, a dispersive spectrometer, a Fourier-transform system, or some other device. The sorted spectral information is then converted by a photodetector into electronic information, which can be processed and which will produce data which would be useful in solving the original chemical problem.

For this scheme to work as a effectively as possible, improved control strategies are necessary. Such control strategies might involve simple feedback of the kind shown in Fig. 2b. In the ultimate implementation of this approach, enough would be known about the sampling procedure, the performance of the source, the characteristics of the spectral sorting device, the transfer function of the detector, and the signal-processing algorithms that each could be optimized and modified on the basis of incoming data. This approach, termed

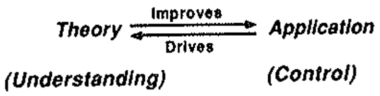

Fig. 1. Diagrammatic illustration of the symbiotic relationship between understanding and control of an analytical application. A developing theory which describes an application improves that application. In turn, the importance of the application drives fundamental understanding about it.

Table 2. Ideal multielement method of analysis

High sensitivity (single atom)
Infinite linear range
Useful for all elements under the same operating conditions
No noise and no drift
No matrix (interelement) interferences
Absolute analysis
Compact
Inexpensive (initial and operating)
Complete elemental coverage
Ease of choice of elements to be determined
No sample preparation required
Micro or macro samples
Spatial resolution possible in solids
Rapid (per sample and per element)
Trivial to operate
Automated
Non-destructive

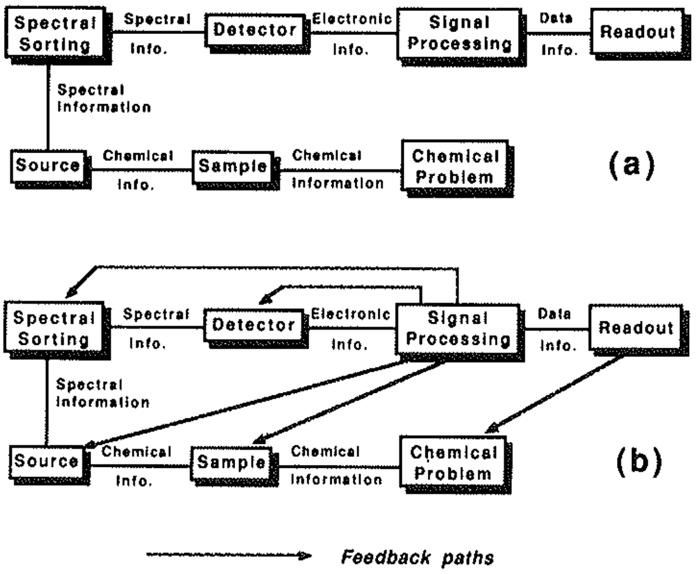

Fig. 2. Information-theory view of an instrument for atomic spectrometric analysis. In (a) the steps of converting information from one domain to another are outlined while in (b) feedback paths are indicated which could assist in real-time experimental optimization and control.

"adaptive control" or "adaptive experimentation" [5] would enable optimized results to be derived from each sample the first time that sample is examined. Clearly, the method is extremely powerful but requires systems that are far better characterized than is commonly the case today.

What are the factors which make the approach in Fig. 2b currently impractical? Where are the weak links in our knowledge? What devices or systems should be controlled? What shortcomings are most serious? To answer these questions, we can begin by identifying the attributes in Table 2 which are most lacking in current instruments or improvement of which would be most beneficial. Although the priorities for improvement could be debated, appropriate characteristics to target would be to reduce noise and drift, to eliminate matrix (interelement) interferences, to minimize sample preparation, and to increase the level of automation. In turn, if noise, drift, and matrix interferences are all reduced sufficiently, absolute (standardless) analysis might become possible.

To decide how these features can most efficiently be improved, let us return to the functional diagram of an atomic spectrometric instrument shown in Fig. 2a. Basically, the functions of the instrument can be separated into three components: atom/ion formation, spectral encoding, and information extraction. Let us consider each of these functions in turn, decide how much is known about each of them, and determine where the greatest gains are to be made.

3.1. *Atom/ion formation and excitation*

Figure 3 shows the pathways by which atoms are formed, excited, and ionized in conventional atomic spectrometric procedures. Three paths are shown, the left pertaining to events that ordinarily occur in a flowing flame or plasma, the center to those involved in hydride or mercury-generation techniques, and the right to those which arise in furnace-based procedures. Additional pathways could be considered but were omitted here for brevity. These other pathways include those which arise in such sources as the high-voltage spark or the glow-discharge lamp.

Of course, it would be impossible in a manuscript of reasonable length to cover in any detail what is known about the fundamental events that lead to atom formation, ionization and excitation in all of the possible sources used in atomic spectrometry. Therefore, let us simply illustrate the level of current knowledge by considering what is known about the events in the left-hand arm of Fig. 3; that is, about the formation of excited atoms and ions in the ICP.

3.2. *Sample preparation*

Sample preparation, the first stage of atom formation, constitutes a group of procedures which collectively are employed to convert a solid sample into a solution of form and

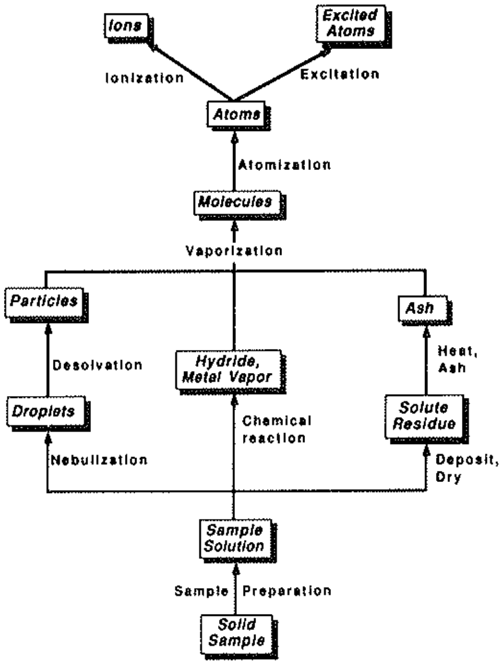

Fig. 3. Stages through which a solid sample can be converted to excited atoms or atomic ions useful for atomic spectrometry. Three paths are indicated, the left-hand one pertaining to events that occur in a flame or plasma, the right-hand branch pertaining to steps in a furnace atomizer, and the central path corresponding to a hydride-generation or free-metal (mercury)-generation procedure.

concentration appropriate for introduction into an ICP. Procedures that are used include wet ashing, dry ashing, the use of fluxes, and other, more exotic approaches. No matter what sample-preparation procedure is used, a number of pitfalls ordinarily arise. These problems include incomplete conversion of the analyte in the sample to the desired form (oxidation state, molecular form, etc.), loss of volatile elements during dry- or wet-ashing, contamination of the sample material or sample solution, unavoidable dilution of the sample, quantitative errors in handling or dilution procedures, and the excessive expenditure of time. Often, sample-preparation operations are the bottleneck in any analytical scheme. Clearly, with this array of problems, sample treatment is an area in great need of improved control.

3.3. *Nebulization*

The next step in the conversion of sample material to free atoms or ions in an ICP is ordinarily the business of transforming a sample solution into a fine spray of droplets. The strengths and weaknesses of existing procedures have been documented elsewhere [6, 7] and need not be repeated here. From that detailed discussion [6, 7] and the efforts of many workers, it is clear that the conversion of a sample into aerosol form is a process in need of dramatic improvement. What would be most desirable is a hypothetical method which would transform a sample solution quantitatively into uniform-sized (monodisperse) droplets, all of which are below two micrometers in diameter. Current devices fall far short of this goal, yield an aerosol whose production is unstable, and are adversely affected by corrosive solvents, changes in solvent character (viscosity, surface tension, and other), and high solute concentration. Extensive aerosol conditioning is ordinarily required, so that the final spray which enters an ICP is often only one per cent of the quantity of sample solution actually consumed.

The production of an aerosol useful for ICP spectrometry really consists of three steps: generation by the nebulizer of the primary aerosol, the conditioning of that aerosol by shattering large droplets through impaction and elimination of remaining large droplets by settling or collection, and transport of the aerosol to a plasma. A better understanding of all these processes is slowly developing. Unfortunately, most methods for generating a primary aerosol do not lend themselves readily to external control and are fundamentally difficult to adapt to the ideal aerosol-generation process just described. For aerosol generation to be improved dramatically, it will therefore require use of a relatively unconventional spraying operation, or a considerable improvement of existing systems, such as the ultrasonic nebulizer, the glass–frit nebulizer, or the monodisperse aerosol generator [8, 9]. As will be illustrated later, these last devices are much more amenable to electronic control and manipulation.

3.4. *Desolvation*

The desolvation of droplets in an aerosol can occur by either of two mechanisms, depending upon whether the evaporation occurs at a relatively low temperature, such as that in a spray chamber, or at a high temperature, such as that found in the plasma itself. Both can be understood with the aid of Fig. 4. In the spray chamber, droplet evaporation is a mass-transfer-controlled event, and is limited in rate by how rapidly solvent molecules can leave the vicinity of a droplet. Accordingly, it is governed by such parameters as the diffusion coefficient of solvent vapor and by the saturation vapor pressure of the solvent at the spray-chamber temperature [6]. In contrast, droplet evaporation in a flame or plasma is controlled by the rate at which heat can reach the droplet surface. As a result, it is determined by such factors as the thermal conductivity of the solvent vapor or the plasma gases, whichever is lower, by the heat capacity of the solvent vapor, and by the temperature differential between the plasma and the droplet surface [10]. With this knowledge, one can manipulate the flame to increase the desolvation and atom-formation efficiencies [11], but the approach is not particularly amenable to interactive or adaptive control.

3.5. *Vaporization*

The vaporization of solute particles is a rather more complex matter than the evaporation of liquid droplets [12]. Depending upon whether the boiling point of a solute mixture falls at, below, or above the plasma temperature, the vaporization might be rate-controlled by either a thermal or mass-transfer process. However, for the majority of solute composites, whose vaporization temperature lies below that of an ICP, and whose size is comparable to the mean-free path of species leaving the particle surface, the event turns out to be mass-transfer controlled and follows a pattern similar to that of Knudsen evaporation [13, 14]. It therefore depends principally on the saturation vapor pressure of the molten solute, over which external control cannot be readily established. Overall, if interelement interferences are dominated by solute vaporization effects, the only means by which they can be reduced is through manipulation of the plasma temperature or the sample composition. Importantly, although many workers have assumed that desolvation and vaporization effects are absent in the high-temperature environment of an ICP, recent evidence suggests the opposite [15, 16].

3.6. *Excitation and ionization*

Most workers agree that interference effects observed in the ICP [17, 18] result from a change in plasma conditions. However, the nature of this change is not clear. What is known is that alkali metals, other easily ionized elements (EIE), and some additional elements alter the spatial pattern of emission from both neutral and ionized atoms of most elements. Significantly, the character of the variation is different for neutral and ionized species. Interestingly enough, the observed changes seem not to arise from an alteration in the electron number density of the plasma [19], at least in the zone from which emission is customarily observed (15 mm above the load coil; see Fig. 5).

It is appropriate to ask, then, what modifications in the plasma might arise from the addition of an easily ionized species and also what the nature of these changes might be, if they do not arise from a change in the number of free electrons in the discharge. There are at least three steps which ultimately lead to analyte excitation in an ICP; these steps can be

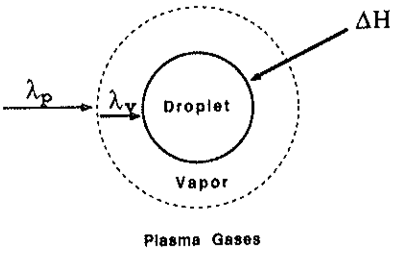

Fig. 4. An aerosol sample droplet is evaporated in a spray chamber at a rate which is governed by how rapidly mass can leave the droplet surface. In contrast, droplet evaporation in the high-temperature environment of an ICP is rate-limited by either the thermal conductivity of the plasma gases (λ_p) or of the solvent vapor (λ_v).

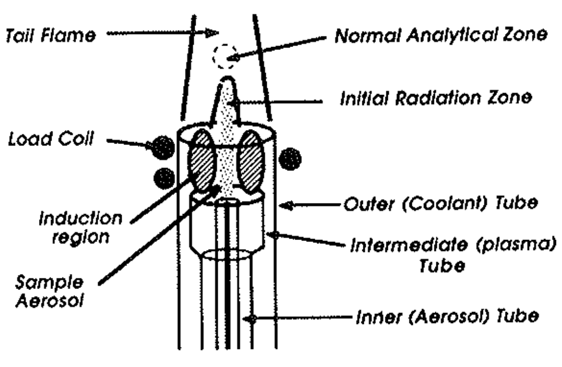

Fig. 5. Diagram of important parts of an inductively coupled plasma, illustrating areas in which radio-frequency energy is coupled and how it can be transported inward and upward into the analyte-containing zones.

understood readily with the aid of Figure 5. Initially, radio-frequency energy is coupled into the discharge within the induction region. If an easily ionized species should alter the electron concentration in that zone, it would no doubt influence the energy-coupling efficiency. Similarly, if the overall impedance of the plasma were altered by a sample concomitant, the energy available in the discharge would be changed.

The next step in the excitation sequence is the transport of plasma energy inward and upward into the analyte-containing channel. In that region, the energy can interact first with the sample aerosol, then with molecules and molecular fragments, and finally with sample atoms and ions. This energy-transport process might be altered by an EIE via either an alteration of the thermal conductivity of the plasma or by a variation in ambipolar-diffusion conditions. These matters perhaps deserve some elaboration.

Recent calculations in our laboratory indicate that the dominant mode of energy transport throughout the ICP involves thermal conduction [20]. Yet, it seems likely that a small number density of unusually high-energy electrons might find their way from the ICP induction region into the center of the plasma; the mode of transport of these higher-energy electrons is by means of ambipolar diffusion [20]. Viewed simply, ambipolar diffusion is just the collective motion of electrons and positively charged ions. Although electrons are smaller and more mobile, and would therefore be expected to diffuse more rapidly than the heavier ions surrounding them, the rapidly moving electrons are retarded in their flight by their positively charged neighbors. The overall result is a collective motion of ions and electrons whose diffusion coefficient is only about twice that of the ions themselves.

Because of the way in which an ICP is sustained, a substantial gradient exists in the concentrations of electrons and ions between the induction region and the analyte-carrying central channel. If ambipolar diffusion is indeed responsible for conveying a small number of high-energy electrons to the central channel, it would be enhanced by even a small number of electrons added to the central channel. Such electrons would diminish the electrostatic gradient which ordinarily limits the rate of ambipolar diffusion; instead, simple energy exchange could take place between the electrons added to the central channel of the plasma and those already present in the induction region. The result would be an increase in the available number of high-energy electrons which could interact with analyte species.

Analyte excitation itself might be affected by the addition of an easily ionized element. This excitation is the final step in the transfer of plasma energy to an analyte species and proceeds by a process which is still not clear. Although some workers favor a charge-transfer mechanism, others argue for direct electron impact or another, more exotic event. Interestingly, most of these hypothesized schemes involve electrons either directly or indirectly and might be influenced not only by electron concentration but also by electron temperature or energy distribution. These latter characteristics might well be affected by the addition of an easily ionized element.

For example, if one assumes that the total charge density in the plasma remains constant even when an EIE is added, the ionization of a sodium atom requires the loss of an argon ion for charge equilibration. Because the ionization energy of sodium is only 5.1 eV while that of argon is 15.8 eV, an energy defect of 10.7 eV remains. This excess energy, added to the plasma indirectly by means of the introduced sodium, might well be carried in a small group of high-energy electrons, which have an undue influence on analyte excitation.

Of course, the foregoing schemes are admittedly speculative and are intended to be so. A number of other hypotheses for the "EIE effect" could be offered. From the standpoint of the present treatment, however, the important fact is that neither the mechanism of analyte excitation nor the cause of observed matrix interferences is well understood. Obviously, a greater level of understanding will be needed before these effects can be controlled.

3.7. *Spectral encoding*

Many different atomic spectrometric methods have been employed to determine elemental concentrations in samples. Among the most common are atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), atomic fluoresence spectrometry (AFS), and mass spectrometry (MS). Other techniques, including coherent forward scattering spectrometry, laser-enhanced ionization, resonance ion mass spectrometry, and others have been used only in special-purpose or exploratory situations. Importantly, because the physical principles of all these spectrometric techniques have been worked out long ago, surprisingly little remains to be learned in this phase of an atomic spectrometric analysis. A noteworthy exception, however, is in the relatively new but rapidly growing combination of plasma-source MS. This technique, the most common embodiment of which is ICP-MS, requires the extraction of analyte ions from an atmospheric-pressure, high-temperature discharge into the relatively cool but low-pressure environment of a mass spectrometer. This expansion, which is accomplished by means of a differentially pumped two- or three-stage interface, is only now becoming well characterized. Investigators disagree on whether charge separation originates in the first stage of the vacuum zone (held at approximately one torr) and on the degree to which the supersonic jet produced by the expanding plasma gases is heterogeneous. Moreover, the ion beam extracted from an analytical plasma such as the ICP is unusually concentrated and reportedly exhibits strong space-charge effects [21]. Because conventional ion-optical systems employed in ICP-MS are not designed for space-charge-limited beams, the existence of substantial interference effects [22, 23] is not surprising. More work is certainly needed to pinpoint the source of these interferences so it can be determined if they can be eliminated rationally or controlled interactively.

3.8. *Where do we stand?*

From the foregoing discussion, it is apparent that rather substantial gaps exist in our knowledge of how the signal conversions diagrammed in Fig. 2a occur. Overall, though, it seems clear that the greatest gain in atomic spectrometric performance could be achieved in the following areas: 1. automating or (better) minimizing sample preparation; 2. overcoming or minimizing interelement or matrix interferences; 3. installing self-checking instrumentation and diagnostic measurements to improve instrument stability and reliability; 4. improving long-term precision and short-term noise; and 5. incorporating additional automation and self-optimizing features into modern instrumentation.

To achieve these gains, it will of course be necessary to better understand and control specific instrumental components and operations. The most critical of these include the processing of raw samples, the generation of the sample aerosol or atomic vapor (in an ablation-based experiment), the ionization or excitation conditions in the analytical source, the ion kinetic energy and jet-expansion characteristics in a mass spectrometer interface, the fidelity of the spectral-selection device and signal-conditioning equipment, and the stability and reliability of detectors or other transducers.

Finally, from these lists of where our greatest gains can be made and which events must be better controlled, we can set down a number of requirements for improved instrument control. First, we will require a computer-compatible instrument. Even today, when microcomputers are installed in virtually every instrument and where the knobs and meters of earlier days are being replaced by keyboards and CRT screens, instruments are still not designed from the standpoint of the computer itself. For example, a computer is able to respond on a time scale far faster than we as human beings can. Yet, most instruments still have incorporated in them relatively long time constants, the argument being that the resultant smoothing is essential for signal fidelity. In contrast, it has long been known [24] that drift can be overcome better by repetitive, rapid scanning followed by signal averaging than by a single slow scan.

In addition, instruments designed for real-time control should incorporate advanced diagnostics. Even the most modern atomic spectrometric instruments have installed in them only rather primitive diagnostic measures and usually possess the capability to detect only catastrophic events. An instrument designed with a computer at its heart would utilize a far broader range of diagnostic tools, so that the condition of the sample-preparation system, the aerosol generator, the atomizing source, and other components could all be monitored continuously. Ideally, nearly instantaneous control could thereby be achieved so drift and error are minimized.

Access to a full spectrum would also be particularly useful for improving the degree of control over an atomic spectrometer. This control would benefit additionally from increased fidelity in both the horizontal and vertical axes of a spectrum, as illustrated in Fig. 6. In all forms of atomic spectrometry, the horizontal axis of a spectrum is associated with the identity of an element. Accordingly, higher resolution and better spectral registration along this axis would result in superior background subtraction, the more unambiguous identification of spectral lines, and improved accuracy in an elemental determination. Similarly, improved fidelity on the vertical axis of a spectrum would result in better signal-to-noise ratios and, accordingly, a lowered relative standard deviation. Added fidelity in both spectral axes would therefore improve the reliability of any control algorithm.

Lastly, what is needed perhaps most of all is intelligent sample processing. Current sample-preparation schemes involve little more than a preliminary classification of a sample into one of several categories, followed by the use of an established "recipe" which is applied to all samples of that type. What would be superior would be a sample-processing approach which can be adjusted in an intelligent, interactive fashion. For example, preliminary investigation of a small specimen of the sample could yield information which could itself help tune the sample-processing operation. Flow-injection approaches might be useful in implementing this concept. With sufficient flexibility, knowledge of sample characteristics, and appropriate feedback paths, it should be possible to optimize the processing of a sample the first time that sample is examined and with no prior knowledge of its character.

Conveniently, a framework already exists within which the requirements just mentioned can be satisfied. Even with imperfect knowledge of the fundamental characteristics of instrumental components and operations, it is possible to determine the so-called "response function" of the instrument to a particular perturbation [25]. These perturbations can be those which involve a change in analyte, a change in sample, an alteration in interferent level, a change in instrument behavior, or whatever is desired. Although such an approach is largely empirical and would be less effective than one based on a fuller knowledge of instrument and technique performance, it is often successful.

With these factors and features now in mind, we are in a position to examine combinations that are currently available for atomic spectrometric analysis and assess whether they lend themselves well to real-time optimization and control. Table 3 lists the sources and detection methods that are frequently employed in atomic spectrometry. Considering first the available sources, we recognize that nearly every device has its own set of shortcomings. For example, the inductively coupled plasma is an admirable device for decomposing samples into their constituent atoms; it does so by means of an extremely high gas temperature and a moderate (atmospheric) pressure. However, these same conditions produce from the ICP a relatively high background emission, generated mostly by ion-electron recombination. This background renders the detection of atomic-emission signals more difficult.

One way to circumvent these problems is through use of a tandem source, one of the options listed in Table 3. In such a tandem source, diagrammed in Fig. 7, two separate devices are employed. The first is optimized for converting a sample into its constituent

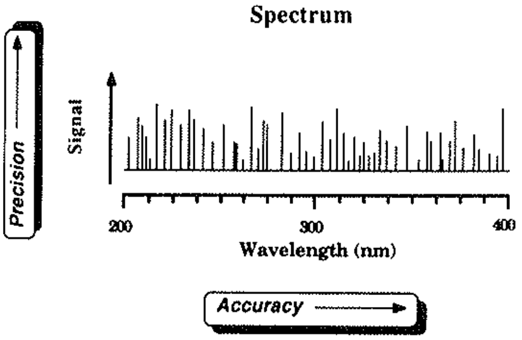

Fig. 6. The horizontal axis of a spectrum is used for *qualitative analysis* and provides accuracy in a determination. The vertical axis is used for *quantitative analysis* and its fidelity is related to precision.

Table 3. Sources and detection methods in atomic spectrometry

Sources	Detection methods
ICP	Absorption
MIP	Fluorescence
GDL	MS
DCP	CFS
Flame	Emission
Tandem sources	
Furnace	MPI
MTES	LEI
e-Beam	PAS
Arc	PBF
HV Spark	

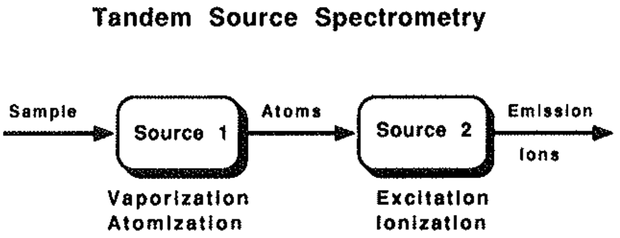

Fig. 7. In tandem source spectrometry, the first source is tailored for quantitative conversion of a sample into free atoms; the second source possesses rather different characteristics and is optimized for ionizing or exciting the resulting atoms.

atoms while the second is tailored for exciting or ionizing those atoms. Because each source possesses a distinct function, it can be configured and controlled to optimize that function. Such an arrangement would clearly be superior from the standpoint of a control strategy.

Any number of tandem sources can be envisioned; a few possible combinations are listed in Table 4. Although several of the listed combinations have already been examined, it is likely that we shall see additional exploration of tandem sources in the future.

Among the detection methods listed in Table 3, the most sensitive is certainly resonance ionization mass spectrometry while the most convenient is probably still flame AAS. For the immediate future, however, it would seem that emission- or mass-spectrometry-based techniques offer much in terms of their combination of sensitivity, convenience, and inherent multielement character.

At present, atomic emission is ordinarily detected with either a direct-reading spectrometer or a slew-scan monochromator system. However, instruments are already available that employ linear and two-dimensional photodiode arrays and individuals have examined the use of interferometric techniques based on Fourier-transform spectrometers or solid-state interferometers of the Fizeau variety. Some investigators are also evaluating encoding-based techniques such as those of Hadamard-transform spectrometry. Which of these many approaches is superior?

For the near term, the three combinations listed in Table 5 seem especially attractive. All three (tandem source–mass spectrometry, tandem source-Fourier transform spectrometry, and tandem source-imaging detector spectrometry) offer many of the features that were decided above to be important if close or adaptive control of an experiment is to be achieved. All three exhibit inherent computer compatibility in many respects, are driven directly by electronic, digitally compatible signals and offer directly electronic, sometimes digital output. The Fourier-transform system suffers somewhat in its relatively slow response time; it requires a finite period to obtain an interferogram and only after the interferogram is processed can a spectrally related feedback signal be generated. All three methods potentially offer high resolution, mass spectrometry in part because its spectrum is relatively

Table 4. Tandem sources in atomic spectrometry

Source 1 (Atomization)	Source 2 (Excitation/Ionization)
ICP	ICP
Flame	MIP
Furnace	e-Beam
Sputtering cell	Metastables
Microarc	Chemiluminescence
Laser ablation	MPI
Arc	Geissler
HV spark	
DCP	

Table 5. A comparison of three atomic spectrometric combinations suitable for use in an adaptive-control strategy

	*TS-MS	†TS-FTS	‡TS-IDS
Computer-compatible instrument	++	++	++
Faster response times	+	—	++
Better diagnostics	+	+	+
Access to full spectrum	++	++	++
Higher spectral fidelity			
precision (vertical)	++	0	++
accuracy (horizontal)	+	++	+
Knowledge of response functions			
instrument	—	+	0
analyte	+	++	++
interferent	—	+	+
time	++	+	+

* TS-MS Tandem source-mass spectrometry.
† TS-FTS Tandem source-Fourier transform spectrometry.
‡ TS-IDS Tandem source-imaging detector spectrometry.

uncluttered. Interestingly, the Fourier-transform device offers perhaps the best spectral (wavelength or frequency) accuracy, but the fidelity of its vertical spectral axis often suffers somewhat from a multiplex disadvantage.

Our knowledge of the three systems differs greatly. Because atomic mass spectrometry is still a developing technique, much must still be learned about its instrumental characteristics. Similarly, the effect of interferents on the mass–spectral signal must be more completely characterized. The imaging-detector spectrometer suffers in a manner similar to that of the mass spectrometer in its relative newness.

The evaluation in Table 5 provides no unambiguous guide about which instruments might be most useful in an adaptive-control arrangement. Although the imaging-detector-based instrument might at first appear to be the most attractive, it is based on technology that is still emerging and whose viability cannot yet be accurately assessed. It will be interesting to watch as these three approaches develop and to observe whether their inherent suitability for instrument control can be usefully exploited.

4. FUTURE PROSPECTS

It seems that implementation of a useful instrument-control strategy must be based on improved understanding of the instrument itself and of the operations it must perform. Although this goal will be difficult to achieve, it would certainly be worthwhile. As Sir

Humphrey Davy once remarked, "Nothing begets good science as much as the development of a good instrument".

To assess whether this concept is practicable, it is useful to recall the five generations of instrumentaion outlined recently by WADE and CROUCH [26]. In their framework, a first-generation instrument is one in which the user employs direct observation, such as was done in atomic spectrometry as early as 1752 when Thomas Melville noted that sea salt imparted a yellow color to a flame. The second-generation instrument of Wade and Crouch utilizes an output device between the user and the chemical system being monitored. Such an arrangement is similar to the flame photometer employed by Lundegårdh in 1928. Interestingly, Lundegårdh himself incorporated a form of automation into his instrument.

A third-generation instrument incorporates a control computer between the user and the instrument or process being run. If one imagines the level of control being rather primitive, this description fits many of the earliest (and some present-day) AAS and ICP spectrometers. A fourth-generation instrument is far more sophisticated and "protects" the user almost completely from the instrument or process. Control parameters and response signals are sent between the instrument and control computer with little intervention on the part of the operator. The most recent AAS and ICP instruments are beginning to approach this level; recent ICP-MS units incorporate it nearly fully.

The fifth-generation instrument of Wade and Crouch still lies in the future as far as atomic spectrometry is concerned and is reproduced here for reference (Fig. 8). Here, the condition of an instrument is monitored continuously and its output data are processed by means of an expert system capable of learning from both the diagnostic information and the data it receives. This expert system, in turn, returns control signals to the instrument to optimize it (ideally) in real time. The user is not so much protected from the instrument or expert system as much as being placed in closer contact with it by means of a man–machine interface (MMI). Through use of cleverly designed graphic-based icons and a "virtual instrument" interface, the user is placed constantly in touch with the instrument's operation and its convergence on the solution of a sample problem at hand.

What kind of modified atomic spectrometric instrument would be capable of being used in a configuration such as that in Fig. 8. We must keep in mind that spectrochemical processes are fast and occur on a time scale of the order of nanoseconds. Accordingly, real-time control is impractical, even for modern high-speed computers. Next, we must recall that intelligent control is possible only through a more thorough understanding of the events which are being controlled. Finally, instrumental modifications will often be necessary in order to place the instrument in closer touch with a control computer or expert system.

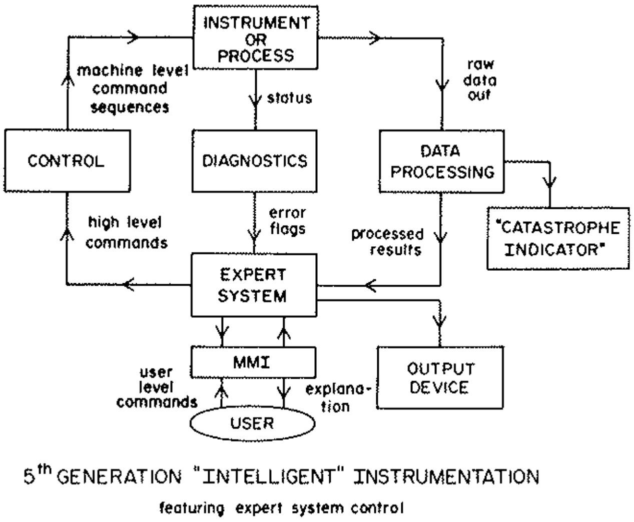

Fig. 8. A fifth-generation "intelligent" instrument for on-line, real-time optimization of an experimental system. Reproduced with permisssion from A. P. WADE and S. R. CROUCH, *Spectroscopy*, 3(10), 24 (1988).

Although nanosecond-level spectrochemical events cannot be controlled in real time, it is possible to achieve a reasonable measure of control by rapid, repetitive sampling. In this arrangement, a solid sample or sample solution would be introduced repetitively into the spectrochemical source, the resulting signal collected, and control signals returned to the source, sample-preparation unit, or aerosol-conditioning device in order to improve the system performance. A new sample specimen or aliquot would then be introduced, the cycle repeated, and the system would tend toward an optimum. Clearly, to minimize sample mass or volume, this procedure would require a microsampling device of great reliability, high speed, and excellent precision. These criteria might be met by laser ablation [27] or by a microspark [28], when solids are examined, or by an isolated microdroplet generator [8, 9, 29] for sample solutions.

Next, we will require diagnostics of our hypothetical system which are truly meaningful. Of course, it would be best if such diagnostics were based on a thorough understanding of the behavior of the instrument. From current knowledge, it would seem that useful diagnostics of an inductively coupled plasma, for example, would be the plasma excitation temperature, ion/atom ratios, based probably on emission values, the overall spatial structure of the discharge, and the temporal behavior of modulated signals. A great deal could be learned from a continuous, detailed spatial examination of a discharge on a real-time basis. Imaging detectors are already available which should make this task relatively straightforward; similarly, image-analysis algorithms are well developed and could be used profitably as a diagnostic tool in emission spectrometry.

To illustrate how useful the temporal behavior of signals might be in a modulated system, consider the interrupted-plasma work of FARNSWORTH [30] and the plasma-modulation studies of OLESIK [31]. From these studies, it is clear that the kinetic behavior of a plasma is far more sensitive to its status than is the steady-state value. Intentional modulation of the plasma or of the sample-introduction system could be used as a sensitive indicator of changing ICP conditions. The stability that such procedures would provide could be supplemented by new types of direct, analog feedback [32] and could be assisted by directly digital control of instrumental gas flows [33] and other parameters.

Sample modulation, especially if implemented with the microsampling approaches mentioned earlier, could also provide important diagnostic information. If repetitive samples taken from a solid or liquid are sufficiently reproducible and if their introduction into an atomic spectrometric source is stable, each microsample should experience the same environment as all others. Because droplet evaporation, particle vaporization, and possibly excitation/ionization in conventional spectrometric sources are all kinetically controlled, a specific temporal pattern should be produced by each microsample that is introduced. A "fingerprint" of this pattern could then be used to deduce whether the sample has vaporized completely, whether matrix interferences exist, or whether atomization or ionization are proceeding in an expected manner. Furthermore, because ionization of liberated atoms necessarily follows the atomization event itself, it might be possible to select a point on the temporal profile of the signal from a microsample which has a higher signal-to-noise ratio than the averaged value.

Interestingly, a system such as that outlined in Fig. 8 can be used in two ways. Not only can it be employed to provide on-line, real-time adaptive optimization of an experiment or instrument, but it can be used to construct a meaningful model of the instrument or even of a sample being examined by the instrument [26]. With a reasonable understanding of the instrument and its operation, a tentative theoretical model could be formulated to describe it. Any detected difference between an experiment and this model could then be used not only to improve the experiment and render its data more reliable, but also to tune the theoretical model more finely. Thus, self-adaptive atomic spectrometers, once they are developed, could be used to improve themselves.

Of course, a calibration problem will arise in a truly self-adaptive atomic spectrometer. If an instrument is tailored or tailors itself optimally for each separate sample, it would have to be re-calibrated under the newly optimized conditions. If this recalibration is inconvenient or time-consuming, much of the gain achieved by adaptive optimization would have been lost.

Because atomic spectrometric signals are ordinarily linear over a broad range, a convenient solution to this problem presents itself. The concept is based on the fact that an *averaged* atomic spectrometric signal is proportional not only to the concentration of the sample, but also to the introduction rate of that sample into the atom reservoir. For example, if the sampling rate of a laser-ablation system [27], a microspark [28], or an isolated droplet generator [8, 9, 29] were varied, a broad range of sample concentrations could be simulated. Simply put, the detected signal would be proportional to the *product* of the standard concentration and the sampling rate. This concept has already been shown to be practicable [34]. With such an arrangement, only a single standard or standard solution would be required, so a newly optimized instrument could be rapidly and efficiently recalibrated.

In conclusion, it must be admitted that much of this account is speculative. Also, some latitude has been assumed in the selection of those figures of merit which are most important in atomic spectrometry. Finally, a number of additional trends, quite likely in future atomic spectrometric instruments, have been ignored. One would hope that our knowledge of atomic spectrometry and the instruments that utilize it will continue to improve and that, ultimately, self-correcting models of such systems can be configured. In such systems, it appears probable that redundancy will exist and that parallel components will greatly enhance reliability. As in many other areas of chemistry and spectrochemical analysis, multidimensional approaches are likely to be more common. Even now, investigators are recognizing the utility of combining OES and MS for greater reliability in a determination. Lastly, human interfaces are bound to grow even more sophisticated and useful so that automation of an instrument does not isolate the user but rather brings him/her closer. In such an environment, real-time, adaptive control becomes even more appealing.

Acknowledgement—A substantial number of the concepts forwarded here had their origins in studies performed by the author and his students in the 1970s. Regrettably, limitations in computers then available precluded their implementation.

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DISCUSSION

One area of discussion dealt with the use of regression techniques in analytical atomic spectrometry. While such techniques have proven useful in mass spectrometry, the much larger number of resolution elements needed in analytical atomic spectrometry have thus far made widespread application of such techniques impractical. As microprocessors become more widespread and more powerful, however, this limitation should diminish. A more serious limitation may be that calibration of these techniques is very material-specific. While the empirical calibrations may be transferable from one kind of sample to another in elemental analysis of metals and alloys, one should not expect that an analytical method calibrated for paper samples would work for polymer films.

There was also some discussion about the role that laser-based techniques will play in analytical atomic spectrometry. At present, laser devices tend to be both complicated to operate and expensive to acquire, so that their deployment in routine analytical instrumentation has been limited. Nevertheless, niches of usefulness have been identified where laser diagnostics provide the only available method for performing a measurement, such as *in situ* measurements in plasmas and flames. A related opinion was expressed that in the coming decades, analytical spectrometry will be primarily need-driven rather than technique-driven: that is, research will be focused on applying available analytical instrumentation to specific determinations, rather than attempting to find applications for new analytical techniques.

Spectroscopy and excited state dynamics of polyatomic molecules in supersonic beams

S. C. WALLACE
Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Abstract—The fundamental aspects of excited dynamics in polyatomic molecules contains many effects, which while understood in the limit of a sparse density of states in a simple diatomic, have long eluded study. With a combination of lasers, supersonic beams to prepare ultra-cold molecules and novel types of spectroscopic approaches, one can begin to observe the dynamics and properties of superposition states which are the basis of phenomena ranging from autoionization, to predissociation, to quantum interference effects and intramolecular vibrational redistribution. This paper will review selected studies on large polyatomic molecules and their clusters.

INTRODUCTION

AS EXPERIMENTAL capabilities and theoretical advances in molecular physics continue their rapid pace of evolution, the distinction between spectroscopy and dynamics has rapidly disappeared. Hence, a total picture, which correlates the interrelation of time and frequency domain studies is the only basis for establishing the fundamental chemistry and physics of light–matter interactions. Lasers and molecular beam techniques have played a major role in reaching new levels of sophistication and understanding in spectroscopy and molecular dynamics (SMD). The possibilities for state-specific excitation and subsequent monitoring of dynamical phenomena have grown exponentially with time.

The range of "spectroscopies" continues to expand as new approaches become experimentally feasible. In this paper, we will discuss recent work on the excited state dynamics (ESD) of large molecules, where we are beginning to bring the same level of sophistication, which in the past existed only for diatomic molecules. Moreover, one also wishes to examine the role of intermolecular interactions on ESD, and so take advantage of the concomitant cluster formation, which comes with free-jet expansions. To these goals, one has two types of molecular beam/laser spectroscopy paradigms. The first is two-laser threshold-photoionization spectroscopy, with detection of bare ions and/or cluster-ions in a mass spectrometer. The relevant potential energy curves and energies are noted in Fig. 1 for the case of a dimer. The sequential excitation through the state for which one is probing ESD therefore permits unambiguous assignment of cluster identities as well as even conformational selectivity because of the sharp ($\leqslant 3\,\mathrm{cm}^{-1}$) photoionization threshold determined [1]. The Franck–Condon principle results in $\Delta v = 0$ propensity rules in most cases, thus allowing one to distinguish coupled isoenergetic states of different vibrational excitation by their increased ionization energy [2]. Finally, multichannel detection (as in Time of Flight Mass Spectrometry) permits simultaneous determination of isotope shifts and dramatic simplification of spectra of species such as rare gases where there are many isotopic possibilities. The second aspect of these studies requires both absorption and emission spectroscopy [3, 4], but with energy and time resolved picosecond fluorescence spectroscopy. This naturally must follow initial spectral characterization via laser-ionization spectroscopy and for certain cases where cluster formation is a rapidly varying function of expansion conditions the laser-ionization beam machine is used as a monitor of the species being excited in the picosecond fluorescence beam experiment. Great care is essential in these emission

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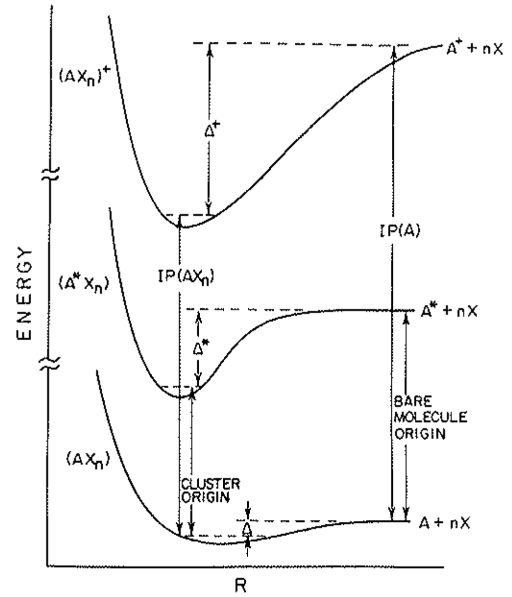

Fig. 1. Schematic potential curves for photoionization spectroscopy in clusters.

experiments, since a large dynamic range (~10^4) is essential to provide the high quality data required for quantitative analysis.

EXPERIMENTAL

The techhniques used to obtain two-colour photoionization spectra and lifetimes have been described in several publications from this group [1, 2]. Briefly, a Q-switched Nd: YAG laser (Quanta Ray DCR-1A) was used to pump a dye laser (Quanta Ray PDL-1), the output of which was frequency doubled in KD*P (Quanta Ray WEX) and used to pump the resonance transition. The ionizing laser (Lumonics HD 300) was pumped by a XeCl excimer laser (Lumonics 860-2). In many cases it proved useful to corroborate the results of fluorescence lifetime work (see below) by using a delayed two-colour photoionization technique.

All of the work reported here utilized a continuous free-jet expansion of helium through a 100 μm diameter nozzle and a backing pressure of 1–2 atm. The vacuum chamber consisted of a stainless steel cube pumped by an Edwards 9B3 vapour booster pump. This system is described in more detail, along with the methods of sample handling and mixing of gas flows for the work with van der Waals complexes, in a previous publication [21].

Dispersed fluorescence exiting the monochromator was detected by a microchannel plate (MCP) photomultiplier tube (Hamamatsu R1564U-02) for time-resolved measurements, or a higher sensitivity side-on photomultiplier (Hamamatsu R1527) when recording emission spectra. Both tubes were operated in the single photoelectron regime, in which each anode pulse is amplified and sent to a fast discriminator. The MCP anode pulses were amplified by a 3 GHz wideband preamplifier with 35 dB gain (Trontech W3GAU-1), while the slower pulses from the side-on tube were amplified with a 1 GHz, 20 dB preamplifier (PRA 1763).

Fluorescence lifetimes were measured by the time correlated photon counting method. The amplified PMT output served as the input signal to a constant fraction discriminator (Tennelec TC 454), and the resulting logic pulses used to start a biased time to amplitude converter or TAC (Ortec 457). The stop pulses were derived by using a photodiode to monitor a portion of the dye laser fundamental beam. The TAC output was directed to the input of a multichannel analyser (TN-7200) operated in pulse height analysis mode. The overall system response times, as determined by the FWHM of a measurement of scattered laser light, were 50 ps when the MCP photomultiplier was used and 500 ps for the side-on tube.

The analysis of fluorescence decay data was performed in one of two ways, depending on the time scale and complexity. For relatively long (>3 ns) single exponential decays a simple linear regression analysis was used, while for more complex decays or shorter decay times an iterative convolute and compare method was used. In both cases the quality of the fit was judged by inspection of the weighted residuals and the magnitude of the χ^2 parameter in the usual way. Instrument response functions were recorded by venting the vacuum chamber and collecting the Raleigh scatter from air at the excitation wavelength.

Fluorescence spectra were recorded by routing the TAC output to a single channel analyser (Ortec 406A) through a 50 Ohm termination. The output of the single channel analyser served as input to the multichannel analyser (MCA), which was then operated in a multichannel scaling mode. In this way the spectra were gated so as to reduce the background level due to PMT noise (roughly 100 counts s^{-1}). The MCA and the monochromator were scanned simultaneously and the resulting spectra calibrated by noting the wavelength at the beginning and end of each scan. With this system it is a simple matter to choose a combination of TAC time base and SCA window parameters to allow recording of time-gated emission spectra. Fluorescence measurements were performed using a synchronously pumped, cavity dumped dye laser as excitation source. A cw-mode locked Nd:YAG laser (Spectra Physics 3460) was frequency doubled to produce 1.1–1.5 W of 532 nm light, consisting of a train of 70 ps pulses at a repetition rate of 82 MHz. This was used to pump an extended cavity dye laser (Spectra Physics 375B) fitted with an acoustic cavity dumper (Spectra Physics 344). A synchronization signal from the Nd:YAG laser's mode locker driver at 41 MHz was electronically frequency doubled (Synergy Microwave XK702AD) and used as a reference frequency for the cavity dumper drive electronics.

The dye laser was cavity dumped at a repetition rate of 4.1 MHz to produce a pulse train of roughly 350 mW at 590 mm with rhodamine 6G, or 340 mW at 575 nm with rhodamine 575. Under these conditions the pulses had an autocorrelation full width at half maximum (FWHM) of just under 8 ps and a bandwidth of approximately 5 cm^{-1}. This was frequency doubled in a 3 cm long KD*P crystal: using an 8 cm focal length lens, some 2–5 mW of the second harmonic was obtained, representing an efficiency of roughly 1%.

The second harmonic beam was collimated, isolated by a corning CS 7-54 filter and focused into the vacuum chamber with a 65 cm focal length lens through Brewster angle windows and 4 mm aperture baffles so as to cross the axis of the free-jet expansion at right angles roughly 20 nozzle diameters downstream. Light from the fluorescing region of the jet was collected along the remaining perpendicular axis with a 7.5 cm focal length *f*/1 quartz doublet and imaged onto the entrance slit of a GCA McPherson 0.35 m, *f*/6.5 monochromator. The imaging lens was chosen to match the *f*-number of the monochromator and thus there is a net magnification of roughly 6.5. The monochromator entrance slit is oriented parallel to the direction of the laser beam and automatically masks off light emanating from other parts of the apparatus, such as laser light scattered from the nozzle. The level of scattered light reaching the detector when the system is properly focused is very low.

VIBRATIONAL AUTOIONIZATION IN ANILINE

The study of high-lying Rydberg states of aromatic systems has been of considerable interest to spectroscopists for many years. It has been only recently, however, that by combining supersonic expansion technology and laser light sources, detailed spectroscopic and dynamic information has been obtained for Rydberg states of molecules such as benzene [5] and toluene [6]. Of particular interest is that Rydberg states lying above the adiabatic ionization potential can couple with the ionization continuum and autoionize [6]. A Rydberg level at such energies is often considered to consist of an excited ion core with various amounts of electronic, vibrational, and rotational energy and a Rydberg electron. Transfer of energy from the excited core to the Rydberg electron often leads to autoionization. The most common mechanism for autoionization of a polyatomic molecule is vibrational autoionization. This process involves conversion of vibrational energy of the ion core to additional excitation of the Rydberg electron producing an ion with less vibrational excitation than that characteristic of the Rydberg state. We have reported the results of a comprehensive investigation of autoionization of high-lying Rydberg states of the aniline molecule prepared by a two-colour excitation process [7]. By preparing an intermediate vibronic level with one laser and tuning the second laser near the ionization threshold, we have identified ions produced by a vibrational autionization mechanism. By exciting different intermediate vibronic states and then photoionizing from these prepared states, one is not limited to a single set of Franck–Condon factors for the ionization step. Furthermore, one can investigate the role of specific vibrational modes in the ionization process.

We have presented photoionization efficiency (PIE) spectra of jet-cooled aniline [1(a)] and discussed the assignments of the direct and autoionization signal. In general, we observe vibrational autoionization [7] only in two-colour spectra corresponding to ionization from vibronic levels characterized by quanta of nontotally symmetric vibrations. From these spectra, we have been able to assign four Rydberg series, all bands of which are located within one ionic ground state vibrational quantum of the direct ionization threshold. The results are discussed within the framework of a simple model of vibrational autoionization based on the breakdown of the Born–Oppenheimer approximation.

The PIE spectra we have obtained when aniline is photoionized from the I^1_1, I^2_0 and I^3_1 $^1B_2$ transitions are shown in Fig. 2. In these spectra there are two distinct photoionization processes: one marked by the direct ionization onset, similar to that illustrated for the 0–0 and $6a^1_0$ bands and one characterized by sharp band structure. We shall consider the direct ionization thresholds first. The ionization onsets exhibiting step-function behaviour are located at $655 \pm 10\,\mathrm{cm}^{-1}$ [I^1_1, Fig. 2(a)], $1320 \pm 15\,\mathrm{cm}^{-1}$ [I^2_0, Fig. 2(b)] and $1980 \pm 15\,\mathrm{cm}^{-1}$ [I^3_1, Fig. 2(c)] above the aniline adiabatic IP. These values are in excellent agreement with the recently determined inversion mode intervals in the ionic ground state. Using MPI photoelectron techniques [8], the first three members of the aniline radical cation inversion mode progression have been estimated to be 645, 1315 and 1960 cm^{-1}, respectively. Thus, the $\Delta v = 0$ propensity for the direct ionization process is maintained for low energy excitation in the inversion normal mode despite the large

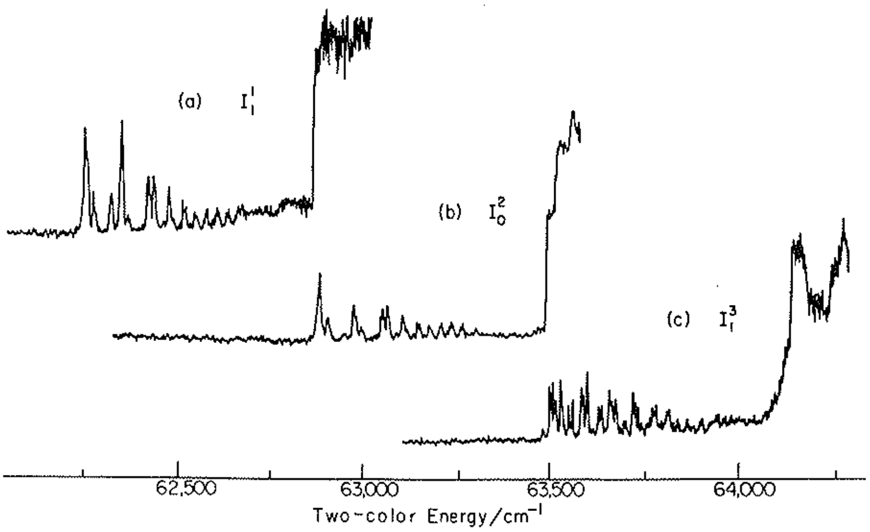

Fig. 2. Photoionization efficiency curves for selected vibrational modes in the $^1B_2$ state of aniline.

changes in vibrational frequency in going from the excited neutral ($I_0^2 = 0 + 760\,\mathrm{cm}^{-1}$) to the ground state ion. In addition, the aniline radical cation is characterized by a harmonic potential for the inversion normal mode through $v = 3$ compared to a quartic potential ($^1B_2$ state) and a double minimum potential ($\tilde{X}$ state) for the two lowest energy electronic states of the neutral molecule.

The band structure in each of the two-colour PIE spectra displayed in Fig. 2 is identified [9] with the autoionization of highly excited states of neutral aniline, in this case, Rydberg states with high principal quantum numbers. Assignment of the Rydberg bands was carried out using the Rydberg equation

$$E = \mathrm{IP} - R(n - \delta)^{-2}$$

From analysis of the bands in the I_1^1 PIE spectrum, we have been able to assign four Rydberg series with quantum defects of $\delta = 0.78 \pm 0.004$ ($n = 14$–21), $\delta = 0.45 \pm 0.02$ ($n = 13$–25), $\delta = 0.41 \pm 0.02$ ($n = 13$–17) and $\delta = 0.22 = 0.02$ ($n = 13$–24), each converging to the LP associated with the same number of quanta in the inversion mode as that of the intermediate state.

The values of these quantum defects imply [10] that the $\delta = 0.78$ series belongs to an s series, the $\delta = 0.45$ and $\delta = 0.41$ bands to a p series, and the $\delta = 0.22$ bands to a d series.

Examination of each of the three spectra in Fig. 2 shows that this structure begins at approximately the same energy relative to the direct ionization onset ($\sim 660\,\mathrm{cm}^{-1}$) regardless of the number of inversion quanta characterizing the intermediate $^1B_2$ state. In addition, one should note that all of the Rydberg structure lie *within* the ionization continuum. Using the value of an ionic ground state inversion mode quantum of $\sim 655\,\mathrm{cm}^{-1}$, one can identify the beginning of the autoionization bands with the energy corresponding to one quantum less excitation in the ion than that produced by direct ionization. This implies that the autoionization process shown in these spectra are characterized by a $\Delta v = -1$ propensity. This is in accord with BERRY's [11] vibrational autoionization propensity rule for the hydrogen molecule. This case in aniline was the first example of vibrational autoionization in polyatomic molecule. Recent theoretical analysis [12] has confirmed the importance of state-selective vibronic coupling.

TORSIONAL SPECTRA OF METHYL SUBSTITUTED INDOLES

Traditionally, torsional spectra have been used to determine conformational information about many molecules. The bulk of data has been provided by I.R., Raman and microwave studies and therefore pertains only to the ground electronic state [13, 14]. Only recently have experiments that probe the internal rotations of the alkyl group within excited electronic states been performed [15 –21].

Indole and the methyl substituted indoles have been the subject of considerable spectroscopic study primarily because indole is the chromophore of the amino acid tryptophan. Work in the condensed phase [22, 23] has established that the near U.V. spectrum of indole and some of the methylindoles is dominated by transitions to two electronic states designated ^1L_a and ^1L_b after PLATT [24]. In the gas phase, however, only one electronic state has been clearly identified, this being assigned to the ^1L_b state [25–27]. To date, however, there is no direct spectroscopic evidence for the assignment of this state to ^1L_b. In principle, the direction of the transition dipole moment would verify this assignment but, even the recent high resolution rotational analysis on the 0–0 band of indole by PHILIPS and LEVY [28] showed that the direction is still ambiguous.

The information provided by the torsional spectra of the methyl substituted indoles should reflect uniquely the behaviour of the excited electronic state. Insofar as the methyl group can be considered a non-invasive probe of gross electronic features, this information will ultimately provide details of the electronic structure of the parent indole molecule. The results of this work are discussed in light of previous findings from this laboratory and others, as well as with past theoretical predictions of the electronic structure of the ^1L_b and ^1L_a states.

The excitation spectra of 1,- 4,- 5,- 6- and 7-substituted methyl-indoles exhibit a number of very low frequency bands which could not be assigned to vibrations of the rigid molecule. These bands have been attributed to the torsional motion of the methyl top. In order to assign the transitions, a simple model for internal rotation was used.

The torsional potential is usually expressed as [13]

$$V(\phi)=\tfrac{1}{2}\sum_n V_n(1-\cos n\phi), \tag{1}$$

where ϕ is the angle of internal rotation. We approximate the molecular system as a rigid rotor attached to a rigid framework. The energy levels for a rigid rotor are given by

$$-B\frac{d^2\Psi(\phi)}{d\phi^2}+V(\phi)\Psi(\phi)=E\Psi(\phi). \tag{2}$$

Here, B is the reduced rotational constant and $V(\phi)$ is given by Eqn (1). For the case of a free rotor, the energy levels are given by Bm^2. We have used the program of LEWIS *et al.* [29] to fit energy levels from our data to the above form of the potential function. The energy levels are obtianed by expanding $\Psi(\phi)$ in a free rotor representation expressed in a sin–cos basis set and diagonalizing the Hamiltonian matrix. The terms in the potential expansion as well as the reduced rotational constant, B, were iterated to give the best fit with the observed energies. Only the V_2 and V_6 terms in the potential function were deemed relevant for the methylindoles. That is:

$$V(\phi)=\tfrac{1}{2}V_3(1-\cos 3\phi)+\tfrac{1}{2}V_6(1-\cos 6\phi). \tag{3}$$

The V_3 term arises from the fact that the equilibrium geometry recurs for every 120° of methyl rotation. In the absence of a V_6 term, V_3 is the height of the potential barrier. The V_6 term is attributed to a methyl C–H bond eclipsing the plane of the parent indole molecule with every 60° of methyl rotation.

The energy levels are labelled by the symmetry species of the C_{3v} point group since the permutation inversion group of the methyl rotor is isomorphic with that point group [30]. The energy levels are also labelled with a rotational quantum number, m. The torsional selectional rules are $a_1\leftrightarrow a_1$, $a_2\leftrightarrow a_2$ and $e\leftrightarrow e$, with $a_1\leftrightarrow a_2$ being allowed only when the overall rotation of the molecule is taken into account.

The intensities may be obtained in the usual way from the Franck–Condon factors. The potential function program generates the eigenvector components assuming a polarizability operator of $\cos\phi$. The intensity distributions of the torsional spectra allow us to obtain the relative torsional coordinate, ϕ, between the excited and ground state potentials [17].

As an example of the various methyl substituted indoles, the 1+1 photoionization spectrum of 5-methylindole is shown in Fig. 3. The ordering and labelling of the energy levels are known for any methyl rotor so the bands could be assigned by inspection. Initially, the observed energy levels were fitted to a potential assuming that splitting between the $0a_1$ and $1e$ levels was too small to be resolved. Later, when approximate potentials were refined. A few of the bands did not fit the torsional scheme and we attribute these to low frequency vibrational motion, possibly ring libration.

To map out the ground state energy levels, dispersed fluorescence spectra of the four strongest bands in Fig. 3 were obtained. These are shown in Fig. 4. Exciting the origin band yielded fluorescence from both the $1e$ and $0a_1$ levels. However, exciting each of the other bands gave pure $e\leftrightarrow e$ or $a_1\leftrightarrow a_1$ spectra. This verified the assignment of the excited state and left us with a simple spectrum to assign to the ground state torsional levels. These energy levels were then used to generate the torsional potential function of the ground state. As with the excited state a few bands could not be assigned and have been attributed to low frequency vibrations or torsions associated with these vibrations.

The potential terms and the B values, along with the observed and calculated energy levels, have been given in detail elsewhere [31]. The B value changes very little upon excitation indicting that the bond lengths and bond angles of the methyl rotor are only minimally affected by the excitation. The potential function was found to be dominated by the V_3 term in both the ground and excited states. The potential functions for the torsional motions of each of these states are depicted in Fig. 5.

In order to ensure self-consistency and to determine the relative positions of the ground and excited state torsional potentials, we have calculated the intensities of the observed transitions as predicted from our model potential. The observation of a long progression of torsional bands implies that upon excitation, there is a large geometrical change involving the methyl rotor. Since no large change in the reduced rotational constant of the methyl rotor has occurred, the torsional progression may be explained as a shift of the equilibrium position of the methyl rotor by 60° relative to the plane of the molecule. If we assume that the potential curves of the excited and ground state are in phase (i.e. the equilibrium geometry of the methyl rotor with respect to ϕ is the same in both the ground and excited states), then the bands from $\Delta m = 0$ transitions are predicted to account for the majority of the intensity. However, if the potential function curves are shifted 60° out of phase we obtain the calculated intensities as depicted in Fig. 4. The agreement with the observed spectra is excellent, verifying the assignments presented in Figs 3 and 4 and showing that the equilibrium geometry of the methyl rotor with respect to the plane of the molecule is rotated 60° in the excited state relative to that in the ground state.

It is to be expected that evidence of methyl torsional motion should appear in the electronic spectra of certain polyatomic molecules. The potentials sampled by a methyl rotor should be different in the ground and excited electronic states. There is growing evidence [21, 32] that the torsional potentials are extremely sensitive indicators of differences in the electronic structure of the two states.

Interactions of the methyl rotor with the π electron density of the ring will lead to characteristic torsional potentials. The most obvious of these is an increase or decrease of the barrier height upon excitation. These changes result from the electron density increases and decreases in the vicinity of the substituent site. A methyl rotor on a planar molecule is expected to exhibit a six-fold barrier; a methyl C–H bond eclipses the plane with every 60° of rotation. In general, the electrostatic potentials in either direction along

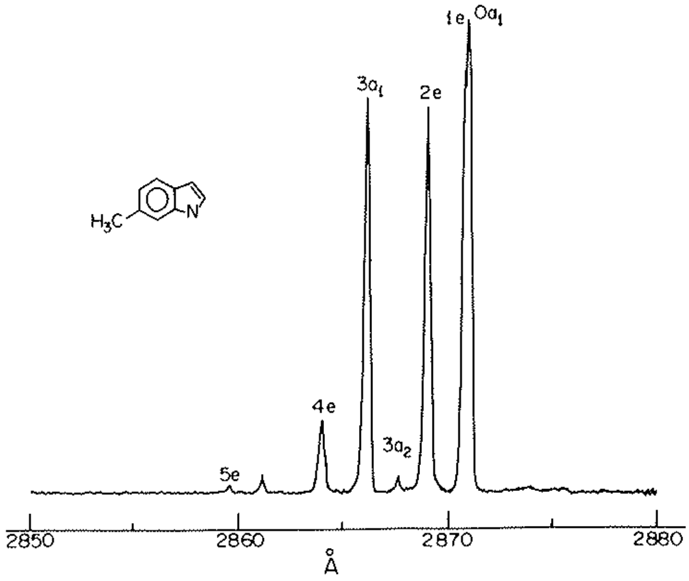

Fig. 3. 5-Methylindole torsional excitation spectra.

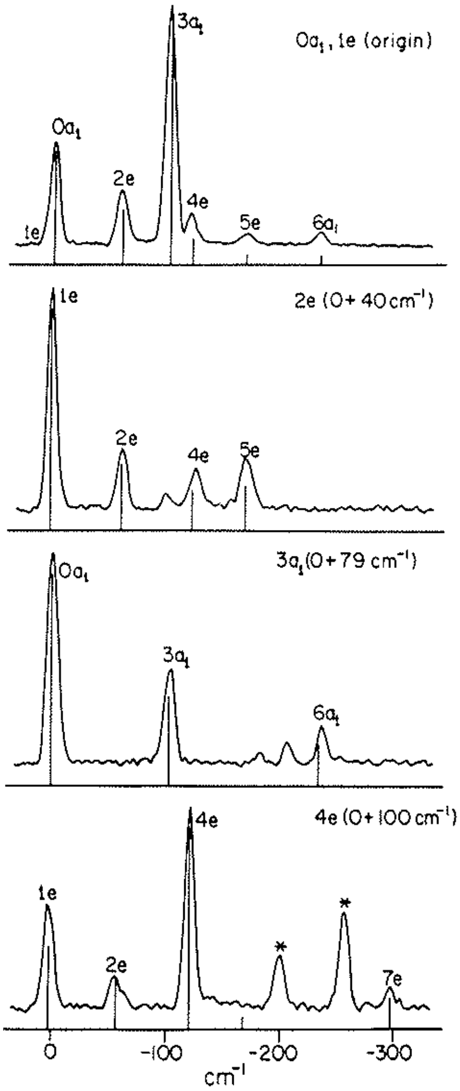

Fig. 4. Selected 5-methylindole emission spectra (see Fig. 3).

the bonds in the plane of the molecule are not equivalent and the methyl rotor will see a threefold barrier. That is, when one of the adjacent ring C–C bonds is eclipsed by a methyl C–H bond the methyl rotor is in the equilibirum position and when eclipsing the other C–C bond the methyl rotor is at a maximum in potential energy. In the excited state, the equilibrium position of the methyl substituent may be rotated 60° relative to the ground state equilibrium position due to the differences in the electronic structure. This results in the observed phase change between the ground and excited state torsional potential functions in 5-methylindole.

By surveying all possible methyl substituted species, the torsional spectra of the methyl substituted indoles have been used as a probe of the electrostatic potential between the methyl rotor and the indole moiety at each substituent site. Although our approach is to infer electronic properties on a qualitative basis, it has the potential to reveal more subtle details about the electronic structure than available through conventional means. Thus, the methyl rotor may be used as a unique probe of the electronic structure of the parent molecule. For the case of the methylindoles, the torsional spectra yield a description of the changes in the electronic structure of the parent indole molecule upon excitation allowing us to confirm the assignment of the first excited state of indole as ^1L_b. More detailed theoretical calculations of the electronic structure of the indole molecule are necessary in order to explain the behaviour of the methyl rotors in a more quantitative

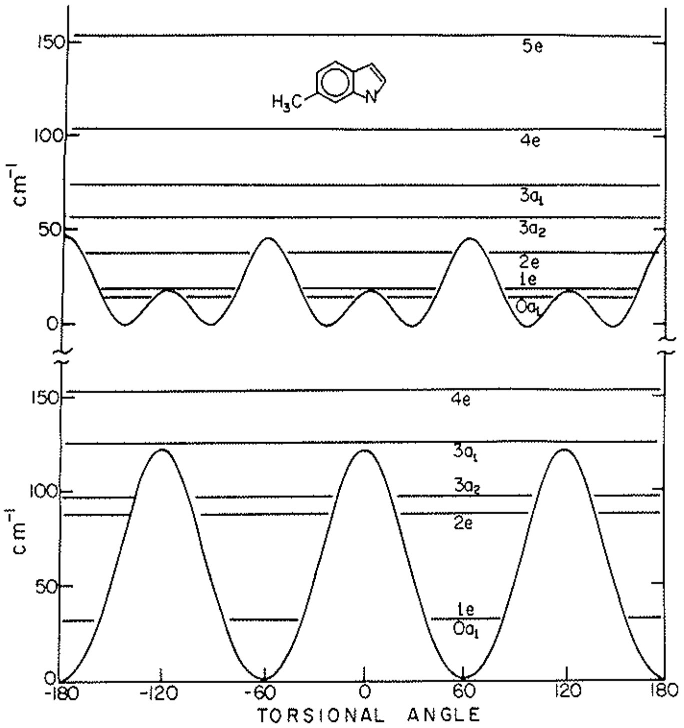

Fig. 5. Ground and excited state torsional potentials for 5-methylindole.

way. However, the results obtained by the analysis of these torsional spectra can be used to test the validity of the theoretical models for many molecular systems.

TIME DEPENDENT STUDIES IN INDOLE

Fluorescence decay curves are obtained for some of the excited state levels by monitoring various bands in their respective fluorescence spectra. The excited state levels studied are the 480, 540, 718, 720, 909 and 969 $\mathrm{cm^{-1}}$ levels. Normal single exponential decays are observed for all excitation bands studied except the 718 $\mathrm{cm^{-1}}$ band. The prominent fluorescence bands due to excitation of the 718 $\mathrm{cm^{-1}}$ band are distinguished in that they show modulated fluorescence decay curves (i.e. quantum beats). The observation of phase shifted quantum beats enables a direct view of Intramolecular Vibrational Relaxation (IVR) [33–39]. Fluorescence bands which exhibit a beat pattern that has a maximum at $t=0$ (+1 phase) arise from direct emission. The direct emission arises from the S_1 level optically accessible from the $v=0$ level of the ground state. Fluorescence bands exhibiting a minimum at $t=0$ (−1 phase) arise from state populated by IVR. The levels that are populated by IVR are not optically accessible from $v=0$ of the ground state and transitions from those levels populated by IVR will terminate on levels different from those involved in direct emission. From the outset we know many of the modes which are prevalent throughout the fluorescence spectra of the lower energy excitation bands. The bands which we expect to show the +1 phase beats will be the bands terminating at the 0, 542, 758 and 1515 $\mathrm{cm^{-1}}$ levels of the ground state.

Two sets of beat patterns were observed from the fluorescence bands after excitation to the 718 $\mathrm{cm^{-1}}$ band which differed only in their relative phases (see Fig. 6). The fluorescence bands that terminate at the 0, 542, 758, 1141 and 1515 $\mathrm{cm^{-1}}$ ground state levels show a +1 phase quantum beat with a single frquency component of 11.5 GHz. The resonance peak and the peak at 945 $\mathrm{cm^{-1}}$ have contributions from the 720 $\mathrm{cm^{-1}}$ excitation as well and the fluorescence decays are thus too poorly modulated to see any

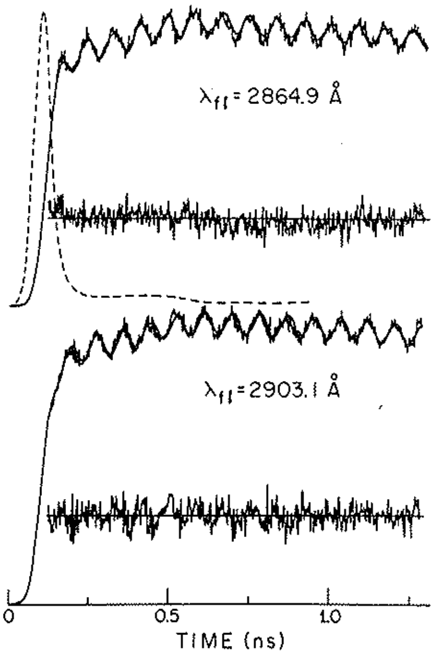

Fig. 6. Energy and time resolved emission from the 718 cm^{-1} band of indole.

beats. The bands that terminate at the 922, 972 and 1056 cm^{-1} ground state levels show a -1 phase quantum beat again with 11.5 GHz modulation.

The parameters necessary to characterize the IVR are easily obtained from the modulated fluorescence decay functions. The phase is evident from an inspection of the rising edge of the decay curve. A Fourier transform of the decay function gives us the beat frequency and dephasing time. The dephasing time is the decay time of the quantum beat envelope relative to the overall fluorescence decay time which arises from differences in rotational constants of the coupled vibrational levels [37]. In our case, the quantum beat period is of the order of the instrument response function so that it is necessary to deconvolute the decay curve in order to determine the modulation depth. A decay function was created with the fluorescence lifetime, beat frequency, phase modulation depth and dephasing time as variable parameters. This function was then convoluted with our experimental instrument response function and compared with the observed decay function. The parameters of the decay function are adjusted until a fit with the observed fluorescence decay was obtained. The results of the fit for two decay functions are shown in Fig. 6.

The fact that only a single beat frequency is observed implies that we are exciting a coherent superposition of only two molecular eigenstates. If that were the case, emission from the redistributed levels should show 100% modulation in the fluorescence decay. However the -1 phase decay functions which we observe show varying degrees of modulation depths; the largest being 70% for fluorescence terminating at the 922 cm^{-1} level. There are a number of experimental limitations which could prevent us from observing the theoretical modulation depth, if indeed we are creating a superposition of only two molecular eigenstates. One consideration could be time base drift. The average decay requires approximately 6 h to accumulate and our modelling procedure for an 11.5 GHz beat frequency shows that a time base drift of only 20–30 ps over that time could account for the modulation depth being reduced to 70%. If the bands in the fluorescence spectrum cannot be completely spectrally isolated (our monochromator bandwidth was 1–2 Å), then contributions from underlying or nearby spectral features could account for the loss of modulation depth as well. That was the case for the 945 cm^{-1} fluorescence band and the resonant fluorescence band.

Assuming that we have excited a coherent superposition of two molecular eigenstates we may calculate the coupling strength and the zero-order energy level separation. The zero-order Hamiltonian matrix [35] is:

$$H_0 = \begin{bmatrix} E_a & V_{ab} \\ V_{ab} & E_b \end{bmatrix}. \qquad 1.$$

Here E_a and E_b are the energies of the two order states $|a>$ and $|b>$ and V_{ab} is the coupling constant. From the modulation depth of the +1 phase decay functions and the beat frequency, it is a simple matter to calculate $|V_{ab}|$ and $|E_a - E_b|$ as outlined by FELKER and ZEWAIL [35]. The best modulation depth which was observed for the +1 phase decay is 25%. We then obtain $|V_{ab}| = 0.12\,\mathrm{cm}^{-1}$. These values are lower and upper limits respectively due to the uncertainty in the modulation depth as discussed above.

We now need to look again at the spectroscopy to determine the zero-order nature of the level coupled to the 718 cm^{-1} in plane mode. The symmetry of the vibrational level coupled to the 718 cm^{-1} mode must be a'. We should be able to determine the identity of the coupled levels from the fluorescence spectrum. If we assume that the 26_1^1 band at 758 cm^{-1} should appear as a false origin, then several bands appear in the fluorescence spectrum with unexpected intensity. Those bands terminate on combinations levels of ν_{42} with the higher frequency a'' modes. All of these bands exhibit −1 phase beats except for the band at 948 cm^{-1} which is a poor case as discussed above. These fluorescence bands arise from the excited state level that is coupled to the 718 cm^{-1} mode. If these bands follow the $\Delta v = 0$ selection rule in the fluorescence spectrum then the coupled level is due to ν_{42} in combination with a mode which is best described as a mixture of the a″ zero-order modes ν_{32}–ν_{35}. A similar fluorescence spectrum was observed for the 990 cm^{-1} excitation band, which was attributed to a mixed level.

A thorough understanding of the spectroscopy has enabled us to describe the coupling that is manifest in the observation of quantum beats for the 718 cm^{-1} level. The complementary nature of the time and energy resolved studies must be stressed. As a result of our work we find that the in-plane 718 cm^{-1} mode couples to a combination of out-of-plane modes. This is a point that is key to our understanding of 1-methylindole lifetime data. The 1-methylindole molecule with the methyl group breaking the plane of symmetry certainly will experience much stronger coupling of the in-plane modes to out-of-plane modes.

The S_1 state of indole exhibits many features which illustrate the transition from a system that can be described in the "spectroscopic limit" [40], through "restricted IVR" [35] and finally to "dissipative IVR" [35]. At low excitation energies the S_1 state can be easily described in terms of the ground state basis and the spectroscopic assignments are straightforward. The excited state a' modes are well described in terms of the ground state at least up to 718 cm^{-1}, while the zero-order description of the excited state a'' modes fails at slightly lower energies as evidenced by the mixed nature of the level coupled to the 718 cm^{-1} level. The 718 cm^{-1} level is the only level that shows dynamical behaviour. However, the spectroscopy is still tractable enough so that we can describe this "restricted IVR" coupling in terms of our zero-order description. At higher energies we see heavily mixed states as we approach the dissipative regime in spite of the absence of dynamical behaviour in the fluorescence decays. All of these levels of description occur below 1000 cm^{-1} in the S_1 manifold of indole.

PRE-SOLVATION CLUSTER EFFECTS ON PHOTOFRAGMENTATION OF 2,3-DIMETHYLINDOLE

One of the most compelling reasons for undertaking the study of indole and its derivatives under jet-cooled conditions is to elucidate the unusual excited state properties which make them useful as fluorescent probes in biological systems. The remarkable sensitivity of the fluorescence quantum yield and emission spectra of these compounds to the environment of the indole nucleus has been used to assess the polarity of the environment of tryptophanyl residues in polypeptide chains, as well as conformational fluctuations which alter that environment on the time scale of the fluorescence lifetime.

Perhaps the most convincing evidence for the presence of two electronic states is due to the work of VALEUR and WEBER [41] and YAMAMOTO and TANAKA [42], who utilized polarized emission and absorption techniques, respectively, to resolve the absorption spectra of indole, 3-methylindole and tryptophan into contributions from two electronic transitions. More recently REHMS and CALLIS [43] have investigated the two-photon absorption spectra of indole, 3-methylindole and 2,3-dimethylindole and have been able to locate the onset of ^1L_a state, though in some cases diffuse features attributed to absorption to that state have been reported [44]. LAMI and GLASSER [45] have stressed that fluorescence quantum yield evidence obtained from experiments carried out on low pressure vapours of a variety of substituted indoles indicate that at certain energies a rapid radiationless decay channel opens, which they attributed to the ^1L_a state. They postulated that it is dissociative and located near the ^1L_b origin, and have mapped out the relative energies of the two states.

Solution phase studies of substituted indoles strongly suggest that in polar solvents fluorescence arises from a highly polar ^1L_a state [41, 43] and it is this which gives rise to the unusual solution phase properties which have prompted so much work on condensed phase and gas phase indole photophysics. The magnitude of the fluorescence Stokes' shift of indoles in aqueous and alcoholic solvents shows that this state is very polar indeed, and it has been likened to the charge-transfer states observed in substituted indolines and aromatic amines. Thus, it is of great interest to examine the properties of dialkylindoles when they are interacting with polar molecules in a supersonic expansion. Here, the degree of solvation can be controlled with some degree of precision, and insight gained into the transition from the isolated molecule to the biologically important solvated molecule.

The RE2PI excitation spectra of 2,3-dimethylindole (2,3-DMI) complexed with the MeOH and trimethylamine (TMA) have been reported previously [27]. They consist of broad absorption features which extend well to the red of the bare molecule origin. We have been successful in obtaining dispersed fluorescence spectra of these complexes, and the results are presented in Fig. 7. Also shown is the spectrum resulting from complexation with ammonia. In every case the emission is characterized by an extreme red-shift of several thousand cm^{-1} and an almost complete absence of vibrational structure, the signature emission from a vibrationally hot species to high-lying vibrational levels of the ground state. The fluorescence lifetimes of these clusters, in some cases were considerably longer than that of the bare molecule origin.

For both solution phase indoles and jet-cooled 2,3-DMI clusters there is observed some relatively diffuse structure in an otherwise continuous excitation spectrum. In the case of solution phase indoles this appears as a shoulder on the long wavelength edge of the absorption band system, while in the clusters it is a rise in the baseline with a few broadened peaks built on it. This might appear to be the remnants of vibrational structure near the ^1L_b origin of the clusters, were it not for the fact that it blends smoothly into a featureless continuum extending to both higher and lower energies, and no differences in either the decay dynamics or the emission spectra were observed upon excitation into the structured or unstructured regions. However, if the ^1L_a state is regarded as being stabilized to a much greater extent then the ^1L_b state, as suggested by condensed phase work, then it is clear that the ^1L_b state will be deeply embedded high in the vibrational manifold of the ^1L_a state. Under these circumstances rapid internal conversion to the ^1L_a manifold is to be expected, if indeed the two states can be treated independently at all. It may be more appropriate to consider these structured regions of the spectrum as simply being due to portions of the diabatic excited state potential surface with enhanced Franck–Condon overlap with the cluster ground states.

Very different behaviour was observed when 2,3-DMI was expanded in the presence of ammonia. At flow rates of ammonia between 0.1 and 4% the fluorescence emission, though relatively weak, was clearly non-exponential and consisted of a 250 ps decay accompanied by longer lived fluorescence which was comprised of several exponential components with lifetimes ranging from approximately 6 to 15 ns. When fitted to two exponential components, the fractional intensities contributed by the fast and slow decays were found to be 17 and 83%, respectively. Increasing flows of NH_3 resulted in an overall increase in signal level while the proportion of fast and slow components varied only slightly. Oddly enough, the fast component became somewhat more pronounced at the higher flow rates. As reported previously [15], the excitation spectrum of even the 1:1 complex was completely featureless, extending at least 1600 cm^{-1} to the red and a few hundred cm^{-1} to the blue of the bare molecule origin and was virtually insensitive to the NH_3 flow rate.

We have measured the time-gated fluorescence of the ammonia complexes in order to determine the emission spectra of the two components and have found that the fast decay component has a maximum approximately 1500 cm^{-1} to the red of the bare molecule origin. The ungated emission spectra shift to the red in response to decreasing excitation energy, but both decay components were present at all excitation wavelengths which were used.

When this experiment was repeated using two-colour laser photoionization techniques it was confirmed that the 2,3-DMI$(NH_3)_1$ complex predominated under the conditions used for the lowest flow rate and had a rather broad ionization onset approximately 2500 cm^{-1} to the red of the IP of the bare molecule. Increasing the ammonia flow resulted in progressive addition of NH_3 to the cluster. At ammonia flow rates of roughly 1%, species comprised of from one to six NH_3 molecules could be detected, in a distribution which peaked at 2,3-DMI$(NH_3)_4$. Ionization was conducted at energies just above the 1:1 cluster IP, at 56 700 cm^{-1}. In experiments with higher ammonia flows the

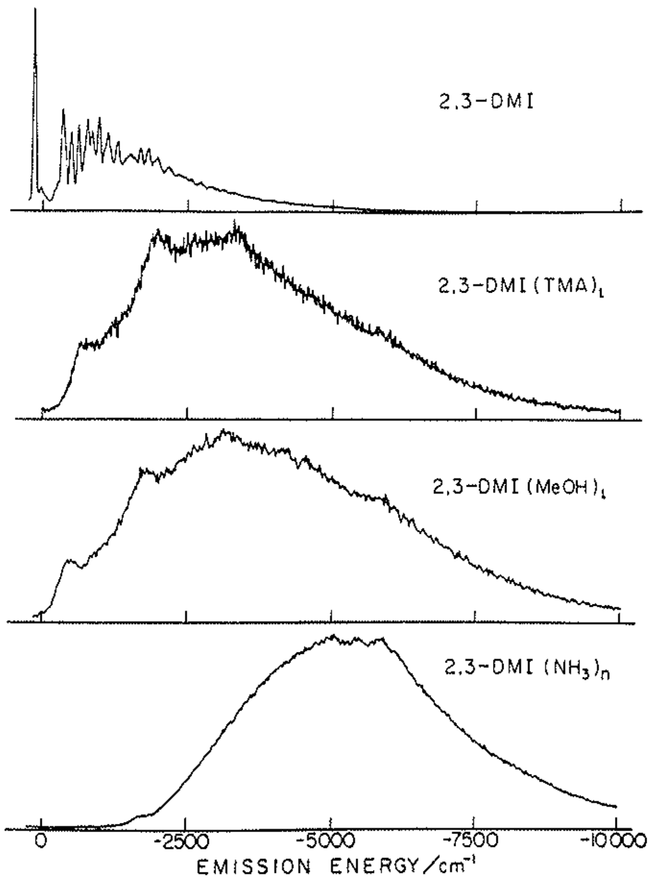

Fig. 7. Emission spectra of 2,3-DMI and complexes.

presence of unclustered 2,3-DMI$^+$ was observed, which is unusual since this ionization energy lies nearly 2000 cm^{-1} below that necessary to ionize the bare molecule.

The mass spectrum observed after the two-colour ionization of these 1% NH_3 expansions proved to be slightly sensitive to the energy of the second (ionizing) photon, and the production of unclustered species grew in importance as the second photon energy approached the bare molecule mass could not be attributed to the excitation of uncomplexed species: the radiation densities used were too low for simultaneous two photon absorption to occur to any appreciable extent, and in any case, all signal was lost when the ammonia flow was reduced to zero.

The production of ions at the mass of the bare molecule is much more likely to arise from fragmentation of the cluster, though whether this occurs before or after the absorption of the second photon we are unable to determine at present. In both cases the production of bare molecule ions is expected to increase with the energy of the second photon, though for different reasons. Dissociation of the neutral, excited cluster would result in a cluster fragment containing a chromophore with less total energy than that imparted by the first photon, by an amount depending on the bond enthalpy liberated and kinetic energy imparted to the departing fragments. To ionize the resulting fragment this energy difference would have to be made up by a more energetic second photon. On the other hand, if the clusters do not dissociate until after ionization, then the degree of fragmentation is expected to increase with excess vibrational energy in the ion and hence, the second photon energy.

The role of hydrogen bonding and vibrational redistribution

The complexation of indole derivatives with polar molecules can be thought of as the result of an interaction between the acidic hydrogen of the ring nitrogen atom and the complexing partner acting as a Lewis base [6]; the resulting hydrogen bond would be expected to weaken the N–H bond of the indole nucleus in proportion to the proton affinity. Since the energy of a hydrogen bond is considerably lower than that of the covalent N–H bond the effect of this interaction on the indole moiety would normally be minimal, but in the case of the 2,3-disubstituted indoles we have already seen that it is this bond which intimately involved with the coupling of the two zero-order electronic potential surfaces. The unusual excited state properties of the 2,3-DMI hydrogen bonded complexes may then be viewed as the result of the interaction between the indolic hydrogen and the lone pair of the Lewis base, which enhances the coupling of the zero-order ^1L_b and ^1L_a states by promoting the extension of the N–H bond.

The excitation spectra observed for these complexes are entirely different from those of indoles in which the ^1L_a state is not expected to play a significant role, and lack the sharp vibrational structure attributed to origin transitions of ^1L_b complexes. There is no evidence in fluorescence for the presence of a picosecond decay component, which would be necessary to explain the broad absorption spectra on the basis of lifetime broadening; rather the structureless absorption must be attributed to extreme vibrational congestion. Thus, in the case of the hydrogen bonded complexes it must be concluded that the hydrogen bonding interaction has such a marked influence on the indole moiety that the nature of the excited state of the complex is fundamentally different from that of the bare molecule, and can be described most readily as a ^1L_a excited state.

If this is the case, then we must address the questions raised by work on the uncomplexed molecules, both by ourselves and elsewhere [3, 27], which indicate that this state is characterized by a dissociative potential. Considering only the hydrogen bonding interactions between 2,3-DMI and its complexing partner, TMA clusters might be expected to have rather similar characteristics to those formed with ammonia. Substituted amines have a somewhat *larger* gas phase proton affinity than NH_3 itself, so that considering a dissociative potential and the hydrogen bond strengths one might expect an even shorter lifetime for the case of 2,3-DMI$(TMA)_1$. This is precisely the opposite of what we have observed: the TMA complex fluoresces quite strongly and has a longer lifetime than 2,3-DMI itself. One should also note the MeOH complexes behave in an essentially equivalent way to those formed with TMA, though its gas phase proton affinity is somewhat lower than that of NH_3. Thus, the relative strengths of the hydrogen bonding interactions alone are insufficient to explain the rapid decay of the ammonia clusters. Furthermore, the characterization of the ^1L_a potential as dissociative must be regarded as questionable, at least in the case of the hydrogen bonded clusters.

We have already noted that the fluorescence of indoles in polar solution is thought to arise solely from the ^1L_a state, so there is no particular reason to assume that this state should be dissociative in the gas phase. In terms of the zero-order state description already discussed for the bare molecule, we can reconcile the present data by postulating that the ^1L_a states of jet-cooled 2,3-DMI complexes are bound states. The role of the N–H bond extension in enhancing the coupling between the ^1L_a and the ^1L_b states would imply that the proposed minimum in the ^1L_a state potential along the N–H coordinates lies at a larger value of r_{NH} than the minimum of either the ^1L_b or ground states. If we assume this to be the case, then vertical transitions from the ground to the excited state terminating on the ^1L_a state potential surface will result in the population of excited state clusters with a relatively high degree of vibrational excitation.

In the case of 2,3-DMI$(NH_3)_1$ the high degree of vibrational excitation could result in a very rapid decay of population as vibrational energy is redistributed into the hydrogen bond and the NH_3 is carried away. Alternatively, if the complexing partner possesses a sufficient density of low-frequency vibrational states the cluster dissociation may be arrested by the dissipation of vibrational energy into the bath of states provided by the complexing partner. In the case of TMA and MeOH a single solvent molecule apparently provides a sufficiently dense set of bath states to inhibit this behaviour, while ammonia does not.

To test this hypothesis two other polar molecules were chosen for a set of experiments similar to those described above: acetonitrile was selected as a "large" partner with a relatively dense vibrational manifold, analogous to TMA and MeOH, while water served as a "small" partner with a more limited number of vibrational modes, analogous to ammonia. The excitation spectra of their 1:1 complexes, obtained by RE2PI methods, were very similar to those of TMA and MeOH reported in Ref. 27. The results of the fluorescence measurements which we obtained were consistent with the idea of the vibrational states of the cluster partner providing an energy sink. The fluorescence lifetime of the 2,3-DMI$(CH_3CN)_1$ complex was found to be 9.2 ns. 2,3-DMI$(H_2O)_1$ exhibited a double exponential decay when monitored at 3300 Å which was strikingly similar to that of 2,3-DMI$(NH_3)_1$, with roughly 20% of the emission being due to a 250 ps component. The slow decay component consisted of a range of lifetimes between 6 and 10 ns. However, higher order clusters exhibited longer-lived and more red-shifted fluorescence in both cases, and those of H_2O did not exhibit the fast decay component observed for the case of NH_3.

Thus, while the 1:1 H_2O and NH_3 clusters were similar in their dynamics, in other ways the NH_3 clusters appear to be unique. For example, the excitation spectrum of the 2,3-DMI$(H_2O)_1$ complex was rather similar to those of the larger complexing partners such as TMA and not at all like the completely featureless continuum of the NH_3 cluster. The fast decay time of the 1:1 H_2O complex was similar to that of the 1:1 NH_3 cluster, but the addition of even one further H_2O molecule brought the cluster lifetime to a value comparable to those of 1:1 complexes with larger complexing partners. At high flow rates of water the fast decay component could be completely obscured by the longer decays of the higher order clusters. In contrast to this, and though many attempts have been made to do so, in the case of NH_3 complexes it was not possible to associate any single decay time with any particular cluster stoichiometry. It appears that even highly clustered species retain a large sub-nanosecond component in their fluorescence decays, and that even the 1:1 cluster displays a multicomponent decay. It is possible that these differences in behaviour are due to differences in the structures of the more extensively clustered species, but since these are unknown in any case further speculation would be fruitless.

Despite these differences in the "small" clusters, in general the excited state decay dynamics which are observed can be considered in terms of the relatively simple model proposed earlier. Thus, we envisage that the vibrational excitation initially "localized" in the chromophore will be redistributed into the vibrational modes of its cluster partner(s). It is clear that the possible fate of these clusters is at least three-fold: they may simply remain "warm" clusters, they may undergo isomerization as a result of the altered dipole moment [1] of the chromophore or they may dissociate. Whatever the case, the chromophore itself will have cooled to some extent, and we will use the term "relaxed" to describe the subsequent state of the 2,3-DMI molecule. Naturally, the simple redistribution of vibrational energy within the cluster cannot actually remove any energy and the degree of vibrational excitation within the indole nucleus would remain much higher than if dissociation were to occur.

A model for the excited state of 2,3-*dimethylindole and its clusters*

Attempting to understand the excited state behaviour of indole and its derivatives in terms of distinct ^1L_a and ^1L_b states reflects the desire of spectroscopists to label the indole excited states according to the classification scheme of PLATT [47]. This model was developed for use in polycyclic aromatic molecules in which the symmetry was rather high and the ground and excited state geometries were similar. It is expected to be applicable if the zero-order states interact only weakly, or what is often synonymous, are well-separated in energy: only in this case is it quite proper to regard them as distinct states, to describe interactions between them in terms of perturbation theory, and to view the resulting excited state dynamics as resulting from transitions between their potential energy surfaces.

In the case of isolated 2,3-DMI and HC the observed excited state dynamics can also be described in the adiabatic representation. Using our experimental observations as a guide, one can speculate on some of the grosser features of the resulting adiabatic potential surface. We also assume that the diabatic potential surfaces, which correspond to the zero-order ^1L_a and ^1L_b states, interact strongly, and are displaced along the N–H coordinate. The prominence of the 0^0_0 band in both the excitation and origin fluorescence spectra indicates that the local minimum of the ^1L_b surface lies at roughly the same position along the N–H coordinates as that of the ground state. The observation of predissociation at the ^1L_b vibrationless level indicates that the potential energy decreases as the N–H bond length increases past a barrier formed by the avoided crossing with the ^1L_a surface. In the region past the barrier the form of the potential surface is contributed mainly by the zero-order ^1L_a surface: it was suggested earlier that while the dissociation energy of this zero-order state must lie to lower energy than the zero-order ^1L_b origin, it may nonetheless be characterized by a bound potential. The previous discussion of the long fluorescence lifetime component in decays of H_2O and NH_3 clusters suggests that this may be the case, hence the rendition of the potential energy curves shown in Fig. 8.

For indole derivatives in condensed phases the transition from non-polar to polar solvent systems is accompanied by a blurring of vibrational structure and a progressive red spectral shift. This is commonly interpreted as result from an inversion of the ordering of the two lowest excited states, with emission occurring from only the ^1L_a state in polar solution. In order to understand the behaviour of the molecule upon complexation we can utilize the expected interaction with the zero-order states to obtain some understanding of the changes which will occur to the diabatic surfaces of Fig. 8. Previous work [27, 45] has shown that the ^1L_b state should be only slightly affected by complexation, while the ^1L_a state will be stabilized more dramatically due to its much larger dipole moment and, hence, interaction with polar solvent species. Complexation is expected to occur in the 2,3-DMI ground state as well [6], resulting in a modest stabilization and extension of the N–H bond due to hydrogen bonding: a similar situation is likely to hold for zero-order ^1L_b states. Evidently the ^1L_a state is stabilized to such an extent that the ^1L_b state lies to higher energy for all values of r_{NH}. Vertical absorption transitions will project the ground state geometry of the complex onto the ^1L_a excited state surface. Due to the displacement of the ^1L_a and ground state potential surfaces this results in the preparation of states with considerable vibrational energy content, as evidenced by the broadened excitation and emission spectra which were observed. The subsequent dynamics which these complexes undergo are driven by this excess vibrational energy and are analogous to those proposed for indoles in fluid solution.

For most of the complexes we have studied, we have described evidence of enhanced intensity in the excitation spectra which occur near the expected location of the ^1L_b origin transitions. Fluorescence spectra and decays obtained following excitation of these features are identical to those obtained after excitation of the continuum to higher or lower energies. This behaviour is reminiscent of that observed upon excitation of the S_2 states of large polycyclic aromatic molecules such as naphthalene. Here, the "intermediate" level coupling between the S_1 and S_2 states leads to broadened S_2 origins which display identical decay dynamics to the S_1 levels which lie nearby. We are thus led to propose that the spectral features which we observe in the excitation spectra of the hydrogen bonded 2,3-DMI clusters reflect the presence of the ^1L_b state origin, which manifests itself as a cluster of molecular eigenstates with enhanced transition probability due to the expected similarity of the ground and zero order ^1L_b state geometries. In the zero-order state description, this corresponds to a very rapid internal conversion between the ^1L_b and ^1L_a states, so that the subsequent dynamics which are observable on our experimental time scale are characteristic of the ^1L_a state.

Our work on the clusters of 2,3-DMI shows that the vibrational energy of the nascent excited state is redistributed not only within the chromophore itself, but is also transmitted to its cluster partner(s). The lifetime of the resulting complex depends on the degree to which vibrational energy can be imparted to the hydrogen bonding partner(s) and we have observed that as the degree of complexation increases, in all but one case (NH_3) so does the lifetime. In addition, the emission spectra invariably shift to the red, implying that more vibrational energy has been removed from the indole nucleus. Thus, the role of condensed phase solvent relaxation in Vavilov's Law has a nice parallel in these jet-cooled experiments. This description of the excited state dynamics provide a convenient bridge between the jet-cooled cluster and polar solution limits.

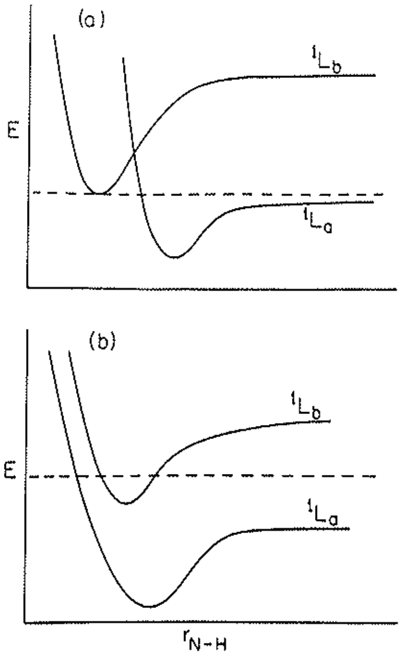

Fig. 8. Schematic representations of sections through the potential surfaces used in discussing the excited states of 2,3-dialkylindoles. (a) The zero-order (diabetic) ^1L_a and ^1L_b excited states of the bare molecule. (b) The zero-order ^1L_a and ^1L_b excited states of the polar complexes. Note we only consider the dependence of the potential on the N–H coordinate.

The close parallel between these results and those from the fluorescence of indoles in polar solution leads us to suggest that we have uncovered a very important part of the connection between jet-cooled and condensed phase indole photophysics. We are currently attempting to link our present results more firmly to those obtained for 3-methylindole$(NH_3)_1$ which we reported previously [27] have been confirmed during the course of this work and more experiments are underway which should help to elucidate the excited state dynamics of this molecule and its connection to the present results.

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Discussion

In response to a question of whether the intramolecular vibrational redistribution (IVR) rate was mode-specific, Professor Wallace responded that he did not like to use the terminology of IVR "rates". The problem is really one of the time evolution of the superposition state initially created by the laser excitation; such a state is, in general, not an eigenstate of the molecular system. In large molecules, the distinction between a rate-equation picture and a coherent superposition model will probably disappear.

A question was also raised of whether the width of O–H and X–H stretching-mode absorption bands in hydrogen-bonded complexes could be attributed to intramolecular vibrational energy transfer from the stretching mode to the weak hydrogen bond, followed by a vibrational predissociation of the complex. Professor Wallace's reply was that recent high-resolution i.r. studies of hydrogen-bonded van der Waals' complexes in cooled supersonic molecular beams have revealed a well-resolved rotation–vibration structure. These features have a residual linewidth which may be due to vibrational predissociation , but these widths are much less than that typical of the earlier low-resolution studies, which suffered from inadequate spectroscopic resolution and unresolved line congestion.

Spectroscopy of surfaces and interfaces—some future prospects

NORMAN SHEPPARD
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

Abstract—The study of surfaces and of surface-adsorbed species at the level of atomic or molecular structure is of great fundamental and technological interest. The spectroscopic methods of studying interfaces are fruitfully complementary to the diffraction and microscopic methods in that they can provide structural and kinetic information about disordered and mobile systems, in addition to ordered and immobile ones. A number of recent developments in experimental techniques hold out much scope for improved spectroscopic studies of interfaces. These include, for example, the use of synchrotron radiation, the use of lasers in the ultraviolet, visible and infrared regions, and the use of high intensity neutron spallation sources. Major progress can be envisaged both in the studies of the surfaces of technologically-important finely-divided materials and of the flat single-crystal surfaces that provide fundamental insights into surface phenonmena. Many of the advances of the past two decades have been in the study of adsorption on solid surfaces in the presence of the very low pressures of gases that are usually required for the use of electrons, ions or atoms as probes. Photons, although intrinsically less surface-sensitive than the latter probes, can still be very effective in selectively studying surface species different from those constituting the bulk phases. They also have the advantage that they can frequently be chosen as probes that are transparent to bulk phases such as high-pressure gases, liquids or solids. It is envisaged that the next few decades will see increasingly effective studies of interfaces between condensed phases, as in colloidal systems, catalysts under high pressure of gas or at solid/liquid interfaces, electrode systems and biological membranes, using the photon spectroscopies allied to laser techniques. Further advances in the understanding of fundamental surface phenomena are likely to come about by the joint applications of spectroscopic with microscopic or diffraction techniques, or by the use of hybrid techniques such as extended X-ray absorption fine structure (EXAFS).

INTRODUCTION

I HAVE been asked to look ahead in this paper towards the future of spectroscopic methods as applied to the study of surface phenomena. It is one of the enduring richnesses of science that over a period reckoned in decades quite new experimental techniques can be invented, which themselves can have quite unpredictable applications to opening-up or re-activating many areas of research. The spectroscopic phenomenon of nuclear magnetic resonance (NMR) is a very good example of this. It was investigated initially some four decades ago as a means of evaluating magnetogyric ratios of nuclei. It was soon found that the precise values measured for the resonances depended also on the electronic environment of the nucleus in question. The term "chemical shift" was invented and was in effect a "physicist's swear-word". In fact this unwanted effect has, in the intervening years, become the basis of the most efficient single physical method for determining the structures of large organic molecules, including the very large biomolecules such as enzymes, in solution. During the past decade the technique has found many applications also in inorganic and solid state chemistry, and it has developed into a major diagnostic tool for medical research. None of these major applications could have been in the minds of the physicists who developed the new technique. All that can profitably be attempted in this article is, of course, to extrapolate with imagination from the already-existing surface-spectroscopic techniques, but the above example leads us to expect that the real advances the next few decades are likely to prove to be much more extensive and exciting than we can imagine.

THE ROLE OF THE SPECTROSCOPIES

If for no other reason than the great technological importance of surface phenomena, e.g. to catalysis, corrosion, adhesion, semiconductor technology in general and to the

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study of biological membranes, we can be very sure that much effort will be devoted in the future to extending the present range of the surface spectroscopies. As in the past two decades, increasingly we shall learn to understand surface properties at the atomic and molecular level. Other families of techniques, particularly the diffraction methods and microscopic methods, will be employed alongside the spectroscopies in enabling such advances to take place.

The diffraction methods, which involve the coherent and elastic interaction of photons or other probes with matter, are at their most powerful when investigating ordered three-dimensional lattices of atoms or molecules in the crystalline state, or ordered surfaces with regular arrangements of adsorbed molecules. It was indeed low energy electron diffraction (LEED) at surfaces that ushered in the era of what is now termed "Surface Science". Electrons rather than X-ray photons of similar wavelength were used because of their stronger interaction with matter and hence higher surface sensitivity. In effect the diffraction patterns give averaged information about relatively large arrays of atomic or molecular species.

The microscopic methods which are capable of atomic resolution, such as high-voltage electron microscopy, field-ion microscopy and the relatively new and potentially exciting scanning tunnelling microscopy, can study matter in more detail. In the surface context they can be used to observe irregularities on surfaces, such as "defects" and "steps", directly and to see how adsorbed molecules interact with these in comparison with surface sites associated with flat atomic "terraces". The main requirement of these super-microscopic techniques is that the atomic complex under observation should stay the same for a sufficient period of time.

The symmetry phenomena associated with regular arrays of atoms are also important in obtaining the maximum information from the spectroscopy of such systems. However, the spectroscopic methods can give very much information in the absence of periodic structures and/or in the presence of mobility, and in this sense are complementary to the diffraction and microscopic methods. The characteristic energy quanta normally studied in spectroscopic experiments—corresponding to the inelastic interaction of photon, electron or other probes with the sample under investigation—can provide information in effect about single atoms or molecules, or small intermolecular or molecule/surface complexes. They also show useful secondary effects relating to the environments of such species. The spectroscopic methods therefore find strong applicability to disordered solid or surface arrays and to mobile liquid, solution or gaseous systems.

HYBRID TECHNIQUES INVOLVING SPECTROSCOPY WITH DIFFRACTION OR MICROSCOPY METHODS

Many of the developments in the future are likely to involve hybrid techniques in which spectroscopic methods are allied to diffraction or microscopic measurements. Thus, at a straightforward level, frequently an electron microscope can be used to focus on a particular interesting part of a target and then Auger electron or photoelectron spectroscopy can be used to determine its atomic composition. Similar very worthwhile experiments are now being carried out on industrially-important inhomogeneous samples by i.r. or Raman spectroscopy by means of which inclusions or impurities of optical microscopic size, in samples such as plastics, minerals or solid catalysts, can be identified in terms of molecular composition.

A particularly interesting hybrid technique of a more fundamental nature, in the sense that the one experiment gives simultaneous spectroscopic and diffraction information, is extended X-ray absorption fine structure (EXAFS) [1]. In this, the absorption of an X-ray photon leads to the ejection of a photoelectron which in turn is diffracted by neighbouring atomic centres. This leads to interference between newly-generated and returning electrons. As the X-rays are scanned in frequency above the initial absorption edge, the energies and hence wavelengths of the photoelectrons vary systematically leading to changing diffraction effects that are recorded as frequency-dependent intensity fluctuations of the absorption band. This structure can be analysed by Fourier transformation to yield information about the distances and scattering strengths of surrounding atoms. The method is applicable to ordered or disordered solids, as the principal diffraction phenomena involve the nearest-neighbour atoms, and has been used to study the bulk and surface structures of metal–catalyst particles. Where a sample has different elements, as with a metal sulphide for example, EXAFS spectra can be obtained at the positions of both the metal and sulphur absorptions to yield complementary information of a self-consistent nature.

THE USE OF SYNCHROTRON RADIATION

The already widely used EXAFS technique provides one example of the increasingly fruitful usage of synchrotron radiation for surface studies [2]. Sources of this type provide intense and continuously-tunable radiation over the vacuum–u.v. and X-ray regions and can also give enhanced intensity in parts of the i.r. region. Synchrotron radiation sources with different and calculable intensity/wavelength characteristics are now available in a number of countries. They require the circulation of electron-beams in magnetic storage rings at relativistic velocities, the range of frequencies/wavelengths covered being dependent on the velocity of the electrons, the diameter of the storage ring and local configurations of "wiggler" magnets. Electrons are circulated in bunches so that synchrotron radiation has also a rapidly pulsed nature that can be used for studies of dynamic molecular or surface processes. Many other applications of synchrotron radiation to absorption and photoelectron spectroscopies of surface species can be envisaged.

SPECTROSCOPIC STUDIES OF FINELY-DIVIDED MATERIALS

(i) *General*

For reasons of sensitivity, the initial spectroscopic applications to the study of surfaces were to finely-divided systems so as to optimize the ratio of signals from the surfaces relative to those from the bulk. Such materials are of widespread technological importance as catalysts, fillers in plastics and pigments in paints, etc. For several decades i.r. spectroscopy led this field, following pioneering work on physical adsorption by TERENIN of the U.S.S.R. in the 1940's [3] and on chemisorption by EISCHENS of the U.S.A. in the 1950's [4]. Even today, this is much the most widely applied spectroscopic method for studying phenomena relevant to the chemically very important area of heterogeneous catalysis by finely-divided solids. However, these spectroscopic results themselves showed that the molecular phenomena at surfaces were much more complex than expected. For example, if a spectrum was obtained to find out what, amongst several possibilities, was the surface species formed by the interaction of a reagent with the surface, it was typically found that not one but three or four different species were present. These could be formed, for example, through interactions with different surface sites available on a polycrystalline catalyst. This type of complexity can nevertheless be unravelled with the help of high sensitivity experiments on simplified systems involving one type of crystal face at a time [5].

(ii) *Infrared spectroscopy*

The i.r. method has proved to be highly applicable to many types of particulate materials such as supported-metal catalysts, oxides, etc. These are normally investigated by transmission methods, with the particles pressed into coherent, but still porous, discs that can be placed in the radiation beam. This type of sample is not only geometrically convenient, but the disc-pressing procedure reduces radiation scattering from individual particles [5]. However, although the relatively small pores in the disc allow contact between a gaseous reagent and the surface, when kinetic measurement are made to determine which of the surface species is catalytically active it often turns out that, for the faster reactions, it is the diffusion of reactants/products into or out of the pores which determines the reaction rate rather than the reactions at the surface. To improve on this situation it is necessary to use loosely-powdered catalysts, such as are employed in practice in industry or the laboratory. During the past two decades there have fortunately been major advances in the sensitivity of i.r. spectrometers due to the use of Fourier transform techniques in conjunction with interferometry. This has enabled a number of spectroscopic sampling techniques to be used which were previously known in principle but considered to be too difficult to use in practice [6]. One of these, diffuse-reflection i.r. spectroscopy, can be used with powdered catalysts in *in situ* reactions at appropriate temperatures. This will be an important advance in the future use of spectroscopic techniques for the study of catalytic reaction mechanisms. These can only be directly evaluated by kinetic methods.

(iii) *Raman spectroscopy*

Raman spectroscopy is well known to be a highly complementary vibration spectroscopic technique to i.r. spectroscopy, as the vibration frequencies which give the strongest Raman bands tend to give the weakest i.r. absorptions and vice versa [7]. Raman spectroscopy has therefore found considerable application to the study of finely-divided oxide catalysts themselves, or of the species adsorbed on them. A recently developed combination of near-i.r. laser excitation of Raman spectra, together with Fourier transform methods [8], has greatly reduced the possibility that the intrinsically weak Raman spectrum will be swamped by much stronger fluorescence emission. The latter can occur from even small amounts of impurities that have absorption bands at the laser wavelength. Fourier transform Raman spectroscopy should lead to a much wider range of studies of surface phenomena, particularly of technical and visibly coloured samples.

Unfortunately, most metal catalysts are matt-black or highly coloured, leading to heating by radiation absorption and the decomposition of surface species as well as much reduced scattering. Where photochemical decomposition is not a problem, it is possible that some of these problems will be overcome by use of carefully planned pulse-laser excitation of Raman spectra, allied to sample rotation techniques.

(iv) *Surface enhanced Raman spectroscopy (SERS)* [9]

This technique has been highly successful in obtaining strong Raman spectra of adsorbed species on the surfaces of a limited number of metals such as silver, copper and gold. The mechanism of this effect is still not fully understood despite much research, but it seems to require a combination of metal particles of appropriate size to give electronic resonances in the laser beam, together with electronic interaction—often of a charge-transfer type—which leads to additional resonance enhancement of the Raman signal. Such overall enhancement can be up to a factor of 10^6 relative to normal Raman scattering. The optical properties of the metal determines whether the particle resonances occur in the visible region, and this is why the technique is applicable to only a few metals. There are hopes that u.v. laser excitation of Raman spectra, obtained through frequency multiplication of intense laser beams in the visible region, may enable SERS to be excited with other metals, such as the catalytically more important transition metals.

A very successful application of SERS has been to obtaining spectra from species adsorbed on electrolytically-roughened electrodes of the metals listed above. Raman spectroscopy has the particular advantage that water has a very weak spectrum so that aqueous work is straightforward. In forthcoming years spectroscopic methods are likely to contribute more and more to the study of electrode reactions, using Raman spectroscopy, i.r. reflection spectroscopy with thin electrolyte layers to minimize solvent absorption and by attenuated internal reflection (ATR) in the i.r. region with partially transparent metal electrodes deposited on i.r. transmitting semiconductors.

(v) *Inelastic electron tunnelling spectroscopy (IETS)* [10]

This is another form of vibrational spectroscopy that can be used to obtain spectra on finely-divided oxides (principally alumina or magnesia) or on metal particles supported on such oxides. Its sensitivity is comparable to those of i.r. and Raman spectroscopy, and absorption onto the porous oxide—from the gaseous, solution or pure liquid state—can be carried out at room or other temperatures. However, a requirement that the sample be held at liquid-helium temperatures during measurement of a spectrum does limit the versatility of this method for studying catalytic processes.

(vi) *Inelastic neutron scattering (INS)* [11]

This is yet another form of vibrational spectroscopy that has been used to study adsorption on finely-divided materials. Because neutrons readily penetrate matter, neutron spectroscopy is far from being a surface-sensitive technique *per se*. However, the hydrogen, ^{1}H, nucleus has a particularly strong cross-section for incoherent neutron scattering, whereas the ^{1}D nucleus is a much weaker scatterer. Hence, the spectrum of hydrogen-containing adsorbates on the surfaces of non-hydrogen containing materials can be successfully observed and identified as such. The vibrational features observed are not only those modes in which hydrogen atoms vibrate against heavy atoms, but also those in which heavy-atoms move but "carry" hydrogen atoms with them. An advantage of INS is that, unlike in i.r. and Raman spectroscopy, the relative intensities of features can be readily calculated from the amplitudes of atomic motions. Until recently, the relatively low neutron fluxes available led to the requirement of large samples and to the limited resolution of the spectra. Also, some neutron sources could cover only limited wavenumber ranges, at the lower end of the region of vibrational fundamentals. The recent construction of an intense spallation-neutron source at the Rutherford Laboratory, U.K., with others being designed elsewhere, gives higher intensities proportional to the increased neutron flux and hence potentially higher resolution spectra over the whole useful vibrational range. Because of the relatively low incoherent neutron-scattering of non-hydrogenic nuclei, INS enables the study of adsorbed species on oxides, or oxide-supported metals, over wavenumber ranges where intense i.r. absorption by the lattice modes of the oxide component much reduce transmission in the lower wavenumber regions. INS shares this facility with Raman spectroscopy and provided that an atom attached to the surface has hydrogen atoms attached, it should make easier the identification of the important low frequencies that are related directly to the strength of bonding of the adsorbate to the surface.

(vii) *General comments on vibrational spectra in surface studies* [12]

From the above account it can be seen that vibrational spectroscopy in its various forms has played a major role in investigating surface adsorption on finely-divided materials. In additional to the wide range of experimental techniques that have been developed for the vibrational spectroscopies since the 1940s, there is the additional theoretical advantage that characteristic group vibration frequencies/wavenumbers, derived from very extensive data bases from compounds of known structures, are very helpful in assigining spectra to possible, and even unexpected, chemical structures of surface-bonded species.

(viii) *Ultraviolet/visible spectroscopy*

Although much less extensively used than i.r. spectroscopy, u.v.–vis electronic spectra have been used for example to detect conjugated adsorbed species such as aromatic polynuclear carbocations formed on acidic oxide surfaces, or carbanions formed from the adsorption of CO to give species of structure $(CO)_n^{x-}$, using diffuse-reflectance techniques on powdered materials [13].

(ix) *Nuclear magnetic resonance spectroscopy* [14]

NMR is, as mentioned in the Introduction, a major tool in general molecular structure determinations, using the group-characteristic chemical shifts from a given type of nucleus (^{1}H, ^{13}C, ^{31}P, etc.) in different chemical environments. There is, however, a general problem of NMR sensitivity, which is much less than for many other spectroscopies, leading to a requirement for surface work of high area materials and substantial sample sizes of a few grams.

Such studies of physical adsorption are not difficult, although the more limited mobility of species adsorbed on a surface to the case in solution leads in general to lower resolution. Much more interesting would be the use of NMR to determine the structures of chemisorbed species. Here, however, there is the additional complication that "anchored" chemisorbed species are not free to reorient in the magnetic field. This leads to non-cancellation of relatively large direct-dipolar interactions between adjacent magnetic nuclei. In solution, molecular "tumbling" leads to such effects, which vary in magnitude and sign depending on the orientation of the internuclear vector with respect to the direction of the externally applied strong magnetic field, averaging precisely to zero. Sophisticated techniques, developed mostly during the last decade, enable high resolution spectra of solids to be obtained when the concentration of adjacent magnetic nuclei of a particular type is not too high and other types of magnetic nuclei can be stimulated to reorient rapidly by strong irradiation at the appropriate resonance frequency. Using such techniques some very useful spectra have recently been obtained from hydrogen itself or hydrocarbon species (using ^{13}C resonances) adsorbed on oxide-supported metal catalysts [15]. We can confidently look for future important developments in this area, involving the use of high-field superconducting magnets and developments in discriminating pulse-sequences.

(x) *Electron spin resonance (ESR)* [16]

This technique of high sensitivity finds particular and important application to the detection and kinetic evaluation of free radical species involved in surface reactions.

SPECTROSCOPIC STUDIES OF SINGLE CRYSTAL SURFACES

The complexities present when spectroscopic studies are made of adsorption on finely-divided solids are such that by the end of the 1960s it was seen to be highly desirable to be able to simplify matters by studying adsorption on one type of crystal surface at a time. However, this requires spectra to be obtained literally from one monolayer or less of the adsorbed species. At that time this seemed to be well beyond the capability of the then available i.r. techniques except in the case of adsorbed species, such as CO or carboxylate ions on metals, which have quite exceptionally high i.r. extinction coefficients [17]. It seemed necessary to use more surface-sensitive probes and techniques and this led, over the next two decades, to the development of a much wider range of new spectroscopies—most of them specifically designed for surface work.

The more surface-sensitive probes now include electrons, atoms and ions, used by themselves or in conjunction with photons. The new spectroscopies to which these have given rise are now much more numerous than the photon spectroscopies which until then had (with the additional example of mass spectroscopy) completely dominated the chemical spectroscopies used for the determination of molecular structures. For example, a recent survey of the Commission of Molecular Structure and Spectroscopy of the International Union of Pure and Applied Chemistry (IUPAC) listed no less than 33 types of spectroscopies involving the use of electrons, and nearly 140 abbreviations and acronyms that have been used for variants of these [18]! The most widely used such spectroscopies include Auger spectroscopy, much used for detecting surface impurities in the form of lighter elements on the surfaces of metals [19]; photoelectron spectroscopy (photons in; electrons out) [20] in the X-ray region (XPES) which probes the core orbitals of adsorbed species and their sensitivity to oxidation state or binding to the surface, e.g. distinction between O^{2-}, O^-, O_2^- and O_2^{2-} oxygen species on metals [21]; photoelectron spectroscopy in the u.v. region (UPES) which probes the valence orbitals or adsorbates as modified by surface interactions [21]; and electron energy loss spectroscopy (EELS) used for studying electronic or vibrational spectra. The latter technique involves the interaction of monoenergetic beams of electrons with a surface and the measurement of the discrete energy losses which correspond to quantized vibrational or electronic excitations of surface atoms or adsorbed species. The vibrational form of electron energy loss spectroscopy (VEELS) is much the most extensively used [22]. The electron as probe has provided the necessary sensitivity to measure the vibration frequencies of monolayers, or less, of chemisorbed species on flat surfaces. The stimulation provided by the many successful applications of VEELS motivated the i.r. spectroscopists to attempt to upgrade their experimental techniques. Recently, through use of Fourier transform spectrometers with improved detectors, i.r. sensitivity improvements now enable spectra of monolayers of a wide range of adsorbed species, such as hydrocarbons, to be determined by reflection–adsorption infrared spectroscopy (RAIRS) [23].

Collectively these new surface-sensitive techniques, allied with their diffraction counterparts, have transformed our understanding of surfaces and adsorbed monolayers on metals and, to a less extent, on semiconductor surfaces. Both of these types of material are often available in good sized single crystals and can be cut to expose different particular crystal planes.

These advantages are less generally available for insulators, such as oxides. With these another difficulty arises because of the build up of electrical charges when particles, such as electrons or ions, are used as entering or leaving probes. The charges present can affect the values of the observed spectroscopic transitions. It is to be hoped that developments in crystal-growing techniques and methods of building up thin layers of insulators on conducting substrates, may overcome some of these difficulties and lead in the future to a wide expansion of surface work with insulators. Epitaxial growth of oxide layers on metal crystals is one way of tackling the insulation problem. However, many of the transition metal oxides that are valuable catalysts operate under non-stoichiometric conditions, i.e. with slight deficiencies of oxygen or metal with respect to the ideal composition. Such non-stoichiometric materials become semiconducting and then the dissipation of charge may no longer cause a problem. Also a small amount of semiconductity can lead to higher quasi-metallic surface reflectances of such materials which may "screen-out" absorptions from the oxide itself in favour of those from adsorbed monolayers.

For a period, the greater sensitivity of electrons, atomic probes etc. to the surface layers of solids led to the view that photons could be downgraded as surface probes. Even when reflected from a surface, photons do penetrate much greater thicknesses of the substrate of the order of a fraction of a wavelength. However if, as is often the case with metals over wide wavelength ranges, little energy is lost by reflection, then absorptions by superimposed adsorbed monolayers can imprint themselves on the reflected beam as in RAIRS [23]. Given this type of circumstance the photons have major advantages. In spectroscopic terms the obvious one is resolution, which can be of the order of $1\ cm^{-1}$ or less for RAIRS, compared with *ca* $30\ cm^{-1}$ or less for VEELS. Also, the very fact that the newer probes interact strongly with matter leads to requirements that all experiments need to be carried out in ultrahigh to high vacuum, partly to avoid scattering in the gas phase. However, for example, most catalytic processes occur with substantial pressures of gases over the surface. Except in regions of outstanding gas-phase absorption (which even so can be minimized by choosing short gas-phase pathlengths) the photons can penetrate the gas phase without difficulty. It is clear, for example, that the way forward for kinetic studies of simplified catalytic reactions is to return to photons as the probes, with single crystal studies using RAIRS providing the possibility of studying the rates and mechanisms of gas-phase catalytic reactions on surface planes with chosen sites. This is likely to be a major spectroscopic theme of surface research in the next decade.

SOME NEW HORIZONS; APPLICATIONS OF LASERS

Renewed interest in photons as probes of surface films raises a number of new important possibilities, such as the study of monolayers at solid/liquid or liquid/liquid surfaces, including biological membranes. Also in the three-dimensional, non-surface spectroscopies, much progress has recently been made using intense pulsed lasers, often probing samples with more than one laser at the same time for the excitation of multiple quantum processes. Apart from the straightforward use of lasers as Raman spectroscopic sources, little use has so far been made of these powerful probes in surface studies.

For example, much effort has been made to obtain Raman spectra from single monolayers [24] because of the important complementary relationship with i.r. spectra. However, in the absence of resonance-Raman effects or intensity-enhancement on roughened surfaces of a few metals (SERS), there is still a general lack of sensitivity for obtaining such spectra other than in exceptionally favourable cases. A two-laser stimulated technique of high sensitivity and excellent fluorescence rejection, that seems yet to be exploited, in an attempt to improve on this situation, is the inverse Raman effect [25].

Frequency-doubling of very intense laser pulses in the visible region can be brought about by interaction with suitable non-centrosymmetric crystals. The asymmetry associated with a surface between two homogeneous statically or dynamically centrosymmetric media, such as between two liquids or a liquid and a centrosymmetric solid, can also give rise to frequency-doubled radiation. In these cases *only* the surface region generates a signal. This technique is known as Second Harmonic Generation. A related second-order effect is the generation of sum or difference frequencies from two intense laser beams of different frequencies brought together at the surface. SHEN *et al.* [26] have recently shown that when a fixed-frequency visible laser and a tunable i.r. laser are focused together on an interface, this can give rise to a beam of frequency ($\nu_{vis} + \nu_{i.r.}$) in the visible region, where detectors are efficient. When the i.r. beam scans through an absorption band at the interface there is a resonance-enhanced emission of this type. This technique is termed Sum Frequency Generation. All that is required is that, between them, the two media on either side of the interface should be transparent to the exciting laser beams in order to enable them to interact at the interface. The very remarkable surface specificity of this second-order technique is shown by the fact that long alkyl chain acids at such an interface seem only to give sum-frequencies involving end group methyl absorptions in the νCH bond-stretching region. Even the CH_2 groups of the long alkyl chain are not detected, presumably because the $-CH_2-CH_2-$ units have static or dynamic centrosymmetry [26]. It has been shown that in addition, the use of different polarization directions for the incident laser beams (between the two of them there are four possibilities relative to the surface) gives intensity information which provides information about the direction of orientation of the alkyl chains with respect to the surface. Vibrational modes which are both i.r. and Raman active can be detected by this technique [26].

A requirement for the wide application of the latter technique is the existence of intense i.r. lasers with sufficiently wide wavenumber tunability. These could also have important applications for RAIRS work. At present, most of those available only cover several hundred cm^{-1} at the high frequency end of the i.r. region [27]. The use of tunable dye lasers in the visible region in conjunction with suitable parametric oscillators, or with frequency reduction using the electronic Raman effect, may be expected to lead to important progress in this direction in the next decade.

COULD A VIBRATIONAL SPECTRUM BE OBTAINED FROM A SINGLE MOLECULE?

Many developments are now taking place in scanning tunnelling microscopy. It has already been shown that, when a probe is positioned over a particular part of a surface, changes of voltage will scan electronic energy levels of the surface atoms. Might it in future be possible to position the probe over a particular adsorbed species and scan its vibrational inelastic electron tunnelling (IETS) spectrum? Such an advance might enable us to unequivocally identify by spectroscopy a single adsorbed molecular species on a particular site!

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PART II

REPRINTS OF "CLASSIC" SPECTROCHIMICA ACTA ARTICLES

CLASSIC PAPERS FROM SPECTROCHIMICA ACTA

IN REVIEWING the back issues of this journal in preparation for the 50th Anniversary Symposium, the editors came across a number of articles which clearly have been of great importance in opening new research areas in spectroscopy and spectrochemical analysis. Fourteen of these articles are reprinted here. Together with the texts of the invited lectures at the Symposium, which appear as the first part of this volume, these reprints provide a unique perspective over 50 years worth of developments in this field of science, and indicate possible new directions for evolution of the field.

Both atomic analytical spectroscopy and molecular spectroscopy are represented in these articles. The first area includes papers by the founders of the field, such as MEGGERS, KAISER, L'VOV and WALSH. Both emission and absorption techniques are described. The molecular papers include a very early description of matrix isolation spectroscopy by the late GEORGE PIMENTEL (see p. XIX). NORMAN SHEPPARD's 1959 paper on infrared spectra of adsorbed molecules, taken together with his contribution to the Symposium on p. 149, represents 30 years of development in the spectroscopy of surfaces and interfaces. RAO's 1962 paper was listed by *Citation Index* as one of the most frequently cited papers in the spectroscopic literature. The paper by SCHACHTSCHNEIDER and SNYDER is also often cited as the first use of computer methods in normal coordinate analysis; we have included their description of the method, but have had to leave out over 50 pages of very detailed specific results on the normal paraffin hydrocarbons.

We are confident that, in the coming 50 years, both Parts A and B of *Spectrochimica Acta* (as well as the new Review and Electronic Sections) will continue to receive and to publish papers of lasting significance, comparable with those reprinted here.

Principals and Principles of Spectrochemical Analysis

By

William F. Meggers.

National Bureau of Standards (Washington).

The history of science abounds with examples of men who observe natural phenomena but are unable to explain or apply them until a " genius " discovers a generalization, principle or law. Once clearly stated such natural laws seem more or less obvious, and the marvel is that they were not recognized earlier. For example, after thousands of years of accidents, wars, and bloodletting is it not strange that *homo sapiens* knew nothing about the circulation of his blood until *William Harvey* discovered it in 1614? Why did the laws of motion and of universal gravitation have to wait for *Newton* to formulate them during the latter half of the seventeenth century? The ancient Greeks made the first observations on electricity and magnetism but it required 2½ millenniums to produce *Faraday*, *Henry*, *Maxwell*, and *Hertz* who perfected the electromagnetic theory. After more than 2000 years of astronomical observation and speculation it remained for *Copernicus* and *Kepler* to announce the true laws of planetary motion.

Since Nature is an open book, for anyone to read who has the wit to understand, it must be concluded that the slowness of scientific progress is at least partly, if not wholly, explained by human stupidity. We owe all progress to the occasional individuals who possess sufficient perseverance, perspicacity, or talents to discover new phenomena or formulate new laws of nature. Only those who have deliberately tried to find such laws know how difficult it is.

What have these introductory remarks to do with spectrochemical analysis? According to the Bible, spectroscopy began when the flood ended, but thousands of years elapsed before man made any practical use of a spectrum. Now everyone knows that, in principle, any chemical element can be detected by a characteristic spectral line, and its concentration determined from the intensity of that line. The actual procedure would be simple indeed if all atomic spectra could be excited in the same light source, if each element emitted only one spectrum, and if all spectral lines had nearly the same properties. However, a century or more of experiments in spectroscopy has demonstrated that no single light source can be designed or operated to excite the spectra of all elements, the same

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elements emit totally unlike spectra under different conditions, and the strongest lines of the different elements or spectra are scattered throughout a wide range of spectrum. In spite of these departures from simple ideal conditions spectrochemical analysis has developed into a practical method of vast importance to science and industry. To find the explanation of this success we must seek out the principal contributors to spectroscopy and examine the principles or laws they enunciated. It will be profitable to do this because spectrochemical analysis is still encumbered with much empiricism and a few misconceptions, and future progress should be based on the tried and true principles of physics.

In 1672 *Newton* reported the first scientific observations on the nature of spectral colors but nearly two centuries passed before the first principle of spectrum analysis was clearly stated and demonstrated by *Kirchhoff* and *Bunsen*. In the meantime many scientific giants (*Herschel*, *Young*, *Wollaston*, *Fraunhofer*, *Talbot*, *Wheatstone*, *Foucault*, *Angström*, *Alter*, *Swan*) experimented with spectra but none of them clearly recognized that emission and absorption spectra are characteristic of the atoms and molecules that produce them. The details and proofs of this statement are omitted here because they have been fully presented by *Kirchhoff*[1] and by *Kayser*[2]. Imperfect spectroscopes, impure light sources, inaccurate measurements and incorrect notions about colored flames retarded the discovery that light emitted by a luminous vapor gives exact information as to its chemical and physical nature.

One hundred and forty-five years passed before *Newton*'s simple arrangement of illuminated opening-prism-lens-screen was improved by *Fraunhofer* who introduced the narrow slit which increased the resolving power and gave rise to the expression " spectral line ".

Twenty-two years later the collimator made its first appearance in a goniometer by *Babinet*. The principles of the present-day spectrometer or prism spectrograph have thus been known and applied for a century and the only important addition to spectrographic apparatus was the invention and production of plane diffraction gratings by *Fraunhofer* in 1822, and of concave gratings by *Rowland* in 1882. The principles of spectrographs now appear to be completely known.

Quite naturally alcohol flames were first employed for spectroscopic observation but with the disadvantage of adding the flame spectrum itself to those of the substances made luminous in the flame. The invention of the *Bunsen* burner in 1857 was a great boon to spectroscopists, but almost simultaneously the electric arc (discovered by *Davy* in 1802) was applied to the excitation of spectra.

Fraunhofer was the first to observe (1817) that highvoltage electrical discharges between metal electrodes produced a discontinuous spectrum. *Wheatstone* found (1835) that sparks, like flames, produce characteristic spectra of different metals. *Ångström* discovered (1855) that spark spectra consist partly of the spectrum of the electrodes and partly of the spectrum of the surrounding gas. When the same yellow lines were always seen in the spectra of different salts this color was ascribed to the water of crystallization until *Swan* in 1857 showed that one-millionth of a grain of common salt was sufficient to produce the " D " lines of sodium with observable intensity. The three chief types of light sources, flames, arcs, and sparks, used by spectroscopists more than 100 years ago are still in common use today: their fundamental principles have never changed but our feeble intellects are still groping to discern and understand them notwithstanding the fact that step-up transformers compared with influence machines, mica condensers compared with Leyden jars, direct-current generators compared with voltaic piles, illustrate important improvements in electrical apparatus applied in the production of spectroscopic light sources.

Practically all the early measurements were made visually with simple glass-prism spectrometers, and spectral lines were distinguished by position numbers on arbitrary scales. *Kirchhoff* measured 463 lines in the spark spectra of 32 elements; his arbitrary numbers were useless to others until *Watts* in 1872 converted them to four-figure wavelengths. *Ångström* in 1868 employed diffraction grating spectroscopes and measured to 4 or 5 figures the wavelengths of 792 lines. This contribution deserves special mention because it provided the first standard wavelengths in spectroscopy and set a precedent for representing all spectral lines on a wavelength scale in angstrom units, thus permitting direct intercomparison and repetition of all subsequent measurements.

The *Ångström* system of standards was discarded about 20 years later when *Rowland* published 6-figure values, and the *Rowland* system after 20 years was in turn displaced by the present international standards which are believed to be correct within ±0.001 A. This high precision in wavelength measurements must be credited to the *Fabry-Perot* interferometer (1897) and to a new principle in wavelength comparisons discovered by *Fabry* and *Buisson* in 1905.

Following the introduction of a wavelength scale the next great advance was the application of photography which enormously extended the range of spectral observation in the ultraviolet, and more recently in the near infrared. Although the ultraviolet was first detected actinically by *Ritter* in 1803, spectroscopic observations were solely visual until about 1880 when, after 40 years of unsatisfactory attempts to exploit *Daguerre*'s process and the collodion wet plate, the gelatine dry plate was sufficiently perfected to yield in the hands of *Lockyer*, *Hartley*, and others, greatly improved data for arc and spark spectra of chemical elements. Between 1 A and 13,000 A the photographic plate is today unsurpassed for recording and measuring wavelengths, but since 1940 considerable progress has been made in improving the bolometer and especially in perfecting direct-reading photoelectric spectrometers.

In principle the human eye, the photographic emulsion, and the photoelectric tube are all highly selective and therefore require calibration when the relative intensities of spectral lines are to be determined. The only non-selective detectors of spectral energy are the devices which are heat engines in principle (like the bolometer invented by *Langley* in 1881) but their efficiency is too low for general use except in the infrared where nothing else will serve.

Most of the spectroscopic measurements now available have been made photographically since 1900 by *Kayser*, by *Exner* and *Haschek*, by *Eder* and *Valenta*, by *Gatterer* and *Junkes*, by the *National Bureau of Standards*, and by the *Massachusetts Institute of Technology*. These contributions represent different approximations to ideal data for spectrochemical identification but no new spectroscopic principles are revealed in them. Compared with *Kirchhoff* the present-day spectrographer has at his disposal more than a thousand times as many lines, measured a thousand times more accurately.

The impressive work of *Kirchhoff* and *Bunsen* founded the science of astrophysics, promptly led to the discovery of four new elements (Cs 1859, Rb 1860, Tl 1861, In 1863), and inspired many scientists to exploit a new method of chemical analysis. In 1874 Lockyer[3] clearly stated for the first time that " while the qualitative spectrum analysis depends upon the positions of the lines, the quantitative analysis depends not upon their position but upon their *length*, *brightness*, *thickness*, and *number* as compared with the number visible in the spectrum of pure vapor." He also pointed out that " the lines of any constituent of a mechanical mixture disappeared from the spectrum as its percentage was reduced," thus foreshadowing quantitative spectrochemical analysis.

In 1882 *Hartley* investigated the intensity and persistency of spectral lines as functions of concentration of the elements sparked in solutions, and thus developed a method of estimating composition. Similar studies with spark spectra of fused minerals and salts led *de Gramont* to select in 1907 the *raies ultimes* for 59 elements, and in 1922 he pointed out that they represented the first members of principal series in simple spectra for which such series were known. This appears to be the first attempt to find a connection between empirical spectrochemical analysis and the physical laws of spectra.

For a half century following *Lockyer* many methods of making quantitative chemical analyses from spectra were suggested but the only one that survived during this period involved the *Hartley* principle of comparing unknown spectra with external standards, that is, with spectra of similar samples having known composition and observed under the same conditions as the unknown. After reviewing the attempts at quantitative analysis up to 1910 *Kayser*[4] concluded " that quantitative spectroscopic analysis has shown itself as impractical ". In 1926 *Konen*[5] reviewed this activity since 1910 and stated: " I have no other alternative but to adhere to the opinion expressed by *Kayser* and me years ago, that a quantitative spectrochemical analysis in the sense of a theoretically well-founded science does not exist." It can now be proved that neither of these statements is any longer valid.

It is true that interest in spectrochemical analysis gradually declined after 1885 until *Löwe*[6] in 1924 referred to it as a "forgotten method." This period also marks remarkable developments in analytical chemistry, and although the general superiority of the spectrographic method for detecting trace elements was recognized, the importance of determining such minor constituents was not then appreciated. Consequently wet chemical analysis prospered and spectrochemical analysis languished. Of necessity spectrographic analysis continued to be applied in astrophysics because there is no other way to determine the chemical composition of celestial objects, excepting meteorites that fall to earth.

Quantitative spectrochemical analysis received a new impetus in 1926 when *Gerlach* showed how most of the difficulties with the *external standard* method could be avoided by employing *internal standards*. Since then " homologous pairs " of all kinds and in great numbers have been empirically selected for practically all types of samples and all types of sources. The simultaneous development of micro-densitometers and improvements in recording photometers brought the *internal standard* method to its present high perfection, especially since a suitable internal standard can always be introduced if the sample itself does not contain one.

During the past quarter century more than 2500 spectrochemical papers have been published.[7] Even a superficial glance at this literature gives an impression of a superfluity of " methods," an excessive multiplicity of light sources and operating conditions, and a purely empirical solution of most problems. It appears that the *applied spectroscopists* (excluding astrophysicists) have scarcely taken any notice of the great advances in knowledge concerning the origin and interpretation of atomic spectra which the *fundamental spectroscopists* brought forth in the period of decline of spectrochemical analysis, 1885 to 1925. Describing a proposed compendium of line pairs and operating conditions used in spectrographic analysis *Hodge*[8] states that these data are usually determined by trial and error by inexperienced workers. Under these circumstances a bewildering variety of methods, sources, lines, and conditions have been employed, and up to the present no serious efforts at scientific refinements or standardization have been made. The primary purpose of this article is to suggest that rapid progress in spectrochemical analysis should result from further consideration of the quantum theory of atomic spectra. The least that can happen is that some confusion will be removed, some misconceptions corrected, and the physical foundations of spectrochemical analysis strengthened. In some cases the fundamental data of spectroscopy (wavelengths, intensities, and atomic energies) are still unknown, incomplete, or unsatisfactory, but the quantum theory is essentially complete and should not be ignored in spectrochemical analysis. In this machine age the most intricate devices are operated by pushing a button, and complex processes are carried out according to cook-book instructions, but it is always true that neither machines nor processes can be intelligently operated or improved without some understanding of the fundamental principles.

Since the physical basis of spectrochemical analysis must be sought in the properties of atoms and in the mechanism of atomic radiation it will be appropriate to review rapidly the well-known principals and the well-established principles of fundamental spectroscopy. Ignoring the early and futile attempts to interpret spectral lines as analogous to fundamentals and harmonics in sound, *Hartley* in 1883 discovered the law of constant wavenumber differences, that is, the same separation is exhibited by certain pairs of lines when their positions are expressed in " wave numbers " ($1/\lambda_{vac}$) rather than in wavelengths (λ); the interpretation of this law came 30 years later. The first significant relationship among widely spaced spectral lines was discovered in 1885 by *Balmer* who fitted a simple formula to the hydrogen lines. A similar but more general formula was discovered in 1890 by *Rydberg* who applied it to series of lines in the relatively simple spectra of alkalis and alkaline earths, and notwithstanding the poor quality of spectral data at his disposal he discovered most of the important properties of spectral series. The important feature of these series formulas is that they accurately represent the wavenumbers of spectral lines as the difference of two quantities, the larger being a constant term called the series limit while the other varies from line to line and is known as the running term. From descriptions of the lines *Rydberg* distinguished three species of series, sharp, principal, and diffuse, superposed in the same spectrum and he recognized that the members of each series were double for alkalis and either single or triple for alkaline earths. To these findings of *Rydberg* the $S\ P\ D$ notation for spectral terms can be traced, and also the concept of even and odd multiplicities.

Attempts to find similar series in more complex spectra were long unsuccessful although constant wavenumber differences were found in many. In particular, in 1899, an obscure man, *Charles P. Snyder*, found a large number of atomic energy levels in complex spectra and submitted them to *Rowland* who admitted that he didn't know what they meant but consented to the publication of a sample.[9] An interpretation of *Snyder*'s results was delayed a quarter of a century.

The most important cue for the interpretation of atomic spectra was given in 1913 by *Bohr* who proposed two postulates, namely, that atomic stationary states exist, and that the radiation frequency multiplied by *Planck*'s constant is equal to the energy difference of two states. The empirically determined spectral terms were thereafter interpreted as quantized energy states characteristic of atoms or ions. In 1914 *Franck* and *Hertz* gave the first direct experimental proof that spectral light is emitted in quanta. Also, in 1914 *Fowler* found the first series in spark spectra but the running term containing *Rydberg's* constant required multiplication by 4. Then in 1919 *Kossel* and *Sommerfeld* enunciated the alternation law and the displacement law of spectra, which indicated that term multiplicities of atoms or ions are determined solely by the number of electrons while atomic charge shifts the spectrum, thus suggesting a direct connection between spectral lines and the electrons and protons in atoms.

The next important step was *Catalán*'s deliberate discovery in 1922 of " multiplets " involving term multiplicities of 5 and 6, thus paving the way for the quantum interpretation of all atomic spectra. Multiplets were promptly found in many complex spectra, and in

1923 *Sommerfeld* invented "inner quantum numbers" to distinguish the levels of polyfold spectral terms. Simultaneously *Landé*, with extraordinary perspicacity, empirically developed a vector model of the atom which disclosed the interval rule and the magnetic splitting factors of atomic energy levels. The rest of the quantum theory was filled in with unusual, almost breath-taking, suddenness. The golden age of spectroscopy came in 1925 when *Russell* and *Saunders* indicated how triplet spectral terms resulted from the addition of orbital moments of two electrons; *Pauli* showed that equivalent electrons produced fewer terms than nonequivalent electrons, and also discovered an exclusion principle which accounted for the electronic structure and periodic properties of atoms; *Hund* generalized the correlation of spectral terms with electron configurations; *Uhlenbeck* and *Goudsmit* suggested that electron spin was responsible for term multiplicities and for half integral quantum numbers; and *Schrödinger* invented wave mechanics which refined the original semi-empirical quantum theory. The details can be found in a dozen or more comprehensive treatises on line spectra, and on their quantum-theoretical interpretation, which were published in the following decade.

Now let me summarize some general principles of spectroscopy that are directly applicable to spectrochemical analysis. If these now seem to be axiomatic or platitudinous remember that they were arrived at after centuries of floundering, fumbling, groping, and experimenting, and that with few exceptions they are less than 35 years old. Aside from the principle that chemical elements possess characteristic spectra and absorb the same frequencies that they emit, first clearly stated by *Kirchhoff* and *Bunsen* in 1859, and *Lockyer*'s statement in 1874 that the lines of any constituent of a mixture disappear from the spectrum as its percentage is reduced, practically all other spectroscopic principles belong to the present generation. We should be proud of this and make the most of it.

1. **Atomic spectra are excited by thermal collision of atoms or ions, by inelastic collisions with electrons, and by absorption of radiation.** A century of spectroscopic experiments with flames showed that relatively few elements could be caused to emit spectra in the alcohol flame but many more could be generated in gas-oxygen or hotter flames. This, combined with the experience that electric arcs produced more intense spectra and melted and vaporized practically all known elements, led to the belief that temperature was the sole condition for producing spectra. High-voltage condensed sparks

intensified certain lines and these enhanced lines were regarded in 1880 by *Lockyer* as proof that chemical elements were not simple but could be dissociated at high temperatures into further elements. Failure to find metalloids in the solar spectrum was also explained by dissociation of these elements by the great heat of the sun. Although *Lockyer*'s explanation of marked changes in elementary spectra was doubted another third of a century passed before the true explanations were suggested by the structural analyses of the different spectra.

Numerous attempts were made to measure the temperatures of these sources even before it was observed that they are far from homogeneous. These inhomogeneities in direct-current arc spectra, for example, may appear as lines of nearly uniform intensity from pole to pole, others enhanced at the poles and some seen only at the cathode. The first group is correctly interpreted as belonging to neutral atoms, the second to singly ionized atoms and the third to doubly ionized atoms. These phenomena which long puzzled and confused the early spectroscopists have been successfully employed since 1914 to separate the spectra of ions from those of neutral atoms. Similar results are obtained by comparing line intensities in arc and spark spectrograms or by comparing spark spectrograms made with different amounts of self-inductance in the discharge circuit. Such experiments forced the conclusion that electrical sources excite spectra partly by collision of atoms where these are in temperature equilibrium, and partly by electron impacts, especially at the cathode where electronic speeds or temperatures are highest. *King*'s furnace is an example of pure thermal excitation. The *Franck* and *Hertz* experiments illustrate pure electronic excitation. There is no evidence that optical excitation or collisions of the second kind are appreciable in the ordinary light sources operated at atmospheric pressure.

2. **Each chemical element is characterized by as many different spectra as the atom has electrons, and the term multiplicities of each are even or odd according as the number of electrons is odd or even.** Thus hydrogen has one spectrum, helium two, lithium three, beryllium four, etc. The spectral terms of the H I spectrum are double, those of He I are single and triple, of He II double, etc. The first spectrum is characteristic of neutral atoms and is the most easily excited. Ionization potentials of neutral atoms range from 24.58 electron volts for He to 3.89 eV for Cs, and the strongest lines[10] range from 584 A to 8521 A. The second spectra, emitted by singly ionized

atoms, are displaced toward higher frequencies or shorter wavelengths as a consequence of the increase of positive charge on the ion when an electron is removed. Insofar as the second ionization potentials are known they range from 75.26 eV for Li^+ to 9.96 eV for Ba^+ and the corresponding strongest lines[11] range from 199 A to 4554 A. With few exceptions the third and higher spectra have no value in practical spectrochemical analysis because their strongest lines are mostly in the extreme ultraviolet, out of reach of ordinary spectrographs. Speaking broadly, flames and arcs favor the excitation of first spectra while high voltage discharges generate higher spectra. Since the strongest lines determine the absolute sensitivity of spectrochemical detection it is obvious that arcs are preferred for trace analyses. This has been discovered empirically many times in the past 20 years.

3. **For all practical purposes the wavelengths of atomic spectra are invariable.** This does not deny the existence of the pressure effect, the magnetic (*Zeeman*) effect, the electric (*Stark*) effect, the gravitational (*Einstein*) effect, and the radial velocity (*Doppler*) effect, but all these wavelength variations are so small that they are of no concern in spectrochemical analysis. This is the basic principle of qualitative analysis, that chemical elements are positively identified by the positions or wavelengths of their characteristic spectral lines. In 1902 *Haschek* suggested that quantitative analyses could be made by measuring the pressure shift of spectral lines as a function of concentration of the elements. Like many other proposed methods based on misconceptions this one is wholly impractical.

4. **Under specified conditions the relative intensities of lines in a particular spectrum are constants of nature.** This is a consequence of atomic structure and quantum theory. The theoretical relative intensities have been calculated for lines in multiplets and many measurements have been made to test the intensity rules. Such theoretical and observed intensities should be useful in spectrochemical calibration but they do not appear to have been applied for this purpose. It cannot be assumed that relative intensities of multiplet lines are immutable except when self-reversal or selective absorption is absent. Fortunately this is always true when concentrations are low and lines are weak.

Radical changes in relative intensities may be observed when lines belonging to *different* spectra are compared. If the lines belong to different spectra of the same element their intensity ratios may vary from point to point in the inhomogeneous light source, and if the lines belong to corresponding spectra of different elements the ratios may vary when excitation is influenced by the sample matrix or by a buffer or other element. The desirability of avoiding or minimizing these radical changes in relative intensity of different spectra should be, and is, obvious to the applied spectroscopist; whereas the fundamental spectroscopist deliberately produces such variations to get information on spectral excitation. For example, if one wishes to differentiate between I and II spectra of a rare-earth element one can do so by comparing intensities of lines in arc and spark spectra of the element. The same separation can be arrived at by comparing intensities of arc spectra of the element in a copper matrix and in a carbon matrix because II spectra are enhanced in the latter.

The most popular method of quantitative spectrochemical analysis rests on the assumption that the intensity of a spectral line is a measure of the number of radiating atoms or ions present in the light source. The usual procedure is to measure the intensity ratio of two lines, one representing the major matrix element and the other the element to be determined, and then obtain the percentage concentration of the latter from the dependence of the intensity ratio upon the concentration as predetermined from measurements on standard or analyzed samples. In 1944 *Van Calker*[12] described " an attempt to establish an absolute quantitative spectral analysis " based on the assumption that various lines of a spectrum differ in concentrational sensitivity so that the intensity ratio or density difference of two lines of an element represents a measure of its concentration in any matrix. To illustrate this method the density differences of two pairs of bismuth lines (2993.3 and 2989.0 A, or 3024.7 and 3067.7 A) were shown to be functions of the bismuth concentration, and the density differences of two magnesium lines (2790.8 and 2852.1 A) were seen to vary with magnesium concentration. It is inconceivable that the first mentioned pair can exhibit any true density or intensity differences because both lines have practically identical excitation potentials and both end on the same level 11418 cm^{-1} (1.41 eV) above the ground state of bismuth. It seems likely that the observed density differences in this case are explained by the *Schwarzschild-Villiger* effect because an intense cadmium line (2880.8 A) in cadmium alloys scatters light into the position occupied by the Bi 2889.0 A line. The second Bi pair consists of a line (3024.7 A) with high excitation potential (1.91 eV) and one (3067.7 A) associated with the ground state. The latter is the strongest line of the Bi I spectrum; it is also the Bi I line most strongly absorbed by unexcited Bi atoms. Self reversal of the first line is probably negligible but it may be expected to increase for the second line as the vapor density increases in the light source. This remark applies also to the magnesium pair, since 2790.8 A is a highly excited Mg II line (12.0 eV) and 2852.1 A is the strongest and most readily absorbed Mg I line. The proposed absolute method is therefore not based upon true differences of intensity or concentrational sensitivity but rather upon differential self reversal as a function of concentration in the light source. Excluding the spurious intensity changes due to self reversal or to photographic saturation there is no evidence that the relative intensities in any spectrum of a given element depend on the abundance of the element.

5. **In addition to wavelength (or wavenumber) and intensity every spectral line is characterized by excitation potentials characteristic of the atoms or ions.** These excitation data are derived from spectral series terms revealed by an analysis of the structure of the spectrum; they are now known for 450 spectra of 82 elements. Although a few spectra of natural elements are still unknown (Po, Ac, Pa) and unanalyzed (Tb, Ho, Er) most of the remainder have been analyzed sufficiently to satisfy the requirements of spectrochemical analysis. The excitation potentials of classified lines are known with the same precision as the measured wavelengths. They are in reality atomic energies proportional to vibration frequencies or wavenumbers but are commonly called potentials because the kinetic energy acquired by a free electron falling through a potential difference expressed in volts provides a simple picture of spectral excitation when atoms or ions collide inelastically with such energized electrons. Spectral term values in wavenumbers are converted to electron volts by the relation $8067.5 \text{ cm}^{-1} = 1 \text{ eV}$. When the excitation potential equals the ionization potential the atom loses an electron, and further increase in excitation produces the second spectrum. The total excitation potential of any II spectrum line therefore exceeds that of any I spectrum line by the first ionization potential, or more. Being aware of the inhomogeneities and fluctuations of spectrochemical light sources it seems obvious that anyone wishing to measure intensity ratios of different elements would avoid comparisons of I and II spectra, and select, insofar as possible, lines of similar excitation characteristics. Unfortunately, very little use appears to be made of excitation data in spectrochemical analysis, except in astrophysics. An indication that this is true is seen in the infrequent mention of excitation po-

tentials in spectrochemical literature. A partial explanation may be found in the existence of an excellent " Multiplet Table of Astrophysical Interest "[13], but no similar compilation meeting the needs of spectrographers is available. The required details can only be found in the original spectroscopic publications references to which were published[14] in 1946.

In 1932 *B. F. Scribner* and the writer began to observe the principal lines of seventy elements on a single, uniform scale of physical intensities, for the purpose of compiling wavelengths, concentrational sensitivities, and excitation potentials for a total of approximately 25,000 lines ranging in wavelength from 2000 to 9000 A. This work was delayed by World War II and by other interruptions but we hope to be able to make the results available to spectrographers in the near future.

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Die Berechnung der Nachweisempfindlichkeit*

Von

H. Kaiser

Mit 4 Textabbildungen

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I. Problemstellung und gegenwärtiger Stand

Die hohe Nachweisempfindlichkeit, die viele spektrochemische Analysenverfahren liefern, ist immer als besonderer Vorzug der spektrochemischen Analyse betrachtet worden. Infolgedessen wurde in den ersten Jahren der technischen Entwicklung viel daran gearbeitet, die Nachweisgrenzen zahlenmässig festzulegen und Verfahren zu finden, die eine möglichst hohe Nachweisempfindlichkeit liefern. Angaben über die erreichten Nachweisgrenzen finden sich in zahlreichen Arbeiten, von denen wir hier nur einige Zusammenstellungen nennen wollen. Die Ergebnisse von *Wa. Gerlach* und seinen Mitarbeitern sind zum grossen Teil in den beiden *Gerlach*schen Büchern wiedergegeben[9;7]. *L. de Azcona* hat einen Atlas der letzten Linien herausgegeben, in dem die Nachweisgrenzen im Lichtbogen stehen[1]. Angaben für Mineralien sind in den Arbeiten aus dem Mineralogischen Institut der Universität Göttingen[10;16], ferner in dem kleinen Buch von *L. W. Strock*[22] zu finden. Die Nachweisgrenzen für Metalle in organischen Werkstoffen bringen *Hess*, *Owens* und *Reinhardt*[11]; für Verunreinigungen in Aluminium hat sie *A. Beerwald* zusammengestellt[3]. Von *O. Schliessmann* stammt eine wichtige Arbeit über die Nachweisgrenzen in Stählen, über sie wird in anderem Zusammenhang noch zu sprechen sein[20]. *H. Lundegardh* hat im zweiten Band seines Buches[15] Tabellen für die Nachweisempfindlichkeit vieler Elemente in der Flamme gegeben.

Ein wichtiges Teilgebiet dieses Fragenkreises betrifft den Vergleich verschiedener Anregungsarten. Hierüber weiss man nur sehr allgemein Bescheid. Sicher ist wohl, dass der Lichtbogen die höchste Nachweisempfindlichkeit gibt, in den Einzelheiten aber ist noch

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* Diese Arbeit widme ich Herrn Prof. *Walther Gerlach*. Wir verdanken ihm neben manchen zweckmässigen Begriffsbildungen die erste systematische Anwendung der modernen Atomphysik auf die Spektrochemie. Die vorliegende Arbeit ist durch frühere Arbeiten von *Wa. Gerlach* mitgeformt worden.

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vieles unklar. Zahlenmässige Angaben über die Steigerung der Nachweisempfindlichkeit beim Puffern der Lichtquelle, beim Vergleich von Glimmschichtmethode und Flammenbogen fehlen fast ganz. (Siehe dazu *Gerlach* und *Rollwagen*[8], *van Calker*[4], *Oftedal*[17], *Ruehle* und *Jaycox*[19], *Kaiser* und *Sohm*[14]).

Dabei ist das Grundsätzliche durchaus bekannt. Es ist klar in den verschiedenen Arbeiten von *Gerlach* ausgesprochen, besonders sei hier auf seinen Madrider Vortrag 1934 verwiesen[6]. Dort wird gesagt, dass die Nachweisempfindlichkeit dadurch begrenzt ist, dass die Nachweislinie des gesuchten Elementes im Untergrund des Spektrums versinkt. Es komme also darauf an, Anregungsarten zu verwenden, bei denen der Untergrund möglichst schwach, die Linie selbst aber möglichst stark erscheint. Ferner müsse man Dispersion und Auflösung des Spektrographen möglichst gross machen, damit der Untergrund gegenüber der Linie verdünnt werde. Durch hart arbeitende Platten könne man ebenfalls erreichen, dass die Linie sich stärker vom Untergrund abhebe. Auch die Frage wird behandelt, ob eine Verlängerung der Belichtungszeit die Nachweisempfindlichkeit erhöhe.

Trotz dieser sehr klaren Einsichten ist in der Frage der Nachweisempfindlichkeit seit Jahren ein Stillstand eingetreten. Das liegt an zwei Schwierigkeiten. Es fehlt im allgemeinen an Proben, bei denen die Gehalte an Spurenbeimengungen so zuverlässig bekannt sind, dass man mit ihrer Hilfe genaue Zahlenwerte für die Nachweisgrenzen ermitteln könnte. Ausserdem aber ist es sehr schwierig zu beurteilen, ob eine Linie, deren Erscheinen man erwartet, tatsächlich noch zu sehen ist. Gerade in der Gegend der Nachweisgrenze, wo die Linie zu verschwinden beginnt, kann man leicht getäuscht werden. Man muss daher versuchen, für die Nachweisgrenze eine Bedingung festzulegen, die von einer Entscheidung des Beobachters unabhängig ist. Diese Schwierigkeit hat *O. Schliessmann*[20] 1941 deutlich gesehen und deshalb die Nachweisgrenze verschiedener Elemente in Stählen so definiert, dass bei der Konzentration der Nachweisgrenze die Schwärzungsdifferenz der Linie gegenüber dem Untergrund 0.1 sein sollte. Diese Festlegung gibt schon eine sehr gute Übersicht. Wie *Schliessmann* selbst aber sagt, kann man die Linie bei viel geringeren Schwärzungsunterschieden noch deutlich sehen, sodass die ermittelten Nachweisempfindlichkeiten zu ungünstig sind. Ausserdem ist aber das gewählte Kennzeichen $S_{L+U} - S_U = 0.1$ nicht nur von der Plattensorte, sondern auch von der Plattenbehandlung abhängig.

Der rechnerischen Behandlung hat sich die Frage der Nachweisempfindlichkeit trotz des klaren Einblicks in die Zusammenhänge bisher entzogen. Das lag daran, dass man noch keine einfachen analytischen Zusammenhänge zwischen Schwärzung und Intensität kannte, auch waren die Fragen, die mit dem Untergrund zusammenhängen, noch nicht genügend geklärt. Beides ist jetzt anders geworden. Auch liegen schon genug Messungen von Eichkurven mit Untergrundkorrektur vor, sodass man über das Verhalten der Eichkurven im Gebiete kleiner Konzentration Bescheid weiss.

In der folgenden Arbeit soll nun gezeigt werden, wie man die Nachweisgrenzen für ein gesuchtes Element bei einer gegebenen Arbeitsvorschrift berechnen kann, wenn eine Eichkurve im Gebiete zuverlässig bestimmbarer, nicht zu hoher Konzentrationen vorhanden ist, und wenn man die mittlere Schwärzungsschwankung auf der Platte kennt. Damit ist zweierlei erreicht. Man braucht keine Proben mehr mit kleinen Gehalten, die nur höchst unsicher bestimmbar wären, und man ist nicht mehr auf die Entscheidung des Beobachters angewiesen, ob die gesuchte Nachweislinie noch zu erkennen ist. An die Stelle der Beurteilung tritt ein Messwert.

Ausser der Frage nach der Nachweisgrenze wird sich noch eine weitere ergeben und auch beantworten lassen, nämlich die Frage nach der «Bestimmungsgrenze». Darunter soll die tiefste Konzentration verstanden werden, bei der mit einer bestimmten Arbeitsvorschrift eine Mengenbestimmung gemacht werden kann, ohne dass die Analysengenauigkeit einen gegebenen Wert unterschreitet. Die Bestimmungsgrenze ist durchaus von der Nachweisgrenze verschieden, auch besteht kein einfacher Zusammenhang etwa der Art, dass die Konzentration der Bestimmungsgrenze ein bestimmtes Vielfaches von der Konzentration an der Nachweisgrenze wäre. Dass es sich hierbei um zwei verschiedene Dinge handelt, ist von *Balz*[2] und von *Owens*[18] klar erkannt worden, wenn sie sich auch nicht des hier gewählten Wortes bedient haben. Bei der Behandlung dieser Frage wird sich ein Zusammenhang mit den im Anfang der Entwicklung von *Gerlach* eingeführten Begriffen «absolut empfindlich» und «relativ empfindlich» ergeben.

II. Die Eichgleichung

Wir bezeichnen wie immer den Logarithmus der Intensität mit Y, den Logarithmus eines Intensitätsverhältnisses mit ΔY. Aus Eichaufnahmen im Gebiet kleiner aber noch zuverlässig bestimmbarer Konzentrationen sei die Haupteichkurve (s. *Kaiser*[13]) für die Bestimmung eines Zusatzelementes Z in einer Grundsubstanz nach einer fest vorgeschriebenen Arbeitsvorschrift gegeben. Die Intensität der Nachweislinie von Z sei in der üblichen Weise bezogen auf die konstante Intensität einer Bezugslinie, die im allgemeinen eine Linie des Grundelements G sein wird. Bei der Berechnung der Intensitätsverhältnisse sei die Intensität des Untergrundes U von der Intensität der Linie + Untergrund $(L + U)$ abgezogen[12]. Es hat sich nun gezeigt, dass derartige Eichkurven im Gebiet kleiner Konzentrationen fast immer geradlinig verlaufen. In vielen Fällen ist ihre Steigung sogar genau 45°; das bedeutet dann, dass die ausgestrahlte Linienintensität der Anzahl der in der Probe vorhandenen und in die Lichtquelle hineinverdampften Atome verhältnisgleich ist.

Für die Haupteichkurve setzen wir die Gleichung einer geraden Linie an:

$$\log k = \eta \cdot \Delta Y_G + \log k_0. \qquad (1)$$

η ist die Steilheit, k_0 die Konzentration am Fixpunkt $(\Delta Y_G = 0)$.

Aus dieser auf eine Grundlinie bezogenen Eichgleichung leiten wir die Gleichung der auf den Untergrund bezogenen Eichkurve ab, indem wir einsetzen

$$\Delta Y_U = \Delta Y_G + (Y_G - Y_{U_Z}).$$

Das gibt:

$$\log k = \eta \cdot \Delta Y_U - \eta\,(Y_G - Y_{U_Z}) + \log k_0. \qquad (2)$$

Darin ist $(Y_G - Y_{U_Z})$ im allgemeinen noch eine Funktion der Konzentration k. Diese Funktion muss bis zu sehr kleinen Werten von k bekannt sein, sonst können wir keine Voraussage darüber machen, wann die Nachweislinie im Untergrund versinkt. Wir könnten z. B. garnichts voraussagen, wenn der Untergrund von irgendwelchen zufälligen Beimengungen in der Probe stark beeinflusst würde.

Wir wollen uns der Einfachheit halber im folgenden auf den wichtigen und häufigen Sonderfall beschränken, dass der Untergrund in Bezug auf die Grundlinie annähernd konstant ist, d. h. $Y_G - Y_{U_Z} = \text{const.}$ Wir nehmen dafür den Mittelwert aus den Eichspektren und erhalten mit der neuen Konstanten

$$\log k_U = \log k_0 - \eta \cdot \overline{(Y_G - Y_{U_Z})}$$

die Gleichung der auf den Untergrund bezogenen Eichgeraden in der Form

$$\underline{\log k = \eta \cdot \Delta Y_U + \log k_U.} \qquad (3)$$

Mit dieser Gleichung werden wir weiterhin arbeiten; da sie aber immer erst am Schluss der Rechnungen benutzt wird, können wir jederzeit auf die allgemeinere Form (2) zurückgehen.

Wir müssen nun noch überlegen, welche Anforderungen wir an das gleichartige Verhalten des Untergrunds in den Spektren der verschiedenen Proben stellen müssen. Für die folgende Theorie ist die Geradlinigkeit der Haupteichkurve (1) die wesentliche Voraussetzung, damit die Eichkurve zu beliebig kleinen Konzentrationen herunter verlängert werden kann. Die Messwerte für die Haupteichkurve werden aber berechnet, indem die Intensität des Untergrundes eliminiert wird. Ob der Untergrund bei den verschiedenen Proben gleich oder verschieden stark ist, spielt keine Rolle. In der Gleichung (1) steckt nichts vom Untergrund. Wir können dann den Übergang zu (3) rein formal ausführen, indem wir alle ΔY_G durch $\overline{Y_G - Y_{U_Z}}$ auf einen mittleren Normaluntergrund beziehen. Auch die so gewonnene Eichgerade (3) kann nach unten verlängert werden.

Es wäre daher ganz falsch, wenn wir bei nicht völlig konstantem Untergrund versuchen würden, die Eichgerade (3) aus den Messungen unmittelbar abzuleiten, indem wir in jedem Eichspektrum das Intensitätsverhältnis der Nachweislinie zu *ihrem* Untergrund bestimmten. Das kann bei schwankender Stärke des Untergrunds niemals eine vernünftige Eichgerade geben, die nach unten verlängert werden kann. Ebenso wäre es falsch, wenn wir bei der Eichung auf die Untergrundkorrektur im einzelnen verzichteten und die Lage der Eichgeraden (1) aus einer Ersatzeichgeraden* berechnen wollten. Mit einer solchen summarischen Untergrundkorrektur kann die Lage der Eichgeraden nicht so genau ermittelt werden, wie es für die sichere Extrapolation zu kleinen Konzentrationen nötig ist, zumal die Nachweislinien in den Eichspektren oft schwach im Vergleich zum Untergrund sein werden, sodass die Schwankungen des Untergrundes sich in der Korrekturgrösse D (s. [12]) kräftig bemerkbar machen können.

Was bedeuten aber — wenn wir von der Lage der Eichgeraden absehen — die Abweichungen der Untergrundintensität in den Spektren der verschiedenen Proben vom mittleren Normalwert für die Bestimmung der Nachweisgrenze? Sie bedeuten nicht viel; das Verschwinden einer Linie im Untergrund ist nur ungenau festzulegen, — wir werden das später noch erörtern — und es macht dabei nicht viel aus, ob der Untergrund etwas stärker oder schwächer als der « Normaluntergrund » ist. Wir sind daher berechtigt, für die Untergrundintensität einen Mittelwert anzunehmen.

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* Siehe dazu eine demnächst erscheinende Arbeit.

III. Die Nachweisgrenze

Die weitere Aufgabe ist nun, festzustellen, wie gross der ΔY_U-Wert ist, bei dem die Linien im Untergrund verschwinden. Wenn man diesen Wert in die Gleichung (3) einsetzt, erhält man die Konzentration $\underline{k}$ an der Nachweisgrenze. (Alle Grössen, die sich auf die Nachweisgrenze beziehen, sollen im folgenden durch einen daruntergesetzten Strich gekennzeichnet werden. Das ist die in der Mathematik übliche Bezeichnung für eine untere Grenze.)

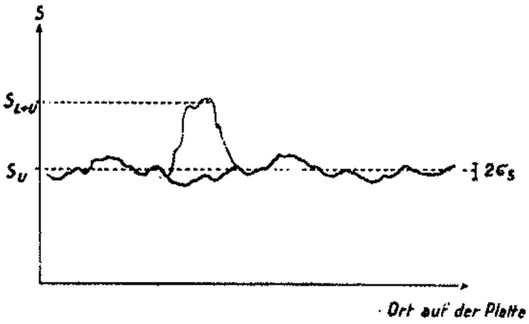

Abb. 1. Schematische Registrierkurve der Schwärzung des Untergrundes mit überlagerter Spektrallinie (punktiert).

Worauf es ankommt, soll die Abbildung 1 zeigen. Hier ist angenommen, dass die Linie auf einem Untergrund liegt, dessen mittlere Schwärzung durch die gestrichelte Linie gegeben ist. Wenn man den Untergrund tatsächlich misst, findet man örtliche Verschiedenheiten in der Schwärzung, die durch die Körnigkeit der photographischen Schicht hervorgerufen werden. Man wird das messen, was durch die ausgezogene unregelmässige Linie dargestellt ist. Dasselbe, was hier als örtliche Schwankungen gezeichnet ist, würde man auch finden, wenn man den Untergrund an derselben Stelle in *verschiedenen* Spektren, die mit gleichen Aufnahmebedingungen gemacht worden sind, ausmessen würde. Über diesem welligen Untergrund erhebt sich nun die Linie mit ihrer Schwärzung. Sie ist punktiert angedeutet. Damit man die Linie mit Sicherheit im Untergrund erkennen kann, muss sie sich deutlich aus den Schwärzungsschwankungen herausheben. Der Schwärzungsunterschied zwischen Linie + Untergrund $(L + U)$ und dem Untergrund muss also ein bestimmtes Vielfaches der mittleren Schwärzungsschwankung σ_S sein. Diese ist am Rande der Abbildung eingezeichnet. Da der Wert für die mittlere Schwärzungsschwankung σ_S (Plattenstreuung) von der Höhe der Schwärzung abhängt, muss sie bei der Schwärzung des Untergrundes gemessen werden oder aus Messungen bei einer anderen Schwärzung errechnet werden (siehe Abschn. IV).

Gemessen werden: S_{L+U}, die Schwärzung, die Linie und Untergrund zusammen erzeugen, und S_U, die Schwärzung des Untergrundes allein.

Ausserdem muss man die « Richttransformation »* ermitteln, die bei der betrachteten Wellenlänge eine vollständig geradlinige Kennlinie ergibt. Im allgemeinen wird das eine verallgemeinerte *Seidel*transformation sein, $P = l \cdot S + (1 - l) \cdot W$.[12] Ausser der Transformation selbst muss man die Steilheit der Kennlinie bestimmen, die wir mit γ_P bezeichnen. Aus den Messwerten berechnet man nun in der üblichen Weise den Wert

$$\Delta Y'_U = Y_{L+U} - Y_U = \frac{1}{\gamma_P} (P_{L+U} - P_U).$$

Bei dieser Grösse $\Delta Y'_U$ ist also der Untergrund noch nicht abgezogen. Das soll der Strich rechts oben andeuten.

Nun muss man überlegen, wie sich die Streuung der Schwärzung in dieser Grösse bemerkbar macht. Dazu braucht man das Fehlerfortpflanzungsgesetz. In der linken Spalte der folgenden Tabelle sind die Grössen aufgeführt, wie sie bei der Rechnung auseinander hervorgehen. In der rechten Spalte steht jeweils die zugehörige Streuung. Da die Schwärzung von Linie + Untergrund an der Nachweisgrenze fast gleich der Schwärzung des Untergrundes allein sein muss, sind die Streuungen für beide einander gleich.

Grösse	*Streuung*
S_U ; S_{L+U}	σ_S
$\downarrow \quad \downarrow$	
P_U ; P_{L+U}	$\sigma_S \cdot \frac{dP}{dS}$
$\downarrow \quad \downarrow$	
Y_U ; Y_{L+U}	$\sigma_S \cdot \frac{dP}{dS} \cdot \frac{1}{\gamma_P}$
$\searrow \swarrow$	
$\Delta Y'_U$	$\sqrt{2} \cdot \sigma_S \cdot \frac{dP}{dS} \cdot \frac{1}{\gamma_P}$

(Die $\sqrt{2}$ kommt bei der Differenzbildung dazu, da nach dem Fehlerfortpflanzungsgesetz die Quadrate der σ zu addieren sind.) Abschliessend ergibt sich also:

$$\sigma_{\Delta Y'} = \sqrt{2} \cdot \frac{1}{\gamma_P} \cdot \frac{dP}{dS} \cdot \sigma_S. \tag{4}$$

---

* In der früheren Arbeit[12] wurde der Buchstabe P nur für den Sonderfall $l = 0{,}5$ benützt, jetzt soll er ganz allgemein gebraucht werden. Um Verwechslungen zu vermeiden, schreiben wir die alte Grösse jetzt $\hat{P}$, also $\hat{P} = \frac{1}{2}(S + W)$. Die Transformationskonstante wurde in der früheren Arbeit anders definiert und a genannt; die jetzt gewählte Art ist zur Berechnung bequemer. Der Zusammenhang zwischen a und l ist: $l = (a + 1)^{-1}$. Der Buchstabe l wurde gewählt, um daran zu erinnern, dass die Richttransformation von der Wellenlänge λ abhängt.

Nun muss der $\Delta Y'_U$ Wert an der Nachweisgrenze ein kleines Vielfaches der Streuung $\sigma_{\Delta Y'}$ sein. Welches Vielfache man wählen soll, ist eine Frage der Zweckmässigkeit. Man muss dann nur bei der einmal getroffenen Festsetzung bleiben. Wir wollen den Faktor 3 nehmen. Bei ganz gleichmässigem Untergrund könnte es sich dann unter 1000 Fällen noch etwa 3mal ereignen, dass man eine Linie mit einer zufälligen Schwärzungsschwankung verwechselte. (Tatsächlich wird diese Sicherheit nicht erreicht werden, denn im allgemeinen ist der Untergrund neben einer Linie nicht ganz gleichmässig, sondern er zeigt eine gewisse Struktur, z. B. von Bandenlinien.) Damit erhalten wir für das $\Delta Y'_U$ an der Nachweisgrenze:

$$\underline{\underline{\Delta Y'_U} = 3 \cdot \sqrt{2} \cdot \frac{1}{\gamma_P} \cdot \frac{dP}{dS} \cdot \sigma_S.} \tag{5}$$

Der so gewonnene Wert muss nun noch durch die *Seidel*transformation (Übergang von log x zu log $[x-1]$) in den Wert $\underline{\Delta Y_U}$ umgewandelt werden*.

Mit diesem Wert geht man dann in die Eichgleichung (3) ein und erhält für die Konzentration $\underline{k}$ der Nachweisgrenze

$$\log \underline{k} = \eta \cdot \underline{\Delta Y_U} + \log k_U. \tag{6}$$

Auf diese Weise kann man zu jeder vollständigen Arbeitsvorschrift die Nachweisgrenzen für die Elemente und Linien ermitteln, auf die sich die Vorschrift bezieht, wenn die in II. genannten Voraussetzungen zutreffen. Es ist sehr nützlich, das bei jeder Eichung eines Verfahrens sofort zu tun; denn es kommt oft vor, dass man derartige quantitative Aufnahmen auch benutzt, um Verunreinigungen nachzuweisen. Kennt man dann von vornherein die zur Arbeitsvorschrift gehörenden Nachweisgrenzen der fraglichen Elemente, so kann man sofort sagen, was es zu bedeuten hat, wenn eine bestimmte Analysenlinie — die nicht die Hauptnachweislinie des betreffenden Elements zu sein braucht — nicht gefunden wird.

Verfolgt man den Gang der obigen Rechnung, so sieht man leicht, wie die beiden in der Einleitung erwähnten Schwierigkeiten überwunden sind: Man braucht keine Proben mit dem kleinen Gehalt der Nachweisgrenze, weil die Bestimmung der Konzentration an der Nachweisgrenze aus der Eichgleichung erfolgt, die im Gebiete zuverlässig bestimmbarer Konzentrationen aufgestellt wird; das Urteil des Beobachters aber ist durch eine Messvorschrift ersetzt, die jederzeit von jedem in derselben Weise ausgeführt werden kann.

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* Für diese Operation hat sich in mehreren Laboratorien sehr bald das bequeme Wort « seideln » eingeführt.

Trotz dieses methodischen Fortschritts kann man eine Nachweisgrenze immer nur der Grössenordnung nach bestimmen. Darüber darf man sich durch den mathematischen Glanz der Gleichungen nicht hinwegtäuschen lassen. Diese liefern zwar formal beliebig genaue Zahlenwerte, aber diese Genauigkeit hat keinen physikalischen Sinn. Eine Nachweisgrenze ist ein Grenz*bereich*, keine Grenz*linie*. Um das deutlich zu machen, berechnen wir die Ableitung $d\Delta Y / d\Delta Y'$, die für die Fehlerübertragung von $\Delta Y'$ auf ΔY massgebend ist. Dazu setzen wir $\Delta Y' = \log x$, dann ist $\Delta Y = \log (x - 1)$ und es wird:

$$d\Delta Y \,/\, d\Delta Y' = x \,/\, (x - 1).$$

Daher ist:

$$\sigma_{\Delta Y} = \sigma_{\Delta Y'} \cdot x \,/\, (x - 1).$$

An der Nachweisgrenze ist aber nach (4) und (5) $\underline{\Delta Y'_U} = 3\,\sigma_{Y\Delta'}$. Die Entwicklung des $\log x$ für kleine Werte von $\Delta Y'$, d. h. $x \approx 1$, liefert $\Delta Y' \approx 0.434\,(x - 1)$. Bringen wir das alles zusammen, dann finden wir für die Streuung an der Nachweisgrenze

$$\sigma_{\Delta Y_U} \approx \frac{0.434}{3} \cdot x \approx 0.145, \text{ da } x \approx 1 \quad \text{ist.}$$

Damit ist: $\sigma_{(\log k)} \approx 0.145 \cdot \eta$, und das bedeutet:

Die Streuung von Gehaltsbestimmungen in der Nähe der Nachweisgrenze ist etwa 40% *vom angegebenen Gehalt* (*für* $\eta = 1$).

Dazu kommt noch etwas anderes: Die Zahlenwerte von σ_S und von γ_P können von Platte zu Platte verschieden sein. Welche Werte soll man nehmen, um die Nachweisgrenzen allgemein anzugeben? Zwar lässt sich γ_P vielleicht noch konstant halten, wenn man sorgfältig auf gleiche Entwicklungsbedingungen achtet, aber σ_S ist nur als statistischer Mittelwert über eine grössere Anzahl von Platten derselben Sorte zu fassen (s. dazu Abschnitt IV). Kleine Änderungen in den angenommenen Werten wirken sich im Ergebnis für $\underline{k}$ wegen des hohen Übertragungsfaktors sehr stark aus. Das zeigt die folgende Tabelle.

TABELLE 1

$\Delta Y'_U$	0.10	0.05	0.03	0.02	0.015	0.010	0.007	0.005
$x/(x - 1$	4,9	9,2	15	22	29	44	63	87

Es hat daher gar keinen Sinn, Nachweisgrenzen auf mehr als eine, in günstigen Fällen zwei Stellen anzugeben.

Die in dieser Arbeit gegebene Definition für die Nachweisgrenzen beruht auf einer photographisch-photometrischen Messvorschrift. Nun werden aber die meisten Spurenanalysen gemacht, indem der Auswertende sich die Spektren in starker Vergrösserung in einem Projektor oder Mikroskop ansieht und prüft, welche Nachweislinien noch zu sehen sind. Das Ergebnis wird sehr von den näheren Umständen abhängen. Durch die Vergrösserung werden z. B. die räumlichen Kontraste vermindert, auf die das Auge (im Gegensatz zum Photometer) anspricht, sodass schwache Linien schlechter zu sehen sind. Auch die Länge der Linien ist von Bedeutung; wenn man schräg auf die Platte blickt, kann man über die Länge integrieren und dadurch schwache Linien besser erkennen. Daher ist nicht zu erwarten, dass die photometrischen Nachweisgrenzen immer mit den visuell ermittelten übereinstimmen werden. Nach den bisherigen Erfahrungen ist aber die Grössenordnung dieselbe. Geplante Untersuchungen darüber konnten nicht mehr ausgeführt werden, wären aber dringend nötig. Solche Untersuchungen müssen an Modellen gemacht werden: Man kann dazu nicht die Hauptnachweislinien nehmen, weil deren Nachweisgrenzen zu tief liegen; man muss schwächere Linien nehmen, deren Nachweisgrenzen im Gebiet zuverlässig bestimmbarer Gehalte liegen. Für die Prüfung mit dem Auge braucht man ja einen Satz passend abgestufter Proben, deren Gehalte oberhalb und unterhalb der Nachweisgrenzen liegen. Solche Proben sind aber für die Umgebung der eigentlichen Nachweisgrenze, die man mit den Hauptnachweislinien erreicht, meist nicht zu beschaffen. Für den Vergleich, auf den es hier ankommt, sind sie auch gar nicht nötig.

Es soll noch einmal betont werden, dass die auf dem beschriebenen Wege ermittelte Nachweisgrenze nur gilt für den Nachweis eines bestimmten Elementes nach einer ganz bestimmten in allen Einzelheiten genau festgelegten Arbeitsvorschrift. Denn nur für eine solche Arbeitsvorschrift gilt ja die Eichgleichung, aus der sich die Nachweisgrenze ergibt. Die Frage, wie man die Versuchsbedingungen abändern muss, um eine möglichst hohe Nachweisempfindlichkeit zu bekommen, bleibt unbeantwortet. Man kann natürlich diese Rechenvorschrift benutzen, um die Nachweisempfindlichkeit von verschiedenen Analysenverfahren, mit denen man die gleiche Aufgabe bearbeiten kann, zu bestimmen und miteinander zu vergleichen. Man kann sich dann das bestgeeignete der betrachteten Verfahren heraussuchen, und kann so eine für die praktische Arbeit wichtige Entscheidung treffen.

Die natürliche Erweiterung dieser Betrachtungen liegt aber in folgender Richtung: Die Eichgleichung (3) und die Grössen $\frac{dP}{dS}$ sowie σ_S, die in der Gleichung (4) stecken, sind von den optischen Daten der Messanordnung und von den Leuchtbedingungen in der Lichtquelle abhängig. Die Grössen in der Gleichung (4) sind dabei insofern von den Leuchtbedingungen abhängig, als sie von der erzielten Schwärzung abhängen. Es ist nun möglich, in diese Gleichungen die Abhängigkeit von den optischen Daten (Lichtstärke, Dispersion, Durchlässigkeit und Spaltbreite des Spektrographen, Plattenempfindlichkeit und Körnigkeit) hineinzuarbeiten, so dass man aus diesen Gleichungen die günstigsten optischen Daten ermitteln kann, bei denen man unter bestimmten Voraussetzungen die höchste Nachweisempfindlichkeit erreicht. Damit wäre wieder eine technisch wichtige Frage gelöst. Wenn man dann noch für die optischen Daten gewisse Normalwerte in die Gleichungen einsetzte, müssten sich Nachweisgrenzen ergeben, die von der Optik unabhängig sind und die nur noch die Lichtquelle selbst kennzeichnen. Damit wäre eine allgemeine Ordnung der Lichtquellen nach ihrer Nachweisempfindlichkeit für die Bestimmung der verschiedenen chemischen Elemente möglich. Die Ansätze zu diesen Rechnungen liegen bereits vor.

IV. Die mittlere Schwärzungsschwankung

Wir haben nun noch etwas über die in Gleichung (4) eingehenden Grössen zu sagen, zunächst über den Differentialquotienten $\frac{dP}{dS}$. Wir nehmen an, dass die Transformation eine verallgemeinerte Seideltransformation ist. Wir führen die Hilfsgrösse r durch die Gleichung $S = \log r$ ein. Damit ist:

$$\frac{dP}{dS} = \frac{r - l}{r - 1}. \tag{7}$$

Nun ist noch die mittlere Schwärzungsschwankung (Plattenstreuung) σ_S bei der Schwärzung des Untergrundes zu ermitteln. Das kann in folgender Weise geschehen: Man nimmt Spektren auf mit der Spaltbreite, mit der auch die Analysenaufnahmen gemacht werden, aber so langem Spalt, dass der Mess-Spalt des Photometers sich zweimal in der Linie unterbringen lässt. Man belichtet so, dass die Schwärzung der Linie gleich der Untergrundschwärzung ist, die bei den Analysenaufnahmen auftritt. An der fertigen Platte misst man die Schwärzung an den beiden Mess-Stellen innerhalb der Linie und bildet den ΔS-Wert. Dieser müsste gleich Null sein, wenn keine Schwärzungsschwankungen vorkämen. Man bestimmt diese Grösse in möglichst vielen Spektren auf der Platte und berechnet daraus nach den Regeln der Fehlerrechnung die Streuung. Die so ermittelte Streuung ist $\sigma_{\Delta S} = \sqrt{2} \cdot \sigma_S$, weil in die Messung zwei Schwärzungswerte mit ihren Schwankungen eingehen.

Macht man diese Messungen an verschiedenen Platten der gleichen Sorte, so wird man feststellen, dass die Werte im einzelnen stark voneinander verschieden sind, weil nämlich die einzelnen Platten hinsichtlich ihrer Gleichmässigkeit verschieden gut sind. Es ist daher zweckmässig, die mittlere Schwärzungsschwankung an einer grösseren Anzahl von Platten der benutzten Sorte zu messen und daraus den quadratischen Mittelwert zu nehmen, der dann für die Plattensorte kennzeichnend ist. Mit diesem Wert rechnet man.

Der Wert von σ_S hängt von der Grösse der Schwärzung ab. Es wäre mühevoll, wenn man ihn auf die vorher angegebene Weise für jede infrage kommende Schwärzung besonders bestimmen müsste. Aus theoretischen Überlegungen von *H. Siedentopf*[21] ergibt sich, dass σ_S proportional der Wurzel aus S sein müsste. Um das nachzuprüfen, wurde die Streuung auf vielen Platten der Sorte Agfa Spektralblau extrahart bei verschiedenen Schwärzungen gemessen. Die graphische Darstellung dieser Messungen, die durch die Kriegsereignisse verloren gegangen ist, ergab Folgendes: Die Punkte lagen nicht auf einer Kurve, sondern bildeten einen Schwarm, durch den man aber immerhin als Leitlinie die *Siedentopf*sche Parabel legen konnte. Bei sehr kleinen Schwärzungswerten war die Streuung aber grösser als die Formel sagte, und es schien daher besser zu sein, die Parabel durch ihre Tangente bei $S = 0.5$ zu ersetzen. Demnach bleibt auch bei kleinen Schwärzungen eine Streuung bestimmter Grösse übrig. Wir können es hier völlig offen lassen, wieweit in dieser Reststreuung ausser den Fehlern der photographischen Schicht noch die zufälligen Fehler der Messungen im Photometer stecken. Wir wollen daher für die Abhängigkeit der Streuung von der Schwärzung folgende Gleichung ansetzen:

$$\sigma_S = \sigma_{(S=0.5)} \cdot (S + 0.5). \tag{8}$$

Aus diesem Ansatz ergibt sich eine wichtige Folgerung: Nach (5) bestimmt nämlich das Produkt $\frac{dP}{dS} \cdot \sigma_S$, wie die Nachweisgrenze von der Untergrundschwärzung abhängt, die bei der Belichtung erreicht wird. Diese Funktion ist in den Abb. 2 und 3 dargestellt

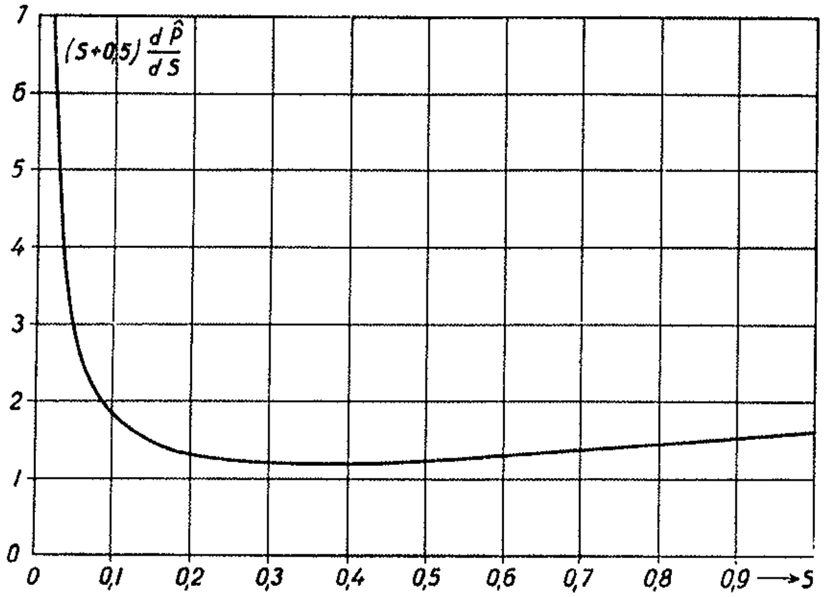

Abb. 2. $\frac{d\hat{P}}{dS}\cdot\sigma_S$ für die $\hat{P}$-Transformation für $(\sigma_{(S=0.5)} = 1)$.

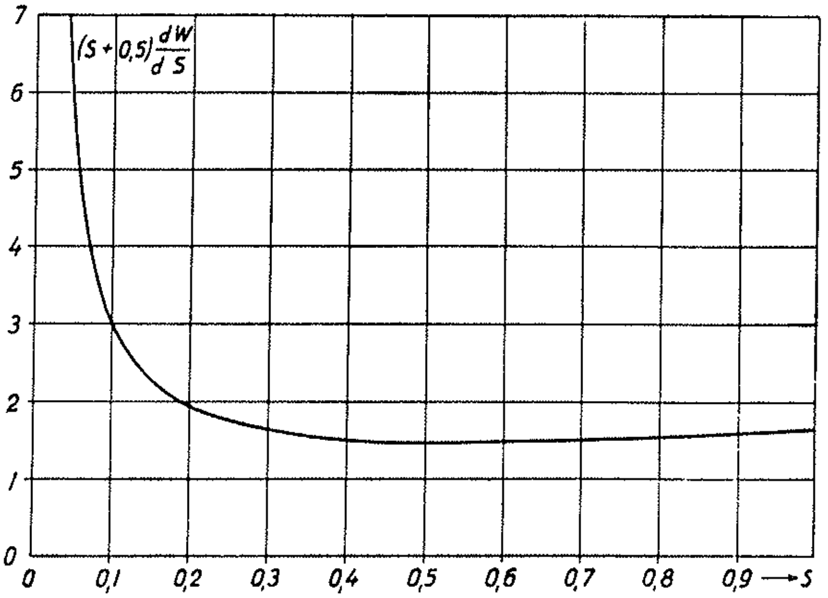

Abb. 3. $\frac{dW}{dS}\cdot\sigma_S$ für die W-Transformation für $\sigma_{(S=0.5)} = 1)$.

und zwar für die häufig gebrauchten Transformationen $\hat{P}$ und W[*]. Die Funktionen sind bei grösseren Schwärzungen fast konstant; sie haben ein flaches Minimum, das für W bei $S = 0.5$, für $\hat{P}$ bei $S = 0.35$ liegt. Der steile Anstieg beginnt für die W-Transformation unterhalb von $S = 0.2$; für die $\hat{P}$-Transformation unterhalb von $S = 0.15$. Das bedeutet: Man hat die volle photometrische Messgenauigkeit der Platte, wenn man dafür sorgt, dass alle Schwärzungen über 0.2 bzw. 0.15 liegen. Da der Zahlenwert für die mittlere Schwärzungschwankung an sich nur ungenau bestimmt werden kann, können wir für das Produkt $\frac{dP}{dS} \cdot \sigma_S$ bei Schwärzungen über 0.2 ungefähr den Wert $1{,}5 \cdot \sigma_{(S\,=\,0.5)}$ annehmen, der für überschlägige Rechnungen genügt.

Um bei einer Spurenanalyse die volle Nachweisempfindlichkeit zu erreichen, folge man der allgemeinen Regel:

Man belichte so lange, dass die ausentwickelte Platte an den Stellen, wo die Nachweislinien liegen, eine Untergrundschwärzung von 0.2 hat. Dann sind alle Nachweislinien zu sehen, die unter den gegebenen Versuchsbedingungen überhaupt aus dem Untergrund heraustreten können.

Diese Regel befolgt man zweckmässig auch bei Aufnahmen zur quantitativen Analyse, die nebenher noch zum Nachweis von Verunreinigungen benutzt werden sollen. Man sollte solche Aufnahmen mit einem Stufenfilter machen und dafür sorgen, dass die Schwärzung des Untergrundes in der Stufe voller Durchlässigkeit 0.15 bis 0.2 beträgt. Die Messungen zur Bestimmung der in höherer Konzentration vorhandenen Elemente muss man dann in den geschwächten Stufen machen, in denen die Schwärzung der Analysenlinien brauchbare, nicht zu hohe Werte hat.

V. Die Bestimmungsgrenze k_B

Die Nachweisgrenze $\underline{k}$ gibt an, bis zu welcher Konzentration herunter man ein bestimmtes Element gerade noch mit Sicherheit nachweisen kann; die Möglichkeit, Mengenbestimmungen mit befriedigender Genauigkeit zu machen, hört schon bei höheren Konzentrationen auf. Es ist eine wichtige Frage, bis zu welchen Konzentrationen herunter man mit einer gegebenen Arbeitsvorschrift kommen kann, ohne dass die Genauigkeit der Mengenbestimmung zu sehr nachlässt. Wir setzten nun fest:

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[*] Da wir in diesen Arbeiten den Buchstaben P für alle verallgemeinerten Seideltransformationen verwenden, ist die in[12] tabellierte Transformation mit der Konstanten $l = 0.5$ hier mit $\hat{P}$ bezeichnet.

Die Bestimmungsgrenze k_B soll diejenige Konzentration sein, bei der schon durch die Schwärzungsschwankungen *allein* eine Streuung von 10% der ermittelten Konzentrationswerte auftritt. Ebenso wie die Nachweisgrenze bezieht sich auch die Bestimmungsgrenze auf eine bestimmte Arbeitsvorschrift. Dass wir diese Grenze gerade durch eine Streuung von 10% festgelegt haben, ist willkürlich, doch entspricht diese Grenze dem, was man bei modernen technischen Metallanalysen verlangen muss. Es macht übrigens gar keine Schwierigkeiten, in den zu entwickelnden Formeln anstatt 10% einen anderen Wert, etwa 20 oder 30% einzusetzen, um Sonderfällen gerecht werden zu können. Damit man aber mit der Bestimmungsgrenze einen festen Begriff verbinden kann, ist es zweckmässig, sich auf einen bestimmten Wert für die zulässige Streuung zu einigen, dafür wird hier 10% vorgeschlagen.

Wir haben die Streuung für die Mengenbestimmung selbst auszurechnen. Aus der Eichgleichung (1) ergibt sich mit Hilfe des Fehlerfortpflanzungsgesetzes

$$\sigma_{(\log k)} = \eta \cdot \sigma_{\Delta Y}. \tag{9}$$

Bekannt ist ferner aus Gleichung (4) die Grösse $\sigma_{\Delta Y'}$. Wir brauchen nun noch den Zusammenhang zwischen $\sigma_{\Delta Y}$ und $\sigma_{\Delta Y'}$. Mit $\Delta Y' = \log x$ und $\Delta Y = \log (x - 1)$ bekommen wir wieder:

$$\frac{d\,\Delta Y}{d\,\Delta Y'} = \frac{x}{x-1} \quad \text{und} \quad \sigma_{\Delta Y} = \sigma_{\Delta Y'} \cdot \frac{x}{x-1}. \tag{10}$$

Nun ist für $\sigma_{(\log k)}$ der Wert einzusetzen, der 10% Fehler in der Konzentration entspricht, also

$$\sigma_{(\log k)} = \log 1{,}10 = 0.0414. \tag{11}$$

Aus (11), (9) und (10) ergibt sich: $\sigma_{\Delta Y_B} = \dfrac{0.0414}{\eta} = \sigma_{\Delta Y'} \cdot \dfrac{x_B}{x_B - 1}$.

Daraus kann x_B bestimmt werden, wodurch dann die Bestimmungsgrenze gegeben ist. Die Auflösung ergibt:

$$x_B - 1 = \frac{1}{\dfrac{0.0414}{\eta \cdot \sigma_{\Delta Y'}} - 1}. \tag{12}$$

Damit wird dann

$$\Delta Y_{U_B} = -\log \left(\frac{0.0414}{\eta \cdot \sigma_{\Delta Y'}} - 1 \right). \tag{13}$$

Dieser Wert ist in die Eichgleichung (3) einzusetzen und liefert die Bestimmungsgleichung für k_B:

$$\log k_B = -\eta \log \left(\frac{0.0414}{\eta\, \sigma_{\Delta Y'}} - 1 \right) + \log k_U.$$

Setzt man darin noch für $\sigma_{\Delta Y'}$ den Wert aus (4) ein, so findet man abschliessend

$$\underline{\log k_B = -\eta \log \left(\frac{0.0414\, \gamma_P}{\sqrt{2}\, \eta \frac{dP}{dS}\, \sigma_S} - 1 \right) + \log k_U.} \qquad (14)$$

Bei der praktischen Berechnung dürfte es am zweckmässigsten sein, schrittweise zu rechnen, und zwar zunächst $\sigma_{\Delta Y'}$ aus (4), dann ΔY_{U_B} aus (13) und dann aus der Eichgleichung (3) die Grösse k_B. Auf diese Weise erhält man den besten Überblick.

Zur Gleichung (13) ist noch eine Bemerkung notwendig. Man sieht, dass diese Gleichung nur verwendbar ist, solange $\eta\, \sigma_{\Delta Y'}$ kleiner als 0.0414 ist. Das bedeutet aber, dass die Messung von Schwärzungsdifferenzen an sich — unabhängig von der Konzentration — keine grössere Streuung als 10% liefern darf, sonst wird unsere Forderung sinnlos. Das wird im allgemeinen erfüllt sein. Ausserdem steckt in der Rechnung, so wie sie hier durchgeführt wurde, die Voraussetzung, dass die Schwärzung von Linie + Untergrund nicht wesentlich von der Schwärzung des Untergrundes verschieden ist; denn wir haben für beide Schwärzungen mit demselben σ_S und demselben $\frac{dP}{dS}$ gerechnet. Da aber das Produkt $\sigma_S \cdot \frac{dP}{dS}$ bei Schwärzungen über 0.2 praktisch konstant ist, kann man bei Schwärzungen oberhalb dieser Grenze von der genannten Voraussetzung sogar beträchtlich abweichen.

Vergleicht man nun die Formeln für die Nachweisgrenze und die Bestimmungsgrenze, so sieht man, dass diese beiden Grössen nicht in übersichtlich einfacher Weise miteinander zusammenhängen. Man kann aber für den Fall, dass $\Delta Y'$ sehr klein ist, eine Näherungsrechnung anstellen:

Setzt man nämlich wieder $\Delta Y = \log x$, so gibt die Entwicklung des Logarithmus $\Delta Y' \approx 0.434\ (x - 1)$. Da $\Delta Y = \log\ (x - 1)$ ist, folgt: $\Delta Y \approx \log \Delta Y' + 0.362$. Setzen wir das in (5) ein, so kommt:

$$\underline{\Delta Y_U} \approx \log \sigma_{\Delta Y'} + 0.839. \qquad (15)$$

Wenn $\eta \cdot \sigma_{\Delta Y'} \ll 0.0414$ ist, kann auch (13) entwickelt werden. Zieht man davon (15) ab, so erhält man die Näherungsformel:

$$\Delta Y_{U_B} - \underline{\Delta Y_U} \approx 0.544 + 10{,}5\, \eta\, \sigma_{\Delta Y'} + \log \eta. \qquad (16)$$

Daraus sieht man, dass der Unterschied zwischen der Bestimmungsgrenze und der Nachweisgrenze vor allem durch die Steilheit η der Eichkurve bedingt ist. Wenn η gross ist, kann es vorkommen, dass die Nachweisgrenze für eine bestimmte Linie tief liegt, die Bestimmungsgrenze dagegen hoch. Eine solche Linie wäre in der von *Gerlach*[9] eingeführten Bezeichnungsweise « absolut empfindlich ». Eine steile Eichgerade wirkt ja nach (6) günstig auf die Nachweisempfindlichkeit. Ist dagegen η klein, so ist die Linie nach *Gerlach* « relativ empfindlich »; denn verhältnismässig kleinen Unterschieden in der Konzentration entsprechen grosse Unterschiede der im Spektrum gemessenen Intensitäten nach (3). Dann liegt die Bestimmungsgrenze nahe über der Nachweisgrenze wegen (16); beide brauchen aber nicht sehr tief zu liegen, denn eine schwache Linie, die nur bei höheren Konzentrationen überhaupt zu verwenden ist, kann sehr wohl relativ empfindlich sein. Wegen der Wirkung von η in (6) widersprechen sich die Begriffe absolut- und relativ-empfindlich bis zu einem gewissen Grade, aber nicht vollständig.

Das von *Gerlach* eingeführte Begriffspaar hat einen fest umrissenen Sinn. Leider sind die beiden Begriffe häufig verwechselt worden, vielleicht wegen des etwas verwaschenen Charakters der beiden Fremdwörter. Daher dürfte es zweckmässig sein, nach bestimmteren Bezeichnungen zu suchen und etwa « nachweisempfindlich » und « mengenempfindlich » anstelle von « absolut- und relativ-empfindlich » zu sagen.

Ein Mass für die Nachweisempfindlichkeit ist die Konzentration an der Nachweisgrenze $\underline{k}$, ein Mass für die Mengenempfindlichkeit die Eichkurvenneigung η.

VI. Beispiel für die Anwendung der Theorie

Im Herbst 1944 wurden Messungen begonnen, um die Theorie in grösserem Umfang an der Erfahrung zu prüfen. Diese Untersuchungen konnten nicht zu Ende geführt werden. Hier soll ein Beispiel daraus gebracht werden: die Ermittlung der Nachweis- und Bestimmungsgrenze für Zink in Reinaluminium bei Verwendung verschiedener Lichtquellen.

Die Lichtquellen waren: Der *Feussner*sche Funkenerzeuger (*FF*) mit 6500 pF Kapazität, 17 kV Entladespannung, einmal mit der vollen Selbstinduktion (0,8 mH) und einmal nur mit der Selbstinduktion der Zuleitungen (etwa $6 \cdot 10^{-6}$ H),* und der *Pfeilsticker*sche Wechselstrom-Abreissbogen (*PA*), betrieben mit 10 A Kurzschlussstrom, 5 Zündungen in der Sekunde und dem Verhältnis 1:3 von Brennzeit zu Pause. Die Elektroden waren Stäbchen von

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* Die erste Entladungsart gibt einen weichen, dem Lichtbogen ähnlichen Funken, die zweite einen stromstarken, harten Funken mit hoher Ionisation.

5 mm ∅, ihre Enden wurden halbkugelig abgedreht, der Elektrodenabstand betrug 3,5 mm. Die Aufnahmen wurden in einem *Zeiss*-Spektrographen Q.12 auf Agfa Platten Spektral-blau-extrahart gemacht; die Spaltbreite betrug 0,035 mm. Vor dem Spalt befand sich ein Dreistufenfilter, die zur γ–Bestimmung verwendeten Stufen hatten ein ΔY_m von 0.137. Die Schwärzungen wurden in einem Schnellphotometer von *Zeiss* gemessen, die gemessene Fläche innerhalb der Linien war $0{,}95 \cdot 0{,}029$ mm^2 = 0,028 mm^2.

Als Nachweislinie für Zn wurde nicht die stärkste Linie 2138,6 Å gewählt, sondern die Linie 3345,0 Å, die in einem photographisch günstigeren Gebiet liegt und bei höheren Zn-Gehalten nicht so starke Selbstumkehr zeigt, wie die Hauptnachweislinie. Die Belichtungszeit wurde bei allen Aufnahmen auf Grund von Vorversuchen so gewählt, dass die Schwärzung des Untergrunds neben der Zn-Linie etwa 0.15 betrug.

Die Proben waren Eichelektroden, von den Wieland-Werken hergestellt und analysiert. Die Tabelle 2 gibt die wichtigsten Daten.

Die drei Proben *P*, *Q*, *R* waren Reinaluminium, jede enthielt insgesamt ungefähr 1% der üblichen Verunreinigungen. Die Probe *W* wurde nur zur Ergänzung hinzugenommen, sie war von der Gattung Al-Mg-Mn und enthielt fast 2% Mg neben anderen Zusätzen.

Die Tabelle 3 bringt das Ergebnis der Schwärzungsmessungen

TABELLE 2

Probe	% Al	% Zn	log *k*
P	99	$0{,}03_3$	− 1.48
Q	99	0,11	− 0.95
R	99	0,21	− 0.67
W	95	0,40	− 0.38

Eichproben.

TABELLE 3

		S			$P_{(l\,=\,0{,}25)}$			
	Probe	Zn	*U*	Al	Zn	*U*	Al	
FF $6 \cdot 10^{-6}$ H	*P*	.192	.177	.562	− .144	− .180	.458	$\Delta P_m =$ .176
	Q	.210	.171	.531	− .102	− .195	.418	
	R	.240	.173	.530	− .039	− .190	.416	γ_P = 1.28
	W	.258	.166	.448	− .004	− .208	.305	
FF 0,8 mH	*P*	.247	.179	1.080	− .025	− .175	1.051	$\Delta P_m =$ .224
	Q	.460	.171	1.055	.322	− .195	1.025	
	R	.640	.163	1.020	.556	− .216	.987	γ_P = 1.64
	W	.567	.146	.488	.465	− .262	.360	
PA	*P*	.541	.143	1.490	.431	− .271	1.479	$\Delta P_m =$ .146
	Q	.969	.151	1.358	.933	− .248	1.339	
	R	1.258	.149	1.343	1.239	− .254	1.328	γ_P = 1.07
	W	1.670	.146	1.363	1.063	− .262	1.344	

für die Zn-Linie 3345 Å, den Untergrund daneben und die Al-Linie 3050 Å. Diese war so stark, dass sie in der schwächsten Stufe des Spektrums gemessen wurde, der Untergrund spielt gegenüber dieser Linie keine Rolle. Um die Y-Werte zu berechnen, wurde eine Kenngrösse P mit der Transformationskonstanten $l = 0{,}25$ genommen. Sie gibt im Gebiet um 3300 Å eine fast gerade Kennlinie, ist also als « Gebrauchstransformation » sehr geeignet, da sie sich als Mittel von $\widehat{P}$ und W aus den Tabellen in[12] leicht berechnen lässt. Die Werte von P sind in der rechten Seite der Tabelle 3 angeführt, dazu noch die ΔP_m und die γ_P.

Die Logarithmen der Intensitäten stehen in der Tabelle 4. In der letzten Spalte sind die für den « mittleren Normaluntergrund » kennzeichnenden Werte $\overline{Y_G - Y_{U_Z}}$ angegeben, sie wurden nur aus den Spektren der Reinaluminiumproben berechnet. Diese Werte wurden zu den ΔY_G der drittletzten Spalte addiert und ergaben so die ΔY_U^* der vorletzten Spalte, die also auf den Normaluntergrund von Reinaluminium bezogen sind. (Auch die Werte für die Probe W).

TABELLE 4

	Probe	Y_{Zn}	Y_U	Y_{Al}	$\Delta Y_U'$	ΔY_U	$Y_G - Y_U$	ΔY_G	ΔY_U^*	$\overline{Y_G - Y_U}$ (ohne W)
FF $6 \cdot 10^{-6}$ H	P	− .112	− .140	.357	.028	−1.177	.497	−1.674	−1.192	.482
	Q	− .079	− .152	.326	.073	− .737	.478	−1.215	− .733	
	R	− .030	− .148	.324	.118	− .506	.472	− .978	− .496	
	W	− .003	− .162	.238	.159	− .354	.400	− .754	− .272	
FF 0,8 mH	P	− .015	− .107	.643	.092	− .672	.750	−1.377	− .633	.744
	Q	.197	− .119	.627	.316	.029	.746	− .717	.027	
	R	.340	− .132	.603	.472	.293	.735	− .442	.302	
	W	.284	− .160	.220	.444	.250	.380	− .130	.614	
PA	P	.405	− .254	1.387	.659	.552	1.641	−1.089	.451	1.540
	Q	.875	− .233	1.255	1.108	1.073	1.488	− .415	1.125	
	R	1.161	− .238	1.246	1.399	1.381	1.484	− .103	1.437	
	W	1.560	− .246	1.261	1.806	1.799	1.507	.292	1.832	

Damit wurden die Eichgeraden der Abbildung 4 gezeichnet. Wir betrachten zunächst nur die Messpunkte der Reinaluminium-Proben. Bei den beiden Funkenarten ist es gleichgültig, ob wir die Eichgeraden mit den ΔY_U oder mit den ΔY_U^* zeichnen. Die Werte unterscheiden sich kaum, wir haben die ΔY_U^* genommen. Schon die Schwärzungswerte zeigen, dass Untergrund und Grundlinie bei den Funkenaufnahmen der Proben P, Q, R wenig schwanken. Das ist bei den Aufnahmen mit dem Abreissbogen anders. Hier sind die

Untergrundschwärzungen gut konstant, dagegen ist die Grundlinie bei der Probe *P* stärker. Das war bei allen Aufnahmen mit diesen Proben so. Die Ursache müsste noch festgestellt werden. Der Messpunkt für diese Probe verschiebt sich daher beträchtlich, wenn der ΔY_U-Wert über die Grundlinie auf einen Normaluntergrund bezogen wird. Nun haben Aufnahmen mit anderen Al-Legierungen gezeigt, dass die Eichpunkte für Zn 3345 Å immer etwas besser liegen, wenn die Intensität der Linie unmittelbar auf den Untergrund und nicht auf die Linie 3050 Å bezogen wird. Aus diesem Grunde und wegen des abweichenden Verhaltens der Grundlinie im Spektrum der Probe *P* wollen wir hier die Eichgerade nach den ΔY_U zeichnen. In Abbildung 4 sind aber die Punkte zu den ΔY_U^* auch eingetragen.

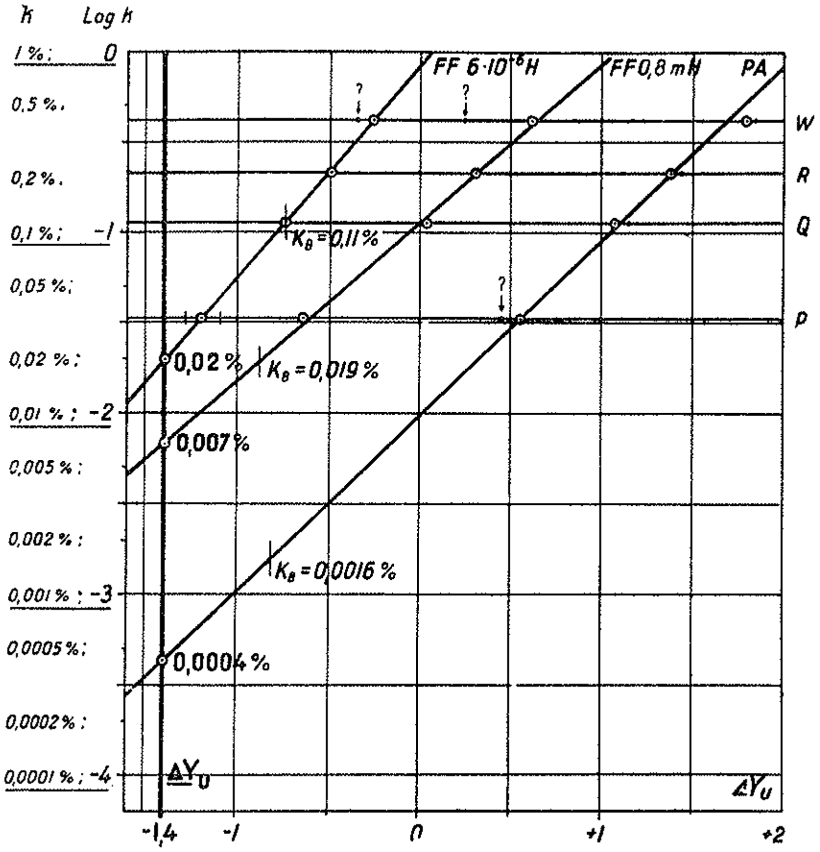

Abb. 4. Eichgeraden, Nachweisgrenzen und Bestimmungsgrenzen für den Nachweis von Zink in Reinaluminium mit *Feussner*-Funken und Abreissbogen.

Nun zur Probe W! Diese Legierungsart verdampft in beiden Funkenarten schlechter als Reinaluminium. Besonders deutlich ist das beim Funken mit 0,8 mH; dort ist die Intensität der Grundlinie nur 0,4 von der Intensität beim Reinaluminium. Der Untergrund dagegen ist nur wenig schwächer. Der Untergrund wird nämlich in den Funkenspektren zum grössten Teil durch das Bremskontinuum der Elektronen hervorgerufen (s. *Finkelnburg*[5]). Er ist deshalb in erster Linie von der Stromdichte abhängig und nicht sehr von der Verdampfung des Metalls. Wir *dürfen* also — wenn wir die Probe W mit den anderen vergleichen wollen — die Zn–Linie gar nicht auf den Untergrund beziehen, wir *müssen* sie auf die Grundlinie beziehen und finden dann über den Normaluntergrund den Anschluss an die Reinaluminium-Proben. Die Abbildung 4 zeigt, dass die Messpunkte dann gut zu den anderen passen. Die Messpunkte zu ΔY_U sind ebenfalls eingetragen, aber mit Fragezeichen versehen.

Beim Abreissbogen ist es wieder anders. Hier passen Untergrund und Grundlinie der W-Probe gut zu denen von Q und R. Anscheinend verdampft die Probe ebenso stark. Trotzdem liegt der Messpunkt nicht auf der von uns gewählten Eichgeraden; besser würde er zur Eichgeraden aus den ΔY_U^* passen. Jedoch haben andere Aufnahmen gezeigt, dass die Eichgerade für die Gattung Al-Mg-Mn anders, vor allem flacher, verläuft als für Reinaluminium. Weshalb das so ist, wissen wir noch nicht; jedenfalls gehört der Punkt für W nicht zu unserer Eichkurve und seine zufällige Lage in ihrer Nähe kann uns nicht sagen, ob wir uns mit den ΔY_U zu der richtigen Eichkurve entschieden haben, die wir ins Gebiet kleinster Konzentrationen fortsetzen dürfen.

Zur späteren Verwendung entnehmen wir aus Abb. 4 noch die Steilheiten η der drei Eichgeraden. Diese sind in der Tabelle 5 mitangegeben.

Wir können jetzt darangehen, die Nachweisgrenzen zu berechnen. Dazu brauchen wir den Wert der mittleren Schwärzungsschwankung σ_S für $S = 0.5$. Für die Plattensorte Agfa Spektral-blau-extrahart und eine Messfläche von 0,028 mm² ergab sich dafür aus sehr vielen Messungen ein durchschnittlicher Wert von 0.003.*

$$\frac{dP}{dS} = 2{,}67 \qquad \text{und nach (8)} \ \sigma_S = 0.002.$$

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* Um dieser Zahl eine anschauliche Bedeutung zu geben, sei erwähnt, dass der Fehler in der Konzentrationsbestimmung, der dieser Plattenstreuung entspricht etwa 1% ist, falls die Steilheiten γ und η von Schwärzungskurve und Eichkurve ungefähr 1 sind.

Die mittlere Schwärzung des Untergrundes ist etwa 0.16; dazu gehört $r = 1{,}45$. l war 0,25. Aus (7) erhalten wir damit:

Für γ_P nehmen wir den mittleren Wert der drei Aufnahmen, also 1,33. (Da γ sehr von den Entwicklungsbedingungen abhängt, hätte es keinen Sinn, die Einzelwerte zu nehmen).

Damit erhalten wir nach (4) und (5)

$$\sigma_{\Delta Y'} = 0.0056 \quad \text{und} \quad \underline{\Delta Y}'_U = 0.017.$$

Die Seideltransformation liefert dann noch

$$\underline{\Delta Y}_U = -1.4.$$

Diese Grenze für ΔY_U ist als senkrechte Gerade links in der Abb. 4 eingetragen. Ihre Schnittpunkte mit den Eichgeraden geben die Nachweisgrenzen $\underline{k}$. Die Werte stehen mit zwei Stellen in der Tabelle 5; es ist aber besser, sie wie in der Abbildung nur mit einer Stelle anzugeben.

TABELLE 5

Lichtquelle	$\underline{\Delta Y}_U$	$\underline{k}$	ΔY_{U_B}	k_B	η
FF; $6 \cdot 10^{-6}$H	– 1.4	$0{,}01_9$%	–.726	$0{,}11_5$%	1,16
FF; 0,8 mH	– 1.4	$0{,}006_8$%	–.872	0,019%	0,87
PA	– 1.4	$0{,}0004_3$%	–.816	0,0016%	$0{,}97_5$

Hätten wir die Eichgerade für den Abreissbogen mit ΔY_U^* gezeichnet, so hätte sich ein höherer Wert für $\underline{k}$, etwa 0,001% ergeben.

Die berechneten Nachweisgrenzen passen recht gut zu den allgemeinen Erfahrungen bei solchen qualitativen Analysen. Bei dem starken Funken sieht man sogar an den Messwerten aus Tabelle 3 und 4, dass die Zn-Linie im Spektrum der Probe *P* gerade noch nachgewiesen werden kann. Diese Nachweisgrenzen gelten nur für Reinaluminium; für die Legierungsart der Probe *W* liegen die Nachweisgrenzen wahrscheinlich etwas höher; im Funken, weil die Linien schwächer im Vergleich zum Untergrund sind; im Abreissbogen, weil die Eichgerade flacher verläuft.

Die berechneten Nachweisgrenzen sind nicht die tiefsten, die man mit den drei Entladungsarten erreichen kann. Sie gelten nur für die gewählten Versuchsbedingungen. Von diesen wirkt besonders die grosse Spaltbreite ungünstig, die aber für die genaue Photometrierung der Aufnahmen nötig war. Bei engerem Spalt liegen die Nachweisgrenzen tiefer, man müsste dann aber länger belichten, um wieder auf die gleiche Untergrundschwärzung zu kommen. Beim Abreissbogen könnte es sein, dass ein Verkleinern der Spaltbreite schliesslich die Nachweisgrenze wieder ungünstig beeinflusste, wenn dadurch eine Bandenstruktur des Untergrundes deutlicher herauskäme.

Sehen wir von dieser Möglichkeit einmal ab, so geben die ermittelten Zahlen das Verhältnis der Nachweisempfindlichkeiten der drei Lichtquellen; denn die übrigen optisch-photometrischen Bedingungen waren bei den drei Aufnahmen dieselben. Insbesondere ist also der Abreissbogen rund 50mal so empfindlich für den Zn-Nachweis in Reinaluminium wie der stromstarke *Feussner*-Funke ohne Selbstinduktion.

Die Tabelle 5 enthält endlich noch die Daten für die Bestimmungsgrenzen, die nach (13) berechnet worden sind. Die Bestimmungsgrenzen k_B sind auch in der Abbildung 4 kenntlich gemacht. Für den stromstarken Funken liegt diese Grenze schon bei der Konzentration der mittleren Probe *R*, sodass der Messpunkt für die Probe *P* schon recht unsicher ist. Die Grenzen des Bereichs der mittleren Schwankung für das ΔY_U der unteren Probe sind durch kleine senkrechte Striche in der Abbildung 4 angedeutet. Sie ergeben sich aus dem $\sigma_{\Delta Y'}$. Für diese Funkenart wäre noch eine Reinaluminiumprobe mit höherem Zn-Gehalt erwünscht gewesen. Da keine vorhanden war, wurde die fremde Probe *W* hinzugenommen, in der Hoffnung damit die Eichgerade etwas sicherer festlegen zu können.

VII. Übersichtsanalysen mit Hilfe der Nachweisgrenze

Die Überlegungen über die Nachweisgrenze eröffnen eine Aussicht, das älteste leitprobenfreie Verfahren zur grössenordnungsmässigen quantitativen Analyse, nämlich das Verfahren der « Zählung der letzten Linien », nach dem *Hartley*, *Pollok*, *Leonard*, sowie *de Grammont* gearbeitet haben, in vervollkommneter Form wieder zu beleben. Bei diesem Verfahren wurde der Gehalt der Probe an einem Element dadurch bestimmt, dass im Spektrum der Probe geprüft wurde, wieviel Analysenlinien des gesuchten Elementes noch zu sehen waren. An Hand von vorher ausgearbeiteten Tabellen konnte dann aus der Anzahl der vorhandenen Nachweislinien die Grössenordnung des Gehaltes ermittelt werden. Die genannten Spektrochemiker haben erfolgreich nach diesen Verfahren arbeiten können. Die Voraussetzung war, dass die Versuchsbedingungen, für die ihre Tabellen ausgearbeitet waren, sehr sorgfältig eingehalten wurden. Eine Zusammenstellung solcher Tabellen haben *Twyman* und *Smith*[23] gegeben. Es ist aber mit Recht beanstandet worden, dass dieses quantitative Verfahren nicht übertragbar ist, weil der Schwellenwert der gesamten Apparatur als Messmittel benutzt wird. Die veröffentlichten Tabellen dieser Art lassen zwar erkennen, wie die Analysenlinien eines Elementes mit abnehmender Konzentration verschwinden; sie sind aber für die Gehaltsbestimmung praktisch wertlos, weil es kaum gelingen dürfte, die ursprünglichen Versuchsbedingungen mit anderen Geräten, Platten und Lichtquellen wieder herzustellen. Daher ist das Verfahren der Zählung der letzten Linien mit der fortschreitenden Entwicklung der spektrochemischen Analyse verlassen worden. Es wurde vor allem durch das *Gerlach*sche Verfahren der homologen Linienpaare verdrängt.

Ein Verfahren zur Übersichtsanalyse, bei dem man nur nachzusehen brauchte, welche Linien des gesuchten Elementes noch da sind und welche nicht, wäre aber wegen seiner Einfachheit sehr erwünscht. Ein solches Verfahren lässt sich heute aufbauen, wenn man die Konzentrationen ermittelt, bei denen verschieden starke Analysenlinien des Elementes im Untergrund verschwinden. Der wesentliche Unterschied gegenüber dem alten Verfahren besteht darin, dass nicht mehr der absolute Schwellenwert der ganzen Anordnung als Messmittel dient, sondern die mittlere Schwärzungsschwankung. Diese ist an und für sich viel weniger veränderlich als der absolute Schwellenwert, sie ist durch die Körnigkeit der Plattensorte und die Grösse der Messfläche bestimmt, ausserdem lässt sich ihre Grösse in jedem Einzelfall ermitteln.

Abgesehen davon, dass ein anderes Messprinzip benutzt werden soll, können heute die Anregungsbedingungen in der Lichtquelle viel besser festgelegt und beschrieben werden als früher. Für die Funkenentladungen des *Feussner*-Funkenerzeugers, den *Pfeilsticker*-Abreissbogen, den Lichtbogen zwischen Kohleelektroden und die Flamme können die Versuchsbedingungen so genau angegeben werden, dass dieselben Anregungsbedingungen, für die Analysentabellen ausgearbeitet wurden, überall wiederhergestellt werden können. Wir brauchen uns hier daher nur mit dem photometrischen Messprinzip zu beschäftigen. Dazu müssen wir die Eichgleichung (3) und die Gleichung (5) beachten. Aus der Gleichung (5) ergibt sich als erste Voraussetzung für das Verfahren die Wahl der richtigen Belichtungszeit. So lange muss belichtet werden, dass die Schwärzung des Untergrundes an den Stellen, wo die Nachweislinien liegen, überall grösser als 0.2 ist. Dann ist das Produkt $\frac{dP}{dS}\,\sigma_S$ praktisch konstant. Seine Grösse hängt natürlich von der verwendeten Plattensorte ab, ebenso wie die Steilheit γ_P. Man wird also die Tabellen zweckmässig ausarbeiten für eine bestimmte, viel verwendete Plattensorte, z. B. für die Agfa-Spektralplatte extrahart, und eine bestimmte Grösse der Messfläche, die bei der Aufstellung der Eichkurven mit Hilfe photometrischer Messung benutzt wird. Es macht aber keine Schwierigkeiten, die Nachweisgrenzen umzurechnen für eine andere Plattensorte, wenn man die Grösse von $\sigma_{AY'}$ und die Konstanten der Eichkurve angibt, die der Tabelle zugrundeliegen. Die Übertragbarkeit auf andere Messbedingungen ist also gewährleistet, jedoch wird es zweckmässig sein, möglichst die vorgeschriebenen zu verwenden.

In der Eichkurvengleichung stecken ausser den Bedingungen der Lichtquelle auch die Daten der optischen Anordnung, vor allem Dispersion und Spaltbreite des Spektrographen. Davon hängt in der Eichkurvengleichung die Konstante k_U ab, in der ja das Verhältnis der Intensität der Linien zur Intensität des Untergrundes enthalten ist. Man muss also dafür sorgen, dass man mit verschiedenen Spektrographen dieselbe Konstante k_U bekommt. Grundsätzlich lässt sich das erreichen, indem man vorschreibt, dass die Spaltbreite so eingestellt werden soll, dass das Intensitätsverhältnis einer bestimmten schwachen Linie des *Grund*elementes zum Untergrund einen vorgeschriebenen Wert bekommt. Auch hier dürfte es zweckmässig sein, die Tabellen für bestimmte weitverbreitete Spektrographentypen aufzustellen, z. B. für einen Quarzspektrographen mittlerer Grösse mit 60 cm Kamerabrennweite. Ehe man sich zu bestimmten Versuchsbedingungen entschliesst, muss man sich genau überlegen, wie man die Bedingungen im einzelnen wählen soll, damit kleine Änderungen möglichst wenig ausmachen und damit für die Übertragung auf andere Geräte genügend Spielraum besteht. Z. B. kann man von vornherein sagen, dass man mit Spaltbreiten arbeiten muss, die grösser als die förderliche Spaltbreite sind, damit die Beugung an der Öffnung des Spektrographen, die bei den verschiedenen Spektrographen verschieden stark sein kann, nur wenig Einfluss auf das Aussehen der Linien hat. Die Aufstellung der Tabellen und ihre Benutzung ist sehr einfach, wenn man sich einmal zu bestimmten zweckmässigen Versuchsbedingungen entschlossen hat. Es dürfte lohnend sein, vor allem für die technisch wichtigsten Metallegierungen, derartige Tabellen zur Übersichtsanalyse zusammenzustellen, weil damit ohne jede photometrische Messung eine Angabe über die Grössenordnung der vorhandenen Gehalte verschiedener Elemente gemacht werden kann. Man muss sich darüber klar sein, dass derartige Tabellen wirklich nur zu Übersichtsanalysen verwendet werden können. Was man bekommen kann, ist vielleicht eine halbe Zehnerpotenz. Genauere Angaben kann man mit Hilfe der Nachweisgrenzen nicht machen, dazu sind diese selbst, ihrer statistischen Definition nach, nicht genau genug bestimmbar. Das vorgeschlagene Verfahren steht auf der untersten Stufe der photometrischen Rangordnung der leitprobenfreien Verfahren[13]. Dem entspricht seine geringe Genauigkeit. Das von *Gerlach* angegebene Verfahren der homologen Linienpaare steht eine Stufe höher. Bei ihm wird bekanntlich die Linie des Zusatzelementes verglichen mit einer Linie des Grundelementes, also wird Gleichheitsphotometrie mit dem Auge getrieben. Infolgedessen lässt sich mit dem Verfahren der homologen Linienpaare auch eine beträchtlich höhere Genauigkeit bei der Gehaltsangabe erreichen, die in günstigen Fällen einer Streuung von etwa 20% entsprechen mag. Es dürfte heute an der Zeit sein, diese Verfahren zur (halbquantitativen) Übersichtsanalyse und zur quantitativen Analyse geringer Genauigkeit neu zu bearbeiten. In ihnen zeigt sich die Leistungsfähigkeit der spektrochemischen Analyse in besonderem Glanz. Notwendig sind genormte Arbeitsverfahren und allgemeingültige Analysentabellen, durch deren Benutzung die mühseligen Vorarbeiten bei der einzelnen Analyse überflüssig würden. Welches Laboratorium verfügt aber heute über die Arbeitskräfte, die nötig wären, um die umfangreichen, einheitlich anzulegenden Reihenuntersuchungen für ein solches Programm auszuführen?

Die Aufnahmen für das Beispiel hat Frl. *Riebe* gemacht, die Aufnahmen zur Untersuchung der Schwärzungsschwankungen Frl. *Richter*. Ihnen beiden möchte ich herzlich danken.

Zusammenfassung

Die spektrochemische Nachweisbarkeit der Elemente ist dadurch begrenzt, dass die Analysenlinien mit abnehmender Konzentration schliesslich so schwach werden, dass sie sich nicht mehr vom Untergrund abheben. In dieser Arbeit wird die «Nachweisgrenze» durch eine Messvorschrift definiert: An der Nachweisgrenze soll der Schwärzungsunterschied, mit dem die Linie sich über den Untergrund erhebt, das $3 \cdot \sqrt{2}$ fache der mittleren Schwärzungsschwankung sein. Die zugehörige Konzentration kann durch Extrapolation aus einer Eichkurve berechnet werden, die im Bereich zuverlässig bestimmbarer Gehalte aufgestellt wird. Man braucht also keine Proben mit den niedrigen Gehalten im Gebiet der Nachweisgrenzen. Die Genauigkeit bei Mengenbestimmungen nimmt mit abnehmender Konzentration ab. Als «Bestimmungsgrenze» wird die Konzentration definiert, bei der die Streuung des Verfahrens infolge der Schwärzungsschwankungen 10% vom angegebenen Gehalt beträgt.

Diese Überlegungen bieten die Möglichkeit, verschiedene Lichtquellen, Anordnungen und Arbeitsvorschriften hinsichtlich ihrer Nachweisempfindlichkeiten zahlenmässig zu vergleichen. Dafür wird ein experimentelles Beispiel, Zn-Nachweis in Al, gebracht. Erörtert wird ferner die Frage, wie man ein einfaches Verfahren zur Übersichtsanalyse aufbauen könnte, wenn man die Nachweisgrenzen verschieden starker Linien des zu bestimmenden Elements als Messmittel benutzt.

Résumé

La détection spectrochimique des éléments est limitée par le fait qu'en diminuant la concentration il arrive un moment où les raies analytiques ne se distinguent plus du fond spectral.

Dans cette communication on précise la notion de «limite de détection» par la définition suivante: La limite de détection est atteinte lorsque la différence de noircissement entre la raie et le fond est égale à $3\sqrt{2}$ fois l'écart moyen des mesures de noircissement.

La concentration correspondante peut être calculée en se servant d'une courbe de dosage établie dans un domaine de concentration facilement mesurable. Il n'est pas nécessaire de recourir à des échantillons de très faible teneur voisine de la limite de détection.

La précision des dosages diminue avec la concentration. On peut définir la «limite de détermination» comme étant la concentration pour laquelle la dispersion des résultats atteint, par suite des variations de noircissement, 10% de la teneur réelle.

Ces considérations permettent de comparer numériquement au point de vue de leur sensibilité spectrale, des sources de lumière, des montages, des modes opératoires différents. Le cas du zinc dans l'aluminium est traité expérimentalement à titre d'exemple.

On traite enfin de la possibilité d'effectuer une analyse rapide en se servant des valeurs connues des limites de détection de plusieurs raies de différentes intensitées des éléments à déterminer.

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Chemische Vorgänge in Kohleelektroden

OTTMAR LEUCHS
Forschungsstelle für Geochemie im Mineralogisch-Geologischen Institut der Technischen Hochschule, München

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Der bei spektrochemischen Analysen häufig verwendete Gleichstromkohlelichtbogen ist schon eingehend beschrieben worden. Für die Auswertung spektrochemischer Analysen genügt es jedoch nicht, nur die Vorgänge im Lichtbogen zu kennen. Das Bild wird erst vollständig, wenn man sich auch über die Diffusionsvorgänge, die die verdampfte Substanz in den Lichtbogen führen, Rechenschaft ablegt. Da die Diffusionsvorgänge mit der Verdampfung einer Substanz einsetzen, ist auch die Kenntnis der chemischen Reaktionen in der Lochkohle notwendig; denn diese Reaktionen bestimmen die Verdampfungstemperatur der Substanzen. Ohne die Berücksichtigung von chemischen Reaktionen und Diffusionsvorgängen bleibt die Auswertung von Analysen mit Hilfe von Eichsubstanzen auf einen sehr engen Kreis gleichartiger Substanzen beschränkt.

Die vorliegende Arbeit geht von der Beschreibung der chemischen Reaktionen aus und bespricht die Auswirkung dieser Reaktionen auf die Diffusion und auf den Nachweis der einzelnen Elemente. Die zu Grunde liegenden Beobachtungen wurden bei der Analyse oxydischer Eisenerze mit Hilfe des Gleichstromkohlelichtbogens gemacht. Daher gelten manche der chemischen Betrachtungen mehr für oxydische als für sulfidische Systeme.

I. Versuche und Beobachtungen

A. VERSUCHSANORDNUNG

Die Versuche wurden unter folgenden Bedingungen durchgeführt:

Schaltung der Lochkohle als Anode	
Stromstärke	5·5–8 amp
Bogenlänge	1·3 mm
Durchmesser der Lochkohle	3 mm
Bohrung der Lochkohle	1·3 mm weit; 5 mm tief
Füllung der Lochkohle	1 Gew. Teil Substanz, gemischt mit 1 Gew. Teil Kohlepulver
Gegenelektrode	Kohlestab, 5 mm Durchmesser
Brenndauer der Lochkohle	100 sec

Die Schaltung der Lochkohle als Anode gestattet eine höhere Erhitzung der Analysensubstanz, als es kathodisch möglich wäre. Die Temperatur des Anodenbrennflecks liegt unter diesen Umständen auf reinen Kohleelektroden bei der Sublimationstemperatur des Kohlenstoffs. Ueber die Höhe der Sublimationstemperatur des Kohlenstoffs gehen die Angaben in der Literatur etwas auseinander. Es wird daher in dieser Arbeit mit rund 3500° C gerechnet. In 5 mm Entfernung vom Brennfleck, d.h. am Grunde der Bohrung der Lochkohle herrscht immer noch eine Temperatur von etwa 1600° C, wie orientierende Messungen mit einem Strahlungspyrometer wahrscheinlich machten. Die Stromstärke von etwa 6 amp genügt, um

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auch Ti und V in Eisenerzen vollständig und ohne Verlängerung der Brenndauer zu verdampfen. Die Gegenelektrode (Kathode) kann sehr kurz gehalten werden, da sie im kurzen Bogen kaum einen Abbrand zeigt, und da der Kathodenbrennfleck nicht zu wandern oder auf die Halterung überzuspringen vermag.

Durch die Mischung der Analysensubstanz mit Kohlepulver nach PREUSS [1] wird ein ruhiger Abbrand gewährleistet. Die geschmolzene Substanz haftet in dünner Schicht am Kohlepulver und kann nicht zu dickeren Tröpfchen zusammenfliessen. Leichtflüchtige Substanzen können leicht absieden. Es gibt verhältnismässig wenige Substanzen, welche auch im unteren Teil einer glühenden Lochkohle noch nicht schmelzen.

Die in den Versuchen 5–6 und 8–10 erwähnte "Universalmischung" enthält als Grundsubstanz Fe_2O_3, welchem je 1% der Oxyde von folgenden Elementen beigemischt wurde: Ag, Al, As, B, Ba, Be, Ca, Co, Cr, Cu, Ga, In, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Sr, Ti, V, Zn, Zr; Grundsubstanz und Spurensubstanzen sind 1 : 1 mit Kohlepulver gemischt.

B. NACHWEIS CHEMISCHER REAKTIONEN

1. Reduktion

1. Versuch

Beim Oeffnen einer im Kurzschlussstrom kräftig geglühten oder erst recht einer einige Sekunden gebrannten Lochkohle, die mit Fe_2O_3/C-Mischung gefüllt wurde, stellt man fest, dass die rostbraune Farbe der Füllung verschwunden ist. Die durchgeglühte Füllung entwickelt mit verdünnter Salzsäure lebhaft Wasserstoff, was sie vorher nicht tut. Das Eisenoxyd Fe_2O_3 wurde also zu metallischem Eisen Fe reduziert.

2. Carbidbildung

a) Calciumcarbid 2. Versuch

Eine mit CaO/C-Mischung gefüllte Lochkohle wird einige Sekunden im Lichtbogen gebrannt, Dann wird der Lichtbogen gelöscht und die Lochkohle sofort in ammoniakalische Kupfer(I)chloridlösung geworfen. Das Wasser entwickelt aus dem in der Hitze gebildeten Calciumcarbid Acetylen, welches sich mit Kupferionen zu rotem, flockigem Kupferacetylid Cu_2C_2 umsetzt. Aus salpetersaurer Silbernitratlösung wird entsprechend weisses, käsiges Silberacetylid Ag_2C_2 gefällt.

b) Zirkoncarbid 3. Versuch

Beim Abbrennen einer mit ZrO_2/C-Mischung gefüllten Lochkohle bildet sich auf der Anode eine Schmelzkuppe von metallischem Aussehen. Der Kohlenstoff der Lochkohle verdampft schneller als diese Schmelze, so dass bald Teile der Schmelze als Tröpfchen seitlich herunterrollen. Der Siedepunkt der Schmelze liegt also oberhalb der Sublimationstemperatur des Kohlenstoffs. Demnach handelt es sich um geschmolzenes Zirkoncarbid, welches Kohlenstoff gelöst enthält. Trotz der Verluste an ZrC durch Abtropfen beträgt die Abbrenndauer ein Vielfaches einer entsprechenden Fe_2O_3-Füllung.

Füllt man die Lochkohle mit TiO_2 oder V_2O_5, dann bilden sich in entsprechender Weise die Carbide von Ti und V; diese haben aber eine wesentlich tiefere Siede- bzw. Zerfallstemperatur, so dass die Brennflecktemperatur zur sofortigen Verdampfung ausreicht. Die Abbrenndauer ist kaum länger als die einer entsprechenden Fe_2O_3-Füllung.

3. Verbindungs- und Legierungsbildung

a) Verbindung mit der Grundsubstanz 4. Versuch

Die erste Lochkohle wird mit As_2O_3/C-Mischung gefüllt, die zweite Lochkohle mit einer Fe_2O_3/C-Mischung, welche 1% As_2O_3 enthält. Im ersten Fall lassen sich auf der Platte nur schwache As-Linien erkennen, während sie im zweiten Fall intensiv hervortreten.

Im ersten Fall gelangt nur ein sehr kleiner Teil des As_2O_3 in den Lichtbogen. Infolge der jähen Erwärmung der Lochkohle beim Zünden sind die Verluste sehr gross. Anders im zweiten Fall. Eisen und Arsen treten nach der Reduktion durch Kohlenstoff zu Fe_2As zusammen [2]. Fe_2As hat eine erheblich höhere Siede- bzw. Zerfallstemperatur als Arsen.

Man ersieht hieraus, dass die Linien ein und desselben Elementes umso intensiver hervortreten, je höher die Verdampfungstemperatur seiner gerade vorliegenden Verbindung ist.

b) Legierung zwischen Spurenelementen 5. Versuch

Zwei Lochkohlen werden in derselben Weise mit der " Universalmischung " gefüllt. Die erste wird direkt abgebrannt, die zweite erst nachdem sie 10 sec im Kurzschlussstrom auf helle Rotglut erhitzt wurde. Die Aufnahme der vorgeglühten Lochkohle zeigt die Linien von Blei und Zink relativ zu den Eisenlinien stärker als die der nicht vorgeglühten.

Man hätte erwartet, dass durch das Vorglühen die relative Intensität der Blei- und Zinklinien sich entweder gar nicht ändert oder etwas kleiner wird, da Blei und Zink verhältnismässig tiefsiedende Elemente sind. (Nach einem Vorglühen von 60 sec sind sie tatsächlich deutlich geschwächt). Doch das Gegenteil ist der Fall. Da Blei und Zink von flüssigem Eisen nicht gelöst werden und keinerlei Verbindungen mit Kohlenstoff bilden, müssen sich also beim Vorglühen Legierungen mit anderen Spurenelementen bilden. Dadurch wird ein Teil der beiden Elemente bei höherer Temperatur verdampft, so dass die Linien der Elemente stärker hervortreten.

C. NACHWEIS EINIGER PHYSIKALISCHER VORGÄNGE

1. Diffusion

a) Diffusion in die Lochkohlewand 6. Versuch

Eine mit einer " Universalmischung " gefüllte Lochkohle wird im Kurzschlussstrom wenige Sekunden auf helle Rotglut erhitzt, aber nicht gezündet, sondern nach Abkühlung sorgfältig geleert und erst dann leer abgebrannt. Die Aufnahme zeigt bevorzugt die leichtflüchtigen, gasförmig in die Lochkohlewand diffundierten Elemente, weniger die hochsiedenden Elemente.

b) Diffusion durch die Lochkohlewand hindurch 7. Versuch

Eine mit Fe_2O_3/C-Mischung, die 10% CaO enthält, gefüllte Lochkohle wird abgebrannt. Das bei der Reduktion von CaO entstehende Ca diffundiert sehr stark, bevor es bei noch höherer Temperatur zu Calciumcarbid gebunden wird. Calcium siedet bereits bei 1487° C, das Gleichgewicht der Reaktion $CaO+C=Ca+CO$ liegt bei 1600° C. Die Carbidbildung beginnt erst bei noch höherer Temperatur. Kommt das gasförmige Calcium nach Durchwandern der Lochkohlewand mit der kälteren Aussenluft in Berührung, so wird es sofort wieder gebunden, etwa zu CaO oder

Ca_3N_2. Es bildet sich dabei in etwa 4·5 mm Entfernung vom Brennfleck ein weisser Ring (Abbildung 1). Dieser verdampft stark; der Anodenbrennfleck springt unter Verlängerung und Verbreiterung des Lichtbogens von Zeit zu Zeit auf ihn herunter und " frisst " ihn auf, wobei er die Lochkohle unter lautem Zischen umkreist. Zugleich erhöht sich die Stromstärke für die Dauer des Zischens. Daraus geht hervor, dass der elektrische Widerstand der Lichtbogengase während des Zischens geringer ist, und dass der Brennfleck eben deshalb auf den Ring herunter springt.

Ersetzt man CaO durch ZnO, dann bildet sich ein ebensolcher Ring aus ZnO. Dieser wird aber nicht vom Brennfleck aufgefressen, wahrscheinlich weil die entstehenden Zinkgase zu schlecht leiten. Der ZnO-Ring wird dicker und dicker, zu einem "Kragen", und bröckelt schliesslich ab, ohne dass dieser Teil der Zinkfüllung in den Lichtbogen gelangt.

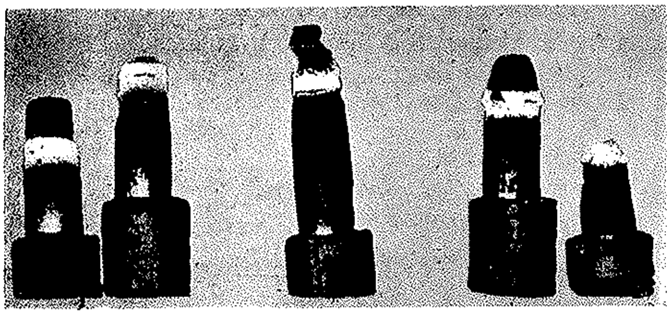

Abb. 1—Ringbildung infolge Diffusion der Füllung durch die Wand der Lochkohle.

1. von links: Lochkohle mit MgO-Füllung nach 80 sec Brenndauer als Anode; 6 amp; 1·3 mm Elektrodenabstand. Tiefliegender Ring aus MgO.—2. von links: wie 1., aber als Kathode; 4 mm langer Bogen, hochliegender Ring.—3. von links: wie 2., aber nur 1 mm langer Bogen. Pilzbildung über der Füllung.—4. von links: Lochkohle mit bröckeligem ZnO-Kragen; sonst wie 1.—5. von links: Lochkohle mit Ca-Mg-Silikatfüllung nach 330 sec Brenndauer als Kathode; 6 amp; 4 mm Elektrodenabstand. Füllung unvollständig verdampft. Eine entsprechende Lochkohle brennt als Anode in 130 sec ohne jeden Rückstand ab.

Im Falle von Calcium und Zink sind die durch die Diffusion hervorgerufenen Verluste infolge weiterer chemischer Reaktionen sichtbar geworden. Sie treten aber bei allen tiefsiedenden Elementen ein und sind umso grösser, je tiefer die Verdampfungstemperatur liegt.

c) *Bestimmung der relativen Grösse der Diffusion* 8. Versuch

Die Bohrung einer Lochkohle wird nur zu einem Viertel mit der " Universalmischung ", im übrigen mit reinem Kohlepulver gefüllt. Dieses wird beim Abbrand zuerst vom Brennfleck erfasst. Es wäre denkbar, dass in der ersten Zeit des Brandes nur Kohlenstofflinien ausgestrahlt würden. Stellt man aber von einem Abbrand nacheinander vier gleichlang belichtete Aufnahmen her, so findet man die tiefsiedenden Elemente, wenn auch mit schwachen Linienintensitäten, ausschliesslich oder hauptsächlich auf der ersten Aufnahme, während die hochsiedenden. Elemente ausschliesslich auf der dritten und vierten Aufnahme zu erkennen sind. Zwischen 1800° und 2600° C siedende Elemente finden sich bevorzugt auf den mittleren Aufnahmen. Durch Vergleich der Linienintensitäten verschiedener Elemente auf den vier Aufnahmen lässt sich die Reihenfolge ersehen, in der die Elemente verdampfen.

Die Arsenlinien sind auf der ersten Aufnahme schwach, auf der dritten Aufnahme kräftig zu sehen; auf der zweiten und vierten Aufnahme fehlen sie ganz. Die erste Aufnahme zeigt durch Eisen nicht gebundenes, in den Lichtbogen diffundiertes Arsen, während die dritte Aufnahme das aus dem Zerfall von Fe_2As frei werdende Arsen erfasst (vgl. 4. Versuch).—Im 6. Versuch findet man ebenfalls etwas Arsen in der Lochkohlewand.

d) Siedepunktsbestimmung aus der Diffusion 9. Versuch

Vergleicht man die Linien der Elemente Blei, Indium und Gallium auf den vier Aufnahmen des 8. Versuches, dann ergibt sich, dass der unbekannte Siedepunkt des Indiums etwa in der Mitte zwischen den Siedetemperaturen des Bleis und des Galliums liegen muss. Das bedeutet etwa eine Temperatur von 1880° C. Der Fehler dieser Bestimmung kann vielleicht ± 100° C betragen und dürfte in speziellen Versuchen sehr zu verringern sein.

e) Reduktionstemperatur aus der Diffusion 10. Versuch

Aus dem 8. Versuch geht weiter hervor, dass Silber und Magnesium in nahezu gleichem Ausmass diffundieren. Diese beiden Elemente verhalten sich so, als hätten sie den gleichen Siedepunkt. Silber siedet bei 2170° C und reagiert weder mit Kohlenstoff noch mit der Grundsubstanz Eisen. Magnesium siedet bei 1102° C und als MgO bei 2800° C. Auch Magnesium wird weder durch Kohlenstoff noch durch Eisen gebunden oder gelöst. Da es bei etwa 2170° C in die Gasphase übertritt, muss dies die Temperatur sein, bei der die Hauptmenge des MgO zu gasförmigen Magnesium reduziert wird, bei der also die Reaktion $MgO+C=Mg+CO$ abläuft. Der Dampfdruck von $(Mg+CO)$ wird hier gleich 1 atm.

2. Kohledampfstrahl und Kohlepilzbildung

11. Versuch

Eine mit Pyrit, FeS_2, und Kohlepulver gefüllte und vorgeglühte Lochkohle wird bei 6 amp oder höherer Stromstärke so abgebrannt, dass der Abstand zur Kathode 1–1·2 mm lang bleibt. Die kältere Kathode kann dann von einem aus der Anode hervorschiessenden Kohledampfstrahl getroffen werden. Der Kohlenstoff kondensiert sich auf ihr in Form eines kleinen, zeitweilig sehr rasch wachsenden Pilzes (Abbildung 2). Der Pilz kann kegelförmige Gestalt mit glatten Seitenflächen (Abbildung 2, links) oder zylinderförmige Gestalt mit zerklüfteten Seitenflächen (Abbildung 2, rechts) oder Zwischenformen annehmen. Er entsteht nicht nur im Hochstromkohlebogen, sondern auch bei 6 amp und zeigt, dass die Verdampfung des Kohlenstoffs sehr rasch vor sich geht.

Abb. 2—Pilzbildung im 6 amp-Lichtbogen auf der Kathode. 1 mm Elektrodenabstand.

3. Beobachtung der Brenndauer

12. Versuch

Unter den eingangs mitgeteilten Arbeitsbedingungen zischt der Lichtbogen laut hörbar, wenn der Bogen in Gasen von hoher Ionisierungsspannung brennt. Elemente mit mittlerer oder niederer Ionisierungsspannung brennen nahezu lautlos ab, sofern ihre Konzentration im Kohlegas genügend gross ist. So ist das

Ende des Abbrandes einer " Universalmischung " am plötzlich einsetzenden Zischen des Bogens in reinen Kohlegasen zu erkennen. Es ist damit ein bequemes akustisches Mittel zur Kontrolle der Brenndauer gegeben.

Beim Uebergang vom lautlosen zum zischenden Bogen erhöht sich einerseits die Temperatur der Lichtbogengase, da die Gase vorher aus leichtionisierbaren Atomen und Molekülen (im Gemisch mit Kohlenstoff) bestehen, nachher aber nur aus Kohlenstoffatomen beziehungsweise -molekülen [3]. Andererseits erhöht sich zugleich der elektrische Widerstand der Gase; die Stromstärke nimmt ab.

II. Die chemischen Vorgänge

In diesem Teil werden die chemischen Reaktionen allgemein besprochen und speziell das Verhalten der einzelnen Elemente in Zwei- und Mehrstoffsystemen (als Grundsubstanzen und als Spurensubstanzen) untersucht.

A. ALLGEMEINES ÜBER CHEMISCHE REAKTIONEN IN KOHLEELEKTRODEN

Die Temperaturen in der Lochkohle übersteigen die eines Hochofens beträchtlich. Daher spielen sich in ihr entsprechende chemische Vorgänge ab. Man kann vier Typen unterscheiden:

1. Die thermische Zersetzung
2. Die Reduktion
3. Die Legierungsbildung
4. Die Verbindungsbildung

Welche Reaktionen im Einzelfalle ablaufen, hängt von den besonderen Umständen ab. So sind die Reaktionen schon verschieden, wenn ein Element* als Sulfid oder wenn es als Oxyd vorliegt. Um den Ueberblick über die nun zu besprechenden Reaktionen zu erleichtern, sei eine Tabelle vorangestellt, aus der die Schmelz- und Siedetemperaturen einiger Elemente, Oxyde und Carbide, soweit bekannt, zu ersehen sind. (Tabelle 1.)

1. Die thermische Zersetzung

Manche Verbindungen zerfallen beim Erhitzen in ihre Bestandteile. So spaltet Pyrit FeS_2 in der Hitze zunächst 1 Atom Schwefel ab, wobei FeS zurückbleibt. Möglicherweise wird dabei Schwefelkohlenstoff CS_2 gebildet. FeS zerfällt bei noch höheren Temperaturen weiter in Fe und S. Silberoxyd Ag_2O zerfällt bereits bei 190° C in Ag und O. Calciumcarbonat $CaCO_3$ zerfällt bei 910° C in CaO und CO_2. Calciumsulfat $CaSO_4$ zersetzt sich zu einem Teil in CaO und SO_3.

Bei diesen Reaktionen werden gasförmige Substanzen gebildet, welche entweichen und damit die Einstellung eines Gleichgewichts verhindern. Der Zerfall geht umso schneller vor sich, je höher die Temperatur ist. Bei einer bestimmten Temperatur erreichen die gasförmigen Zersetzungsprodukte den Dampfdruck von 1 atm; bei dieser Temperatur wird die Verbindung instabil.

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* Anm.: Der Begriff "Element" soll alle chemischen Bindungszustände eines Elementes (z.B. Ca, CaO, CaC_2 usw.) zusammenfassen, während der Begriff "Metall" den elementaren oder metallischen Zustand (z.B. Ca, Mg, Fe usw.) von den gebundenen Zuständen unterscheidet. Das Metall kann fest, flüssig oder dampfförmig vorliegen.

Tabelle 1

Schmelz- und Siedepunkte einiger Metalle, Oxyde und Carbide in °C. Erste Ionisierungsspannung in Volt. (Nach D'ANS-LAX, Taschenbuch für Chemiker und Physiker und REMY, Lehrbuch der Anorganischen Chemie.)

	Element		*Oxyd*		*Carbid*		*1. Ionisierungsspannung*
	Smp	Sdp	Smp	Sdp	Smp	Sdp	
Ag	961	2170	—	—	—	—	7·58
Al	658	2500	2046	2700	1400	—	5·94
As	—	616	—	321	—	—	10·05
B	2300	2550	294	—	2350	3500	8·21
Ba	710	1638	1923	2000	1773	—	5·21
Be	1280	2967	2530	—	2100	—	9·3
C	—	ca3500	–205	--191·5	—	—	11·24
Ca	850	1487	2570	2850	2300	—	6·25
Co	1492	3185	1810	—	—	—	7·8
Cr	1920	2327	1990	—	1820	—	6·7
Cu	1084	2595	1336	—	—	—	7·67
Fe	1535	2730	1530	—	1837	—	7·83
Ga	29·5	2064	1741	1900	—	—	5·97
In	156	—	—	—	—	—	5·76
K	63·5	776	—	1300 (KOH)	—	—	4·32
Mg	657	1102	2642	2800	—	—	7·63
Mn	1221	2156	1560	—	1245	—	7·41
Mo	2622	4800	795	—	2690	4500	7·2
Na	97	883	322	(NaOH) 1390	—	—	5·09
Ni	1453	3177	1990	—	—	—	7·6
Pb	327	1750	890	1470	—	—	7·37
Si	1414	2630	1477	2230	2700	—	8·14
Sn	232	2430	—	18–1900	—	—	7·54
Sr	757	1364	2430	—	1773	—	5·68
Ti	1727	3000	1775	—	3140	—	6·81
V	1720	3000	658	1970	2830	3900	7·74
W	3380	6000	1473	—	2860	6000	—
Zn	419	906	—	1725	—	—	9·37
Zr	1860	2900	2700	4300	3530	5100	6·92

Die Zerfallstemperaturen der Oxyde und Carbide sind zum grössten Teil unbekannt. Es werden angegeben:

Ag_2O	190	Al_4C_3	ab 2100	Fe_3C	2220
In_2O_3	1000	BaC_2	ab 1750	SiC	ab 2200
V_2O_5	1750	Be_2C	ab 2200		

2. Die Reduktion

Kohlenstoff ist bei hohen Temperaturen ein starkes Reduktionsmittel. In der Lochkohle ist er im Ueberschuss vorhanden, so dass er reduzierbare Substanzen, d.h. besonders die Oxyde aller Elemente, bei genügend hoher Temperatur zu den

Metallen reduziert*. Darauf dürften A. RUSANOW und Mitarbeiter bereits hingewiesen haben [4]. Die Reduktionen verlaufen vollständig, da gasförmige Reaktionsprodukte entstehen. Je höher die Temperatur ist, desto schneller verläuft eine Reduktion. So wird z.B. aus Magnetit Fe_3O_4 primär metallisches Eisen. Magnesiumoxyd wird zu Magnesium, Calciumsulfat $CaSO_4$ wird zu einem Teil zu Calciumsulfid CaS reduziert. Dieses CaS wird bei noch höherer Temperatur thermisch zersetzt. Die Reduktion der Oxyde erfolgt bei umso tieferer Temperatur, je edler das Metall ist. Die unedelsten Metalle werden erst oberhalb 2000° C reduziert.

3. *Die Legierungsbildung*

Liegen in der Lochkohle zwei oder mehrere Metalle nebeneinander vor, so ist zu überlegen, ob diese in flüssigem Zustand mischbar sind (Fe/Mn) oder nicht (Fe/Ag), und welcher Art diese Mischung dann ist. Es können sich höherschmelzende und damit möglicherweise auch höhersiedende, intermetallische Verbindungen (Fe/Al), oder tieferschmelzende, eutektische Mischungen (Fe/Mn) bilden.

Die Siedeverhältnisse sind im einzelnen leider noch weitgehend ungeklärt. WEIBKE und KUBASCHEWSKI weisen auf einige intermetallische Verbindungen hin, die sich beim Mischen der metallischen Schmelzen unter Abgabe von zum Teil ganz erheblicher Reaktionswärme bilden. Ueber die Siederscheinungen wird aber nichts gesagt [5].

4. *Die Verbindungsbildung*

a) Temperaturbeständige Verbindungen—Während die intermetallischen Verbindungen, soweit bekannt, thermisch nicht besonders stabil sind, gibt es bei den Verbindungen zwischen Metallen und Nichtmetallen oder unter den Nichtmetallen Verbindungen, welche sich durch ausserordentlich grosse Temperaturbeständigkeit auszeichnen. Zu diesen gehören in erster Linie einige Carbide, Boride und Nitride, weiter Silicide, Phosphide, Arsenide und vielleicht auch einige Sulfide und Oxyde. Von diesen nehmen in unserem Falle die Carbide eine bevorzugte Stellung ein, da Kohlenstoff immer im Ueberschuss vorhanden ist. Dagegen sind die anderen Nichtmetalle nicht immer und in wechselnder Menge vorhanden, so dass sich dadurch grosse Verschiebungen in den Verdampfungstemperaturen ergeben können.

Die Nichtmetalle führen durch ihre variablen Verbindungsbildungen — ähnlich und stärker noch als die Legierungsbildungen — jene Unsicherheit herbei, die dazu zwingt, für jede Analyse eine der Analysensubstanz möglichst ähnliche Eichsubstanz zu suchen. Es kommt auf die immer wieder andere Kombination der verschiedenen Elemente an.

b) Die Carbide—Die temperaturbeständigsten Carbide sind die sogenannten Einlagerungsverbindungen des Kohlenstoffs [6]. Die Zersetzungs- bzw. Siedetemperaturen der Einlagerungsverbindungen liegen meistens weit über der Sublimationstemperatur des Kohlenstoffs (Tabelle 1). Andere Carbide zerfallen bereits früher; so bildet das reduzierte Eisen nur unterhalb etwa 2200° C Zementit, Fe_3C. Die Zersetzungstemperatur des Calciumcarbids CaC_2 ist nicht bekannt, dürfte aber zwischen 2400° und 2700° C liegen. Aehnlich ist es bei Carborundum, SiC.

Die Carbidbildung ist eine ausgesprochene Gleichgewichtsreaktion, bei der im allgemeinen keine flüchtigen Nebenprodukte entstehen. Die Lage des Gleichgewichts hängt ab von der Temperatur, dem Mengenverhältnis der Reaktionsteilnehmer, und von der Gegenwart weiterer Elemente, die einen der Partner

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* Anm.: Im folgenden wird das Beimischen von Kohlenstoff nicht mehr ausdrücklich erwähnt. Die Füllung einer Lochkohle "mit Fe_2O_3" bedeutet also immer die Füllung "mit einem Gemisch von 1 Gew. Teil Fe_2O_3 und 1 Gew. Teil Kohlepulver".

binden können. Die Beständigkeit der Carbide kann grösser oder kleiner sein als die von Legierungen. Die bei einer tiefen Temperatur gebildeten Carbide zerfallen wieder bei höherer Temperatur. Manche Carbide vermögen Kohlenstoff aufzulösen. Da die Carbidbildung in allen Fällen in gleicher Weise wirkt, werden durch sie bestimmte Elemente aus dem Wechselspiel in der Schmelze der Legierungen und Verbindungen abgefangen. Der Nachweis solcher Elemente wird dadurch unabhängiger von der Grundsubstanz.

B. SPEZIELLES ÜBER CHEMISCHE VORGÄNGE IN KOHLEELEKTRODEN

Die Verhältnisse in den Kohleelektroden sind am einfachsten zu übersehen, wenn man Zweistoffsysteme betrachtet, in denen der Kohlenstoff jeweils die eine Komponente bildet. Die Lochkohlefüllung soll also z.B. aus der Mischung eines reinen Oxydes mit Kohlepulver bestehen. Die gleichen chemischen Vorgänge wie hier werden im allgemeinen auch in den Fällen ablaufen, in denen das Oxyd als Grundsubstanz durch kleine Mengen von Spurensubstanzen verunreinigt ist.

Ist aber andererseits das Oxyd als Spurensubstanz in einer Grundsubstanz enthalten, dann spielen bei Betrachtung des Oxydes ausser den Reaktionen mit Kohlenstoff noch diejenigen mit der Grundsubstanz eine Rolle. Dann handelt es sich um ein Dreistoffsystem.

Für die folgenden Ueberlegungen ist es zweckmässig, den Begriff der "effektiven Siedetemperatur" eines Elementes einzuführen (vgl. Anm., S227). Es soll darunter der Temperaturbereich verstanden werden, innerhalb dessen die Hauptmenge eines Elementes verdampft. Es ist dabei also gleichgültig, ob das Element in metallischer oder gebundener Form, aus der Schmelze einer Legierung oder bei der Zersetzung einer Verbindung in die Gasphase übertritt. Die effektive Siedetemperatur kann identisch sein entweder mit der Siedetemperatur des Metalles (z.B. Eisen) oder einer Verbindung (z.B. NaOH, MoC), oder mit der Reduktionstemperatur des Oxydes (z.B. MgO) oder mit der Zerfallstemperatur des Carbides (z.B. CaC_2). Die effektive Siedetemperatur eines Elementes liegt in Mehrstoffsystemen meistens höher als die Siedetemperatur des Metalles.

1. Zweistoffsysteme (Grundsubstanzen)

Die bei hohen Temperaturen durch Zerfall oder Reduktion entstehenden Metalle unterscheiden sich durch ihre Fähigkeit, mit Kohlenstoff zu reagieren. Danach lassen sie sich in folgende vier Gruppen einteilen:

Grundsubstanzen 1. Gruppe—Die Elemente der 1. Gruppe bilden mit Kohlenstoff Carbide, deren Siedepunkte über der Sublimationstemperatur des Kohlenstoffs liegen (z.B. die Einlagerungsverbindungen von Ti, Zr, V, Mo, W). Innerhalb der Lochkohle lassen diese Elemente keine Diffusion erkennen. Einige von ihnen lassen sich von Kohleelektroden bei 6 amp nicht vollständig verdampfen (Zr, Mo, W).

Grundsubstanzen 2. Gruppe—Die Elemente der 2. Gruppe bilden weniger beständige Carbide, die bereits zerfallen oder verdampfen, bevor die Temperatur von 3500° C erreicht ist. Ihre Zerfallstemperatur liegt über der Siedetemperatur des betreffenden Metalles. Solche Elemente werden durch Kohlenstoff "fixiert", d.h. bis zu höheren Temperaturen in festem oder flüssigem Zustand festgehalten (z.B. Ca, Sr, Ba). Die Diffusion wird durch die Carbidbildung verringert.

Grundsubstanzen 3. Gruppe—Die Elemente der 3. Gruppe bilden noch weniger beständige Carbide. Diese zerfallen bereits unterhalb des Siedepunktes des betreffenden Metalles. Die effektive Siedetemperatur ist dann die gleiche wie die Siedetemperatur des Metalles (z.B. Be, Al, Mn, Fe). Die Diffusion dieser Elemente im Gaszustand wird durch die vorübergehende Bindung an Kohlenstoff im flüssigen Zustand nicht beeinflusst.

Grundsubstanzen 4. Gruppe—Die Elemente der 4. Gruppe bilden mit Kohlenstoff überhaupt keine Carbide. Die effektiven Siedetemperaturen sind entweder gleich der Siedetemperatur des Metalles (z.B. Cu, Ag, Sn, Pb) oder gleich der Siedetemperatur der unzersetzten Verbindung (z.B. NaOH, KOH) oder aber gleich der Reduktionstemperatur der Substanz (z.B. MgO).

2. *Mehrstoffsysteme* (*Spurensubstanzen*)

Mit der Reduktion der Grundsubstanz wandelt sich für die Spurensubstanzen das ganze sie umgebende System. Oxyde, die in der Grundsubstanz löslich waren, brauchen in dem reduzierten Metall der Grundsubstanz nicht mehr löslich zu sein, auch nach ihrer eigenen Reduktion nicht. Besonders empfindlich sind diejenigen Metalle, die schon bei verhältnismässig tiefer Temperatur sieden, und die nicht vom Kohlenstoff fixiert werden.

Das Verhalten der Spurensubstanzen ist von vier Faktoren abhängig:

1. von der Siedetemperatur der Grundsubstanz
2. von ihrer eigenen Siedetemperatur
3. von der Reaktion mit Kohlenstoff und
4. von ihrem Verhalten zur Grundsubstanz

Die Siedetemperatur der Grundsubstanz ist deshalb so wichtig, weil es von ihrer Höhe abhängt, ob chemische Reaktionen überhaupt eintreten bzw. wie weitgehend sie ablaufen.

Spurensubstanzen in niedrig siedenden Grundsubstanzen—Siedet die Grundsubstanz besonders niedrig, d.h. unter etwa 1000° C, so wird sie sehr rasch verdampft. Dabei werden alle Spurensubstanzen, unabhängig von ihren physikalischen oder chemischen Eigenschaften, mitgerissen. Sie gelangen auf diese Weise im richtigen Verhältnis in den Lichtbogen. HASLER und unabhängig von ihm ROST haben dies in ihren "Sprühmethoden" angewandt [7].

Spurensubstanzen in mittelsiedenden Grundsubstanzen—Bei zwischen etwa 1000° und 2200° C siedenden Grundsubstanzen besteht in der Lochkohle ein Abstand von mehreren Millimetern zwischen dem auf dem festen Kohlepulver der Füllung aufsitzenden Brennfleck und der Siedezone der geschmolzenen, am Kohlepulver haftenden Grundsubstanz. Hochsiedende Zusatzelemente in geringen Mengen werden je nach ihrem Partialdruck zusammen mit der Grundsubstanz verdampft. Bei grösseren Mengen tritt eine echte Anreicherung nur dann ein, wenn die maximale Brennflecktemperatur nicht zur sofortigen, vollständigen Verdampfung genügt.

Spurensubstanzen in hochsiedenden Grundsubstanzen—Siedet die Grundsubstanz über 2200° C, so stellen sich vor der Verdampfung der Spurenelemente die chemischen Gleichgewichte ein. Besonders diejenigen leichtflüchtigen Elemente, die an keinem solchen Gleichgewicht wesentlichen Anteil haben, werden in der ihren Siedepunkten entsprechenden Reihenfolge herausfraktioniert. Es handelt sich also hauptsächlich um Spurenelemente, die als Grundsubstanzen der 4. Gruppe angehören. Der Verteilungszustand dieser Elemente ist von Einfluss auf die Fraktionierung; aus durch Verreiben hergestellten Eichmischungen findet die Verdampfung schneller statt als aus gewachsenen Mineralen. Elemente mit mittlerer, effektiver Siedetemperatur unterliegen der Fraktionierung in geringerem Ausmass. Hochsiedende Spurensubstanzen verdampfen zusammen mit der hochsiedenden Grundsubstanz.

Die Reihenfolge, in der die einzelnen Elemente im Lichtbogen erscheinen, ist von den effektiven Siedetemperaturen und damit von den chemischen Reaktionen abhängig. Eine in allen Grundsubstanzen gültige Reihenfolge kann es nicht geben. Mit jeder neuen Grundsubstanz liegt ein anderes System für die Spurenelemente vor. So werden durch Eisen die Metalle Al, Si und besonders As, nicht aber Zn, Pb und Ag gebunden. Nickel bindet Al und As, Kupfer bindet Al, Sn und Zn.

3. Reaktionen zwischen den Spurensubstanzen

Auch Spurensubstanzen können sich untereinander binden. Dann kann der Fall eintreten, dass ein tiefsiedendes Spurenelement durch ein anderes, in geringerer Menge vorhandenes Spurenelement nur zu einem Teil fixiert wird. Ein Teil des Elementes siedet dann bei tieferer und ein Teil bei höherer Temperatur. Der bei höherer Temperatur siedende Anteil gelangt vollständiger in den Lichtbogen und ruft dadurch eine verhältnismässig kräftigere Schwärzung der Platte hervor als der tiefersiedende Anteil (vgl. 4. und 8. Versuch). Das Unangenehme ist, dass das Verhältnis beider Anteile durch die zunächst unbekannte Menge des anderen Spurenelementes gegeben ist. Achtet man nicht darauf, dann können bei den Analysen Fehler von mehreren Zehnerpotenzen auftreten (z.B. eine As-Bestimmung in Gegenwart kleiner, variierender Mengen von Fe).

4. Die Lage der Siedezonen in der Lochkohle

In A663 (s.12) 3 ist der Zustand veranschaulicht, der sich in einer Lochkohle einstellt, wenn man die erwähnte "Universalmischung" abbrennt. An dem Querschnitt der Lochkohle sind links der Massstab und in der Mitte der wahrscheinliche Temperaturverlauf angegeben, wie er sich unter den Bedingungen dieser Arbeit einstellt. In der Lochkohle befindet sich die in kleinen Tröpfchen am Kohlepulver haftende Eisenschmelze. In dieser Schmelze stellen sich in kurzer Zeit die Verdampfungsgleichgewichte der Spurenelemente ein. Es bilden sich die jeweils thermisch beständigsten Verbindungen.

Rechts neben der Lochkohle sind die einzelnen Elemente in der Höhe ihrer Siedezone angeführt, entsprechend dem bei der Verdampfung vorliegenden Bindungszustand. Verbindungen der Spurensubstanzen untereinander sind nicht berücksichtigt. Die Reihenfolge der Verdampfung aus jedem Tröpfchen der Schmelze lässt sich von unten nach oben ablesen.

Einer Temperaturerniedrigung am Brennfleck um 500° C entspricht in 5 mm Entfernung, das ist etwa am Grunde der Bohrung, nur eine viel geringere Temperaturabnahme von höchstens 50° C. Durch eine solche Temperaturerniedrigung wird also die Verdampfungsgeschwindigkeit der hochsiedenden Substanzen sehr stark, die der tiefsiedenden dagegen kaum nennenswert beeinflusst.

Die Siedezone eines Elementes ist als Basis für die Diffusion anzusehen. Je näher die Siedezone dem Brennfleck liegt, desto grösser ist der Prozentsatz der Gase, der in den Lichtbogen und damit zur Anregung gelangt.

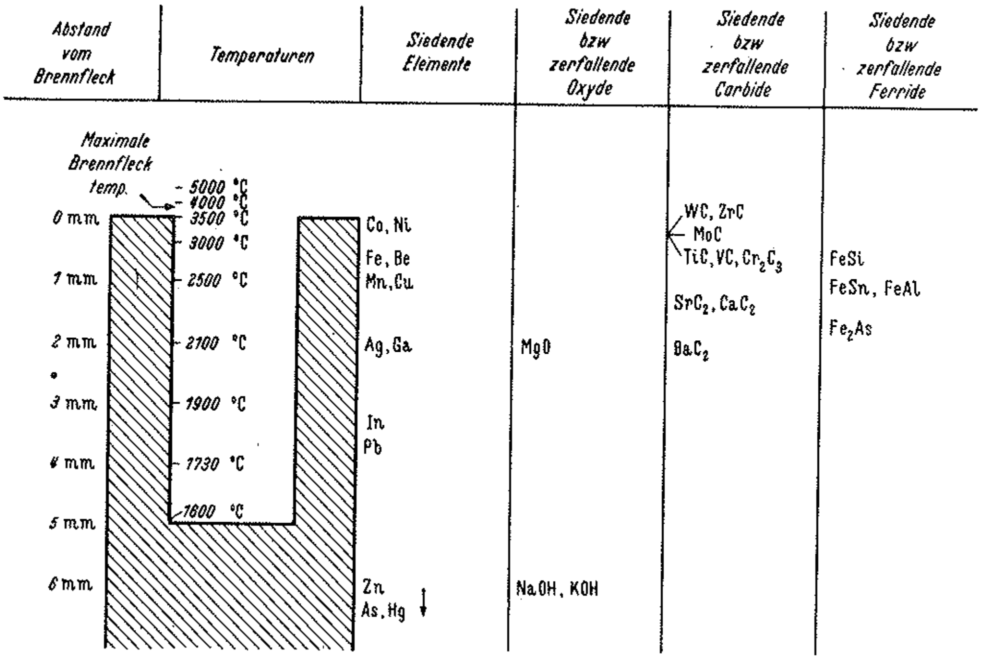

Abb. 3—Querschnitt durch eine Lochkohle. Links der Abstand vom Brennfleck; in der Mitte die wahrscheinlichen Temperaturen in der Lochkohle; rechts die in Fe_2O_3 als Grundsubstanz zu je 1% enthaltenen Spurenelemente etwa in der Höhe ihrer Siedezone und in dem bei der Verdampfung vorliegenden Bindungszustand. Gültig unter den eingangs erwähnten Abbrandbedingungen. Zusammengestellt nach dem 8. Versuch.

III. Einige physikalische Betrachtungen

In diesem Teil werden die Vorgänge verfolgt, durch die die chemischen Reaktionen in der Lochkohle mit den physikalischen Erscheinungen des Lichtbogens zusammenhängen.

A. DIE DIFFUSION

1. *Der Verdampfungsvorgang*

Mit dem Verdampfungsvorgang beginnt die Diffusion der gasförmigen Metalle in der Lochkohle. Da aber eine Verdampfung auch schon bei Temperaturen unterhalb der eigentlichen Siedetemperatur stattfindet, verdampft ein Teil einer Substanz schon vor dem Erreichen der eigentlichen Siedezone. Liegen mehrere, verschieden hochsiedende Substanzen nebeneinander vor, so beschleunigt das Abströmen der Gase der tiefer siedenden Elemente ausserdem die Verdampfung der höher siedenden. Aus diesem Grunde lassen sich hochsiedende Elemente als Spurensubstanzen viel besser verdampfen als als Grundsubstanzen. Die Lage der Siedezone hängt somit nicht nur von den Abbrandbedingungen, sondern auch von der Menge eines Elementes in der Lochkohle ab.

Das geht auch aus einem Vergleich der Abbrennzeiten des 3., 4. und 5. Versuchs hervor. Der 3. Versuch zeigt, dass infolge des hohen Siedepunktes des Zirkoncarbids die Abbrenndauer sehr verlängert ist. Die Abbrennzeiten des 4. und 5.

Versuchs sind aber untereinander fast gleich und betragen beide etwa nur 20% von der des 3. Versuchs. 1% ZrO_2 in Fe_2O_3 verlängert also den Abbrand des Fe_2O_3 nicht, obwohl das ZrO_2 vollständig verdampft wird.

2. Abhängigkeit der Diffusion von der effektiven Siedetemperatur

Der 8., 9. und 10. Versuch haben gezeigt, wie man die effektiven Siedetemperaturen durch Beobachtung der Diffusion ermitteln kann. Die Diffusion eines gasförmigen Elementes findet in allen Richtungen statt, nicht nur nach oben durch das Kohlepulver auf den Brennfleck zu, sondern auch seitlich in die Kohlewand hinein und durch sie hindurch, sowie nach unten in den Sockel der Kohle (vgl. auch 7. Versuch). Je näher die Siedezone dem Brennfleck liegt, desto grösser ist der Anteil des Gases, der in den Lichtbogen und damit zum Nachweis gelangt. *Man sollte daher alle Elemente bei möglichst hoher effektiver Siedetemperatur in die Gasphase übertreten lassen,* denn dann ist die Menge, die in den Lichtbogen diffundiert, die grösstmögliche und der Nachweis am empfindlichsten. Ausserdem erreicht man damit noch ein Zweites: Die Gegenwart anderer, verschieden stark bindender Metalle wird belanglos, wenn das Element mit der grössten Bindekraft in ausreichender Menge zugegen ist. Die Nachweisgenauigkeit wird unabhängig von dem Wechselspiel der Legierungsbildungen.

Für den Nachweis eines Elementes wie Arsen ist Kohlenstoff als Elektrodenmaterial infolge seines hohen Sublimationspunktes so lange ungeeignet, als das Arsen nicht fixiert ist. As wird durch C nicht gebunden, siedet sehr tief und besitzt zu allem eine sehr hohe Ionisierungsspannung, benötigt also zur Anregung eine hohe Lichtbogentemperatur. So sind die Verluste durch Diffusion ausserordentlich hoch, solange nicht Elemente wie Fe oder Ni—welche auch in den Tiefen der Erde As binden — das As fixieren.

Die Verluste durch Diffusion werden bei sehr tiefsiedenden Substanzen zusätzlich durch das Abströmen der Verbrennungsgase CO und CO_2 erhöht. Alle verwendeten Lochkohlen sollten sich in ihren Abmessungen und in ihrer Porosität gleichen, damit die Diffusionsverluste die gleichen sind.

3. Zündverluste

Beim Zünden eines Lichtbogens stellen sich die hohen Temperaturen in der Lochkohle sehr rasch ein (innerhalb 1–2 sec). Diejenige Menge eines Elementes bzw. einer Verbindung, die sich in der Lochkohle oberhalb der Siedezone befindet, wird sofort verdampft (4. Versuch). Sie wird damit vom Lichtbogen unter anderen Bedingungen erfasst als der Rest des Elementes, da die Konzentration im Kohlenstoffgas grösser und damit die Lichtbogentemperatur geringer ist.

Die Zündverluste an tiefsiedenden Substanzen sind umso grösser, je tiefer in der Lochkohle die Siedezone liegt, und je gröber der Verteilungszustand ist. Die Fixierungen treten dann nicht schnell genug ein. In durch Verreiben hergestellten Eichmischungen sind daher die Zündverluste grösser als in natürlichen Mineralen.

4. Anreicherungen

a) Scheinbare Anreicherungen—Während des Abbrandes einer Lochkohle wandern die Siedezonen in der Lochkohle nach unten. Ein bestimmtes Tröpfchen einer Schmelze wird also allmählich immer heisser. Die leichtflüchtigen Anteile destillieren zunächst heraus. Dadurch wird eine scheinbare Anreicherung von höhersiedenden Elementen im Tröpfchen bewirkt. Man sollte jedoch besser von einer

Verarmung an leichtsiedenden Substanzen sprechen, da nur die Konzentration, nicht aber die Menge der höhersiedenden Anteile im Tröpfchen ein wenig grösser wird. *b) Echte Anreicherungen*—Befinden sich in der Füllung grössere Mengen sehr hochsiedender Substanzen, so verharren diese so lange an ihrer Stelle im Kohlepulver, bis sie vom Brennfleck erfasst werden. Genügt die Brennfleckenergie, um diese Substanzen auf ihre Siedetemperatur zu erhitzen, dann werden sie sofort verdampft. Reicht die Brennfleckenergie aber hierzu nicht aus, dann wird sich der nichtverdampfte Teil der Substanz im Brennfleck ansammeln; dadurch können schliesslich auf dem Sockel der Lochkohle in echter Anreicherung Schmelzkuppen entstehen (vgl. Bild 1, 5. Lochkohle von links).

B. DIE VORGÄNGE AN DER ANODE

1. Der Anodenbrennfleck

a) Die Brennflecktemperatur—Die Temperatur des Anodenbrennflecks ist eine Funktion des auf die Anode aufprallenden Elektronenstromes (Anzahl und Geschwindigkeit der Elektronen, Dichte des Elektronenstromes). Bei geringer Stromstärke erzeugt der Elektronenstrom eine Brennflecktemperatur unter 3500° C, so dass der Kohlenstoff im Brennfleck einen Dampfdruck von unter 1 atm erhält. Die Kohleanode brennt sehr langsam ab. Durch Erhöhung der Stromstärke lässt sich auf reinen Kohleelektroden die Brennflecktemperatur höchstens bis auf den Sublimationspunkt des Kohlenstoffs steigern. Bei weiter anwachsender Stromstärke bleibt die Brennflecktemperatur die gleiche. Es steigert sich aber die Verdampfungsgeschwindigkeit des Kohlenstoffs. Enthält die Lochkohle eine Füllung, die wie ZrC im 3. Versuch oberhalb 3500° C siedet, dann wird der Brennfleck von dieser Füllung übernommen. Es entsteht dann eine entsprechend höhere Temperatur auf der Füllung. Man kann diese Temperatur die maximale Brennflecktemperatur nennen.

b) Der Kohledampfstrahl—Die gesteigerte Verdampfungsgeschwindigkeit des Kohlenstoffs ist an dem aus der Anode hervorschiessenden Kohledampfstrahl zu erkennen (11. Versuch). Bei geringem Abstand der kälteren Kathode kondensiert sich der Kohlenstoff auf dieser in Form eines Pilzes (Abbildung 2). Die Erzeugung des Pilzes gelingt besser, wenn die Lochkohlefüllung aus FeS besteht, als wenn Fe_2O_3 gewählt wird. Finkelnburg hat Kohledampfstrahl und Kohlepilz im Hochstromkohlebogen von einigen 100 amp beschrieben, in dem die gleichen Erscheinungen bedeutend eindrucksvoller zu beobachten sind [8].

2. Die Abbrennzeit der Analysensubstanz

Die Abbrennzeit einer Lochkohlefüllung hängt von der Verdampfungsgeschwindigkeit der höchstsiedenden Substanz ab, falls diese in genügender Menge vorliegt. Die Verdampfungswärme wird durch die Brennfleckenergie geliefert. Sie ist nach der Troutonschen Regel umso grösser, je höher die Verdampfungstemperatur einer Substanz liegt. Enhält eine Lochkohle keine Substanzen, die oberhalb 3500° C sieden, dann ist die Abbrennzeit bei gleicher Brennfleckenergie nur durch die Verdampfungsgeschwindigkeit des Kohlenstoffs bestimmt. Liegt die effektive Siedetemperatur einer Kohlefüllung dagegen über 3500° C, dann wird eine höhere Verdampfungswärme benötigt; die Abbrennzeit wird entsprechend verlängert (3. Versuch).

ERGEBNIS

Mit den hier entwickelten Anschauungen lässt sich jetzt verstehen, weswegen sich einer absoluten spektrochemischen Analyse bisher so grosse Schwierigkeiten entgegengestellt haben, d.h. weswegen die absolute Linienintensität nicht bedingungslos der Substanzmenge proportional ist, auch wenn die Arbeitsbedingungen die gleichen sind. Der Grund liegt darin, dass man bisher die chemischen Reaktionen in der Lochkohle unberücksichtigt gelassen hat. Die chemischen Reaktionen richten sich nach Art und Menge der insgesamt vorhandenen Elemente. Sie beeinflussen über die effektive Siedetemperatur bzw. über die Siedezone, über die Verluste durch Diffusion und damit über die Konzentration eines Elementes im Lichtbogen die Schwärzung der photographischen Platte. So wird man sagen können, dass eine Analysenprobe mit einer Eichprobe nur dann verglichen werden darf, wenn in beiden Proben dieselben chemischen Reaktionen ablaufen und die Siedezonen damit den gleichen Abstand vom Brennfleck haben. Wenn ausserdem Gerlachs Forderung nach gleicher Lichtbogentemperatur erfüllt ist [9], dann sollte die Verdampfung der Substanzen in derselben Weise vor sich gehen.

Das Ziel der weiteren Forschung wird sein, einerseits durch geschickte Zugabe geeigneter Substanzen störende chemische Reaktionen zu verhindern und damit die Materialzufuhr und die Konzentration der gesuchten Elemente im Lichtbogen besser in die Hand zu bekommen. Andererseits wäre es denkbar, aus einer Analysenlenie nicht nur die Intensität, sondern auch die Lage der Siedezone zu entnehmen und auszuwerten.

Zusammenfassung

Die Arbeit bringt im ersten Teil eine Reihe von Versuchen, mit welchen der Ablauf einiger chemischer Reaktionen in der Kohleelektrode sowie die Diffusion der verdampften Substanz verfolgt werden kann. Im zweiten Teil wird versucht, eine allgemeine Uebersicht über das Verhalten der verschiedenen Elemente als Grundsubstanzen und als Spurensubstanzen zu gewinnen. Es werden thermische Zersetzungen, Reduktionen durch Kohlenstoff, Legierungsbildungen und die Bildung hochtemperaturbeständiger Verbindungen unterschieden. Diese Reaktionen werden besonders im Hinblick auf die durch sie hervorgerufenen Aenderungen der Siedetemperaturen besprochen. Der dritte Teil befasst sich mit der Bedeutung, die die chemischen Reaktionen für die physikalischen und physikalisch-chemischen Vorgänge in der Lochkohle und damit für die Methodik der spektrochemischen Analyse haben. Denn die Konzentration eines Elementes im Lichtbogen ist auch von den chemischen Reaktionen in der Lochkohle abhängig.

Summary

A series of experiments to test the various types of chemical reaction and of diffusion which take place in a boring in a carbon arc electrode is described. The high-temperature chemical reactions between various elements and carbon are described in detail. Some of these reactions lead to non-volatile compounds, others may take varying courses according to the composition of the mixture being analysed. A general view of the behaviour of various elements when present as the main constituent or as traces is outlined, and the work concludes with some observations on diffusion processes in the carbon and other physical variations in arc behaviour.

Résumé

On décrit d'abord une série d'essais qui ont pour but de mettre en évidence les réactions chimiques ainsi que les phénomènes de diffusion qui ont lieu à la température élevée de l'arc électrique entre électrodes de carbone.

On considère ensuite en détail quelques unes de ces réactions notamment celles qui tendent à la formation de dérivés non volatils tant pour les éléments présents comme constituants majeurs que lorsqu'ils n'interviennent qu'à l'état de traces.

On reprend enfin l'examen de quelques uns des processus physiques qui jouent un rôle dans l'arc.

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The application of atomic absorption spectra to chemical analysis

A. Walsh
Chemical Physics Section, Division of Industrial Chemistry,
Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

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Summary—The theoretical factors governing the relationship between atomic absorption and atomic concentration are examined and the experimental problems involved in recording atomic absorption spectra are discussed. On the basis of the discussions, it is shown that such spectra provide a promising method of chemical analysis with vital advantages over emission methods, particularly from the viewpoint of absolute analysis. It is also suggested that the absorption method offers the possibility of providing a simple means of isotopic analysis.

1. Introduction

The application of atomic spectra to chemical analysis has proved so successful over such a wide field that there is a tendency to overlook some of the basic limitations of existing methods. In spite of the remarkable advances in technique which have resulted in press-button analyses of high precision at fantastic speeds, there has been practically no progress whatsoever in solving the fundamental problem of devising an absolute method, i.e., a method which will provide an analysis without comparison with chemically analyzed standards or synthetic samples of known composition. In routine analysis for production control this problem is of little consequence, since it is only necessary to have a limited number of standards, and in such work modern direct-reading methods leave little to be desired, except on the score of complexity of equipment and associated expense. When analyses of miscellaneous materials are required, the task of providing the required range of standards becomes insurmountable and the spectrochemical method then loses its accuracy, since accurate analyses generally necessitate the use of standards which are closely similar in composition to the sample for analysis. In some analyses it is also essential that the sample and standards be similar as regards physical condition. For example, the intensity of the spectrum of a metal or alloy may vary with the metallurgical history of the sample. This difficulty may be overcome by taking the sample into solution, but accurate and sensitive methods of analyzing solutions are only available for the limited range of elements, having a low excitation potential, which can be estimated by flame photometry. In this method, also, it is necessary to use standard solutions having compositions closely similar to that of the test solution.

The possibility of adapting any of the existing methods to absolute analysis does not appear to be promising. In the first place, there seems to be little prospect of developing a light source which is such that the emission spectrum of a given element is not affected by the presence in the atomic vapour of atoms of other elements. Secondly, even if these interelement effects were eliminated, there remains the problem of absolute intensity measurement and the associated problem

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of determining the distribution of atoms over the various energy states. In practice there is the third difficulty that electrical discharges of the type now in use do not give a stable output of radiation; modern methods conceal these erratic variations in output by integrating, photographically or photoelectrically, the radiation over a period of several seconds. Finally, there are other problems arising from self-absorption and self-reversal, and from the fact that the processes of vaporization and excitation are not isolated from each other. A review of these and other aspects of source behaviour has been given elsewhere [1].

At the present stage of its development there is no doubt that the major obstacle to further progress in the technique of spectrochemical analysis is the occurrence of interelement effects, since if these could be eliminated it would be possible to use the same set of standards for the determination of any one element in any material. With existing emission methods the intensity of a given spectrum line due to one particular concentration of an element in different materials varies greatly. For example, Prokof'ev [2] reports that for the same concentration of silicon the intensity of the silicon lines in the spark spectrum of steel is eight times as great as in brass, and in duralumin the intensity is even less. Many other examples of interelement effects have been published.

No satisfactory explanation of these effects has yet been given, nor can one be expected, since the phenomena occurring in the arc and spark discharges used as light sources are far too complex to permit of any theoretical analysis, and the approach to the subject seems likely to remain essentially empirical. It seems possible, however, to arrive at certain broad conclusions. Since interelement effects are usually of the same order of magnitude for different spectrum lines of a given element, corresponding to transitions between different energy states, they probably arise from changes in the concentration of atomic vapour rather than changes in the excitation conditions. However, such changes cannot occur in sources in thermal equilibrium at a constant temperature. Thus, if thermal equilibrium is assumed, then interelement effects must necessarily be due to a change in the temperature of the atomic vapour. Whilst the behaviour of the electrical discharges used in spectrochemical analysis shows that it is not justifiable to assume thermal equilibrium or to ascribe a temperature to the discharge, it is instructive to consider the effects of changes in temperature on a mass of atomic vapour in thermal equilibrium.

Consider the emission of a spectrum line due to the transition from an excited state j, of excitation energy E_j, to a ground state of energy $E_0 = 0$. Then if P_j and P_0 are the statistical weights for the excited state and ground state respectively, the number of atoms in the excited state, N_j, is related to the number of atoms in the ground state, N_0, by the relation

$$N_j = N_0 \frac{P_j}{P_0} e^{-\frac{E_j}{kT}} \qquad (1)$$

and, neglecting self-absorption and induced emission, the intensity of the emitted line is proportional to N_j.

In order to illustrate the magnitude of N_j/N_0, the calculated values for resonance lines of various elements at different temperatures are given in Table 1.

Table 1. Values of N_j/N_0 for various resonance lines

Resonance line	*Transition*	P_j/P_0	N_j/N_0			
			$T = 2{,}000°$K	$T = 3{,}000°$K	$T = 4{,}000°$K	$T = 5{,}000°$K
Cs 8521 Å	$^2S_{1/2} - {}^2P_{3/2}$	2	$4{\cdot}44 \times 10^{-4}$	$7{\cdot}24 \times 10^{-3}$	$2{\cdot}98 \times 10^{-2}$	$6{\cdot}82 \times 10^{-2}$
Na 5890 Å	$^2S_{1/2} - {}^2P_{3/2}$	2	$9{\cdot}86 \times 10^{-6}$	$5{\cdot}88 \times 10^{-4}$	$4{\cdot}44 \times 10^{-3}$	$1{\cdot}51 \times 10^{-2}$
Ca 4227 Å	$^1S_0 - {}^1P_1$	3	$1{\cdot}21 \times 10^{-7}$	$3{\cdot}69 \times 10^{-5}$	$6{\cdot}03 \times 10^{-4}$	$3{\cdot}33 \times 10^{-3}$
Zn 2139 Å	$^1S_0 - {}^1P_1$	3	$7{\cdot}29 \times 10^{-15}$	$5{\cdot}58 \times 10^{-10}$	$1{\cdot}48 \times 10^{-7}$	$4{\cdot}32 \times 10^{-6}$

It will be seen that in nearly all cases the number of atoms in the first excited state is only a small fraction of the numbers of atoms in the ground state. The fraction only becomes appreciable at high temperatures for states of low energy. Since most elements have their strongest resonance line at wavelengths below 6,000 Å, and since we shall be concerned mainly with flames or furnaces having temperatures below 3,000°K, we may regard N_j as negligible compared to N_0. The fraction of atoms in higher excited states is much less than those given above, and thus ΣN_j is also negligible compared with N_0, and the latter can be considered as equal to the total number of atoms, N.

Thus, whilst the number of excited atoms varies exponentially with temperature, the number of atoms in the ground state remains virtually constant and therefore the integrated absorption $\int K_\nu \, d\nu$ due to transitions from the ground state is independent of temperature. (This discussion only applies to atoms having a ground state well removed from the lowest excited state; the case of atoms having a multiplet ground state is discussed in Section 2.)

On the basis of the above discussion it would appear that atomic absorption spectra would have important advantages over emission spectra as a means of chemical analysis. It is therefore surprising to note that the research in this field has been devoted almost exclusively to emission spectra; the annual review [3] of progress in spectrochemical analysis is, in fact, given under the general title of "emission spectroscopy." Apart from the special case of estimating the contamination of room and laboratory atmospheres by mercury vapour, the application of atomic absorption spectra to chemical analysis appears to have been confined to astrophysical work on the determination of the composition of the solar and stellar atmospheres.

The purpose of this paper is to examine the theoretical factors governing the relationship between atomic absorption and atomic concentration and to discuss the experimental problems involved in recording atomic absorption spectra. On the basis of these discussions, it is shown that such spectra provide a promising method of chemical analysis with vital advantages over emission methods, particularly from the viewpoint of absolute analysis. It is also suggested that the absorption method offers the possibility of providing a simple means of isotopic analysis.

2. Variation of atomic absorption with atomic concentration

The relationships between atomic absorption and atomic concentration, under various conditions, are fully discussed in several papers, mainly in astrophysical journals, and in standard reference books [4–6]. For the purpose of this discussion it is sufficient to consider only the most fundamental of these relationships. In this section the discussion will be further restricted by assuming that atomic absorption lines possess no fine structure; the case of isotopic hyperfine structure is discussed later in Section 4.

Consider a parallel beam of radiation of intensity I_{0_ν} at frequency ν incident on an atomic gas or vapour of thickness l cm. Then if I_ν is the intensity of the transmitted beam, the absorption coefficient K_ν of the vapour at frequency ν is defined by

$$I_\nu = I_{0_\nu}\, e^{-K_\nu l} \tag{2}$$

The dependence of K_ν on ν, i.e., the shape of the absorption line, is determined by the nature of the transition involved in the absorption and on the physical conditions such as temperature, pressure, and electrical fields, to which the atoms are subjected during the measurement.

According to classical dispersion theory, the relationship between absorption and concentration is given by

$$\int K_\nu\, d\nu = \frac{\pi e^2}{mc} N_\nu f \tag{3}$$

where e is the electronic charge, m the electronic mass, c the velocity of light, N_ν the number of atoms per cm^3 which are capable of absorbing in the range ν to $\nu + d\nu$, and f, the oscillator strength, is the average number of electrons per atom which can be excited by the incident radiation. Equation (3) is not valid for strong absorption lines, since it assumes that the refractive index is of the order of 1 over the breadth of the absorption line.

For a resonance line due to a transition from a ground state which is well separated from the lowest excited state, N_ν can be considered as equal to N, the total number of atoms per cm^3 (see Table 1). If, however, the transition does not originate in the ground state, or if there is a multiplet ground state, then the number of atoms capable of absorbing is given by

$$N_\nu = N \frac{P_i e^{-\frac{E_i}{kT}}}{\sum P j e^{-\frac{E_j}{kT}}} \tag{4}$$

where i denotes the initial state involved in the transition, and the summation in the denominator extends over all possible energy states. In practice, of course, the summation can be restricted to the low-lying levels.

In terms of transition probabilities the equation corresponding to equation (3) is

$$\int K_\nu\, d\nu = \frac{\lambda^2 P_j}{8\pi P_i} \cdot N_\nu A_{ji} \left(1 - \frac{P_i}{P_j}\frac{N_j}{N_\nu}\right) \tag{5}$$

where λ is the wavelength at the centre of the absorption line, P_i and P_j are the statistical weights of the lower and upper states, respectively, involved in the transition, and A_{ji} is the Einstein coefficient of spontaneous emission for the $j \rightarrow i$ transition. N_j is the number of atoms in the upper electronic state, and will generally be negligible compared with N_ν, and in this case equation (5) reduces to the well-known relation:

$$\int K_\nu \, d\nu = \frac{\lambda^2 P_j}{8\pi P_i} N_\nu A_{ji} \tag{6}$$

In the general case N_ν is given by (4), but for resonance lines is equal to N. Similarly, if the transition from the jth to ith state is the only one which can occur, as in the case for resonance lines, $A_{ji} = 1/\tau$, where τ is the mean life of an atom in the excited state j.

Equations (3) and (6) provide simple relationships between absorption and concentration, and it is now necessary to investigate whether they can be applied to a practical method of spectrochemical analysis. Since the intensities of spectrum lines are usually expressed in terms of oscillator strengths, it is convenient to consider equation (3).

Firstly, it is necessary to know whether suitable absorption lines occur in regions of the spectrum which are amenable to measurement. In terms of sensitivity, it is obviously desirable to use the strongest resonance lines, and in general these will correspond to the strongest lines occurring in emission spectra. These are listed in a paper by **Meggers** [7], and reference to this shows that with the exception of the rare gases, hydrogen, mercury, the halogens and the metalloids, all elements have their most sensitive lines in the region 2,000–9,000 Å. Thus the lines for all the more common elements all lie in regions of the spectrum where measurements are simple to make.

The oscillator strengths of some of these lines have been determined, and are listed in Table 2. Theoretical calculation [8–14] of f-values is possible for atoms having simple electronic structures, but has not yet been carried out for heavy atoms having a complex structure. **Bates** and **Damgaard** [15] have described a simplified theoretical method and have published tables from which the absolute strengths can be rapidly obtained. The method has been shown to give accurate results for all transitions in the lighter simple systems, but there are insufficient experimental data to enable one to judge to what extent the method can be applied to the more complex electronic structures.

It is interesting to note that the oscillator strength for the strongest copper line is approximately the same as for the alkali metals, in spite of the fact that the closed 3d shell of the copper atom is not nearly so tightly bound as the inner electron shells of the alkali metals. By comparison with the f-values of other elements in Group 1, it seems probable that rubidium, silver, and gold will have f-values of the order of 0·7 for their strongest resonance lines. Similarly, the Group 2 elements Zn and Sr may be expected to have f-values of the order of 2 for their strongest lines.

It does not appear possible at the present time to make any corresponding estimates of the oscillator strengths of spectral lines of other elements, particularly those such as iron and cobalt, with complex electronic structures and multiplet ground states. The possibility of determining approximate f-values for such elements by a simple experimental method is discussed in Section 4.

For those elements for which the oscillator strengths are known, the atomic concentration can be determined from the integrated absorption coefficient, using equation (3); the experimental problems involved in measuring such coefficients are discussed below.

Table 2. List of f-values

Resonance line	*Transition*	f	*Reference*
Li 6708 Å	$^2S_{1/2} - {}^2P_{3/2}$	0·50	[9]
Na 5890	$^2S_{1/2} - {}^2P_{3/2}$	0·70	[16]
K 7665	$^2S_{1/2} - {}^2P_{3/2}$	0·64	[17]
Cu 3247	$^2S_{1/2} - {}^2P_{3/2}$	0·62	[18]
Cs 8521	$^2S_{1/2} - {}^2P_{3/2}$	0·66	[19]
Be 2349	$^1S_0 - {}^1P_1$	1·82*†	[11, 13, 14]
Mg 2852	$^1S_0 - {}^1P_1$	1·74*	[13, 14]
Ca 4227	$^1S_0 - {}^1P_1$	2·28*†	[12, 13, 14]
Cd 2288	$^1S_0 - {}^1P_1$	1·20	[20]
Ba 5535	$^1S_0 - {}^1P_1$	2·10	[21]
Hg 1849	$^1S_0 - {}^1P_1$	1·19	[22]
Tl 2769	$^2P_{1/2} - {}^2D_{3/2}$	0·20	[23]
Cr 4254	$^7S_3 - {}^7P^0_4$	0·084	[24]
Ni 3415	$^3D_3 - {}^3F^0_4$	0·02	[25]
Fe 3720	$a^5D_4 - z^5F_5$	0·013	[29]

* Theoretical values.

† Biermann and Trefftz [13] state that these values should be corrected according to the method described in ref. 14. See also the values quoted in ref. 30.

Footnote. Since the purpose of this table is to indicate the order of the f-values for various lines, the values obtained by different observers are not included. They are discussed by Korff and Breit [26] and by Mitchell and Zemansky [4].

3. Experimental determination of atomic absorption coefficients

The shape of an atomic absorption line is determined by (a) the natural width of the line due to the finite lifetime of the excited state; (b) the Doppler contour due to the motions of the atoms relative to the observer; (c) pressure broadening, either by atoms of the same kind giving rise to resonance broadening or to foreign gases;

and (d) Stark broadening due to external electric fields or to neighbouring charged particles. The natural width of an atomic spectral line is of the order of 10^{-4} Å, and for the purposes of this discussion is negligible compared to the width due to other causes.

The Doppler width of a line is given by

$$D_\lambda = 1{\cdot}67 \frac{\lambda}{C} \sqrt{\frac{2RT}{M}} \tag{7}$$

where R is the universal gas constant and M is the atomic weight. Typical values of D_λ are given in Table 3.

Table 3. Values of D_λ at various temperatures

Element	λ	M	D_λ		
			1,000°K	2,000°K	3,000°K
Na	5890	22·3	0·028 Å	0·039 Å	0·048 Å
Cu	3247	63·6	0·0092 Å	0·0013 Å	0·016 Å
Zn	2139	65·4	0·0060 Å	0·0085 Å	0·010 Å

If we assume that a temperature of 2,000°K is required to produce sufficient vapour, then the Doppler width is of the order of 0·01 Å. The accurate measurement of the profile of such a line would require a resolution of about 500,000, which is beyond the performance of most spectrographs. In addition, if it is desired to use photoelectric methods of intensity measurement, then it is scarcely feasible to use a continuous source, since the energy emitted over such a small spectral slit-width would be too small to give a high enough signal/noise ratio. In the past this difficulty has often been overcome by using the method of total absorption, in which the energy removed from the incident beam is measured. This method has the advantage that the measurement is independent of the resolution of the monochromator, but suffers from the disadvantage of giving a complicated relation between N and f, according to the region of the curve of growth in which the measurement is made. However, if the absorption is so strong that it is not possible to make an accurate measurement of the absorption coefficient, as in astrophysical work, then the curve-of-growth method is the only one available. The method has been successfully applied to the measurement of oscillator strength from furnace absorption spectra by KING [18] and by ESTABROOK [24, 25].

From the point of view of spectrochemical analysis, a more attractive method appears to be to measure the absorption coefficient at the centre of the line, using a sharp-line source which emits lines having a much smaller half-width than the absorption line. If the shape of the latter is determined entirely by Doppler broadening, we have [27]

$$K_{\max} = \frac{2\lambda^2}{D_\lambda} \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{\pi e^2}{mc^2} Nf \tag{8}$$

where D is the Doppler width. Thus in this case also there is a linear relation between absorption and concentration.

If such a sharp-line source is used, it is now no longer necessary to use a spectral slit-width of the same order as the half-width of the absorption line. The requirement now is the ability to isolate a selected line from other lines emitted by the source. Thus spectrographs having the same resolution as those used in conventional emission methods are adequate. In many cases it may be sufficient to use filters.

Various methods of producing such sharp-line sources are available. In our work it has been found convenient to use hollow-cathode discharge tubes, and it has proved possible to make sealed-off tubes about the size of a photomultiplier tube.

There is one other experimental difficulty. In many cases vaporization of the sample will result in the emission of radiation at exactly the wavelength where it is desired to make the absorption measurement. This difficulty can be overcome by modulating the incident radiation before it reaches the atomic vapour and amplifying the output of the detector by an amplifier tuned to this modulation frequency. Thus the radiation emitted by the atomic vapour, which is not modulated, produces no signal at the output of the amplifier.

So far it has been assumed that the line shape is determined solely by Doppler broadening, and this is sensibly true if the vapour is produced by a vacuum furnace, such as that used by KING, and if the vapour pressure is so small that resonance broadening is negligible. Another convenient method of vaporizing the sample is to atomize a solution of the sample into the air supply of a Meker burner, as in emission methods of flame photometry. In this case there is broadening due to foreign gases, and, although we have not made accurate measurements for the flame we have used, its magnitude is probably of the same order as that due to thermal motions. Once the broadening due to pressure is known, the corresponding correction to equation (8) can be applied, using the tables published by ZEMANSKY [28]. As an example, if the pressure broadening width is equal to the Doppler width, the maximum absorption is 43 per cent of that due to Doppler broadening alone.

IV. Discussion

The above discussion of atomic absorption spectra has indicated the attractive possibilities of using them for chemical analysis and of developing a method which will provide a useful complement to emission methods and in many cases may well supersede them. One of the main attractions of this absorption method is that, theoretically, it is expected to be much less susceptible to interelement effects. In so far as effects observed in emission are due to variations in the distribution of atoms over the various excited states, they would have no counterpart in absorption where this is due to a transition from the ground state. Similarly, absorption will not be critically dependent on the temperature of the atomic vapour, since the Doppler width only varies as $T^{1/2}$, whereas small changes in temperature produce large changes in the intensity of the emitted radiation. In addition, the integrated absorption coefficient is independent of wavelength, in marked contrast to the emission intensity, which will vary according to Planck's law.

Whilst the discussion has been limited to the ideal case of a vapour in thermal equilibrium, in practice there may be effects due to a sheath of cool vapour. But whereas in emission spectroscopy this causes self-reversal which reduces the peak intensity, in absorption it will contribute to the absorption and will in no sense reduce the sensitivity. Incidentally the self-reversal observed in emission spectra provides a good indication of the sensitivity of the absorption method. Another cause of deviation from thermal equilibrium is chemiluminescence; this may well produce a number of excited atoms, which is comparable with that due to thermal excitation, but will not produce any significant change in the number of unexcited atoms. Thus the effects on the absorption spectrum are negligible compared to those on the emitted radiation.

On the experimental side, the important advantage of the absorption method lies in the fact that the measurement of the absorption coefficient consists of measuring the ratio of two intensities, which is much simpler to achieve than the measurement of emission intensities in absolute units.

The possibilities of absolute analysis have been discussed and the use of a relative absolute method may also be noted. For example, if the sample solution is atomized into a flame, then a calibration for one element would serve to deduce the approximate calibration of other elements, provided the oscillator strengths are known. In this connection it would appear that, using standard solutions, this method could be used to determine oscillator strengths, at least to within an order of magnitude.

Finally, the absorption method may prove suitable for isotopic analysis. If sources emitting spectra of only one isotope are used, then an analysis for this isotope can be obtained directly, since the oscillator strength is the same for each component of the hyperfine structures of the excited level. If no pure isotope is available, then sources having different concentrations of isotopes may be used. Alternatively, an isotopic filter containing the vapour of one or more isotopes may prove satisfactory.

The results of some preliminary experiments have been in full accord with the conclusions arrived at in this paper, and future papers by J. P. SHELTON and the author will describe the construction of an atomic absorption spectrophotometer and its application to various analytical problems.

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Determination of the order of atoms in a linear molecule

E. Bright Wilson, Jr.
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts, U.S.A.

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Abstract—The force constants determined from the infra-red or Raman spectra of a sufficient number of isotopic species can decide between alternative arrangement of atoms in a linear molecule. A convenient method of calculation of force constants is given which uses as co-ordinates all the interatomic distances whether bonded or not. A diagonal force-constant matrix in these co-ordinates has the correct number of independent elements. Large values indicate bonded distances; small ones non-bonded distances. Advantage is taken of the fact that the G matrix is of the same form whether the co-ordinates used are dependent or not.

Introduction

Infra-red spectroscopy has several times [1,2] been used to determine the order of the atoms in linear molecules. By comparing the values of the force constants obtained from analysis on the basis of alternative models, a choice can sometimes be made.

The purpose of this paper is to point out a convenient way of carrying out the calculations involved in such problems.

Method

The basic idea is to use a co-ordinate system for setting up the secular equation for the stretching frequencies, which is independent of the order of the atoms. Such a system is the set of changes in all interatomic distances, whether bonded or non-bonded. For example, in linear XYZ (or ZXY, YZX), one would use the co-ordinates Δr_{xy}, Δr_{yz} and Δr_{zy}, where r_{xy} is the distance from X to Y. There are $\frac{1}{2}n(n-1)$ such co-ordinates, if n is the number of atoms. Only $n-1$ of these are independent, but all will be used nevertheless.

The potential energy is taken to be diagonal, i.e. in the example

$$2V = f_{xy}(\Delta r_{xy})^2 + f_{yz}(\Delta r_{yz})^2 + f_{zx}(\Delta r_{zx})^2 \tag{1}$$

and therefore has $\frac{1}{2}n(n-1)$ force constants. These are linear combinations of the $\frac{1}{2}n(n-1)$ force constants (including interaction constants) in terms of an independent set of co-ordinates. The force constants introduced above are independent, even though the co-ordinates are not.

The secular equation will be obtained by the use of the G matrix [3]. This can be written down by the usual rules whether the co-ordinates employed are independent or not. In the present instance a diagonal element, say $G_{xy,xy}$, is the sum of the reciprocal masses of the two atoms, i.e. $(1/m_x) + (1/m_y)$. A non-diagonal element will vanish unless the two co-ordinates share one atom, in which case $G_{xy,yz} = \pm(1/m_y)$. The minus sign appears when the shared atom is between the other two atoms.

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The secular equation can be written in expanded form conveniently, since the force-constant matrix F is diagonal. It is

$$\sum_{s=0}^{n} (-1)^s \lambda^{n-s} \Sigma G^{(s)} F^{(s)} = 0 \tag{2}$$

where $G^{(s)}$, $F^{(s)}$ are s-rowed diagonal minors of G and F and the inner sum is over all such s-rowed diagonal minors [4].

The F and G matrices are independent of the order of the atoms except for the signs in G. Interchange of order of a pair of atoms will not change the value of any diagonal minor of G, so the secular equation is independent of the order of the atoms.

From experimental observations on the stretching vibrations of a sufficient number of isotopic forms of the molecule, the $\frac{1}{2}n(n-1)$ force constants are determined. Those associated with bonded distances will ordinarily be larger than those associated with non-bonded distances, thus yielding the information necessary to determine the order of the atoms.

Example. The sum of roots of the secular equation in HCN is

$$\Sigma\lambda = (\mu_C + \mu_H) f_{CH} + (\mu_C + \mu_N) f_{CN} + (\mu_N + \mu_H) f_{NH} \tag{3}$$

in which $\mu_x = 1/m_x$. Data is available [5] for $H^{12}C^{14}N$, $D^{12}C^{14}N$ and $D^{13}C^{14}N$ so that there are three equations for the three unknowns. From these one obtains

$$\Delta\mu_H(f_{CH} + f_{NH}) = \Delta\Sigma\lambda \tag{4}$$

$$\Delta'\mu_C(f_{CH} + f_{CN}) = \Delta'\Sigma\lambda \tag{5}$$

if Δ represents the change HCN to DCN and Δ' that from $D^{12}CN$ to $D^{13}CN$. Numerically,

$$f_{CH} + f_{NH} = 5{\cdot}6 \times 10^5 \text{ dyn/cm.}$$

$$f_{CH} + f_{CN} = 25{\cdot}5 \times 10^5$$

From these and equation (3) one obtains

$$f_{CH} \simeq 6{\cdot}1 \times 10^5$$

$$f_{NH} \simeq -0{\cdot}5 \times 10^5$$

Consequently H is bonded to C and C to N, as expected.

If the molecule is known to have a centre of symmetry, symmetry co-ordinates may be used. For example, with $Ag(CN)_2^-$, the evidence [2] shows that there is a centre of symmetry. The infra-red active modes are antisymmetric. As co-ordinates one could use

$$\begin{aligned} (\tfrac{1}{2})^{\frac{1}{2}}(\Delta r_{AgC_1} - \Delta r_{AgC_2}) &= R_{AgC} \\ (\tfrac{1}{2})^{\frac{1}{2}}(\Delta r_{AgN_1} - \Delta r_{AgN_2}) &= R_{AgN} \\ (\tfrac{1}{2})^{\frac{1}{2}}(\Delta r_{C_1N_1} - \Delta r_{C_2N_2}) &= R_{CN} \end{aligned} \tag{6}$$

In terms of these the G matrix is easily found, and consequently the antisymmetric factor of the secular equation. The sum of the roots for this is

$$\lambda_3 + \lambda_4 = (2\mu_{Ag} + \mu_C)F_{AgC} + (2\mu_{Ag} + \mu_N)F_{AgN} + (\mu_C + \mu_N)F_{CN}$$

in which the F's are the diagonal force constants in terms of the symmetry coordinates. If Δ represents the change due to substituting the carbon isotope and Δ' the change due to the nitrogen isotope, one has

$$\Delta(\lambda_3 + \lambda_4) = \Delta\mu_C(F_{AgC} + F_{CN})$$
$$\Delta'(\lambda_3 + \lambda_4) = \Delta\mu_N(F_{AgN} + F_{CN})$$

In published work [2] on $Ag(CN)_2^-$ both frequencies were given for the normal compound but only the high frequency for the isotopic species. However, the product rule [6] (which is also independent of the order of the atoms) can be used to determine the low frequency and thus give the sum of the roots. The result is

$$F_{AgC} + F_{CN} = 18{\cdot}3 \times 10^5 \text{ dyn/cm.}$$
$$F_{AgN} + F_{CN} = 16{\cdot}7 \times 10^5 \text{ dyn/cm.}$$

which shows that $F_{AgC} > F_{AgN}$ and therefore supports the structure with Ag–C bonds. However, because of the relative weakness of the Ag–C bonds, the evidence is not as conclusive as would be desirable. The whole argument as given neglects anharmonicity.

If the expressions involving the sum of the roots do not suffice because of lack of data, the other invariants can be employed to assist in the determination of the force constants. However, these will require the solution of quadratic or higher equations and can lead to multiple solutions. It can happen that one solution supports one structure while another solution supports a different order of the atoms. In such a case the bending frequencies may be decisive or more isotopic data may be required.

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The promise and problems of the matrix isolation method for spectroscopic studies

GEORGE C. PIMENTEL
Chemistry Department, University of California, Berkeley, California, U.S.A.

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THE matrix isolation method was developed at the University of California to permit the leisurely spectroscopic study of extremely unstable species, including free radicals. In the technique it is desired to prepare a suspension of the species of interest in a suitable solid matrix, that is, in a solid material which is chemically inert, rigid with respect to diffusion, and transparent in the spectral region of interest. In these laboratories the matrix materials selected were nitrogen, argon, and xenon, since the infrared spectral region was considered to be of primary importance. In other laboratories [1, 2, 3, 4] where the technique was developed independently, interest was directed toward ultraviolet-visible studies and matrix materials used included the familiar glass-forming organic mixtures (e.g. "E.P.A.", *iso*pentane-3-methyl pentane). In our use of nitrogen or a rare-gas matrix, the solid sample is prepared by freezing quickly a gas mixture of a small amount of some material of interest in a very large amount of the matrix. Suitable coolants are liquid hydrogen (20°K) or liquid helium (4°K) but not liquid nitrogen (77°K).

In the course of experimentation it became apparent that a variety of types of study were made possible by the matrix technique. These are enumerated and examples given.

(a) *Band narrowing*. The infrared spectrum of a monomolecular dispersion of a compound in solid argon consists of very narrow lines. This reduction of band widths sometimes aids in verifying the existence of overlapping, accidentally degenerate bands. This spectral behavior is of particular importance in the study of the hydrogen stretching modes of hydrogen bonded species. The large band breadths observed in spectra of solutions prevent identification of frequencies characteristic of hydrogen bonded polymers of various sizes. In matrix studies of methanol in nitrogen, for example, it was possible to assign characteristic O—H stretching frequencies to dimers, trimers, tetramers, and higher polymers. The pattern of frequency shifts is informative of the structures of these polymers [5].

(b) *Free radicals*. Two methods are in use for the preparation of suspensions of free radicals. The free radicals may be prepared in the gas phase and quickly frozen with the matrix on a cold surface. Another technique is to produce the free radicals after deposition by photolyzing a suitable starting material. For example, hydrazoic acid has been suspended in solid nitrogen at 20°K and then photolyzed. As the HN_3 is decomposed by photolysis, various products are revealed by the appearance of new infrared bands. One of these products is certainly ammonia, suggesting that the NH radical produced in the primary dissociation extracts hydrogen atoms from other HN_3 molecules in successive secondary reactions. This scheme supports the identification of a band at 1290 cm^{-1} attributed to the bending mode of NH_2 radical [6].

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(c) *Primary act of photolysis.* The matrix method provides a method of studying the photolytic process. In principle, the photolytic process can be stopped without secondary reactions, thus providing direct information on the primary act of photolysis. For example, studies have been made of the photolysis of methyl nitrite in solid argon. The product identified was formaldehyde in a yield of one mole per mole of methyl nitrite photolyzed. No nitric oxide was detected, but one unidentified band is in a reasonable spectral region for an absorption of HNO. The data are informative concerning the production of formaldehyde in the photolysis of gaseous methyl nitrite, for which a yield of about one half mole per mole of methyl nitrite photolyzed is obtained.

(d) *Kinetics.* The matrix method provides a means of bringing together reactive species at very low temperature as well as a means of isolating them. With spectroscopic observation, it is possible to make direct kinetic studies for reactions with unusually low activation energies, probably in the range 1–3 kcal. For example, the rate of disappearance of a band assigned to *cis*-nitrous acid has been measured at 20°K. This disappearance is attributed to the *cis* to *trans* isomerization of nitrous acid. Assuming zero entropy of activation leads to an enthalpy of activation of 1·4 kcal/mole.

In attempting to exploit these possible applications of the matrix technique, a variety of practical and interpretive difficulties have been discovered. Two of these are discussed.

In interpreting the spectra obtained by the matrix method, it is necessary to estimate the extent to which the results are determined by the matrix. The infrared spectra of a number of stable molecules in nitrogen or argon matrices have been examined and it is clear that the sharp bands obtained are very close in frequencies to the corresponding bands observed in gas-phase studies. It is implied that the matrix disturbs neither the structure nor the vibrational force constants of the suspended molecules. An exception is provided by ammonia. The symmetrical bending mode of ammonia is observed at about 975 cm^{-1} in a nitrogen matrix instead of near 950 cm^{-1} as in the gas phase. This shift, in the wrong direction for a dielectric effect, is considered to reflect the loss of inversion doubling because of constraint by the matrix.

Similarly, there is uncertainty in the interpretation of kinetic measurements. The constraints of the matrix could affect the activation thermodynamics so as to make the results of doubtful applicability to the reaction kinetics under more normal conditions. The *cis-trans* isomerization provides a striking example, since the best previous estimate of the activation energy for isomerization is 10 kcal, seven times larger than the value deduced here. Another possible kinetic measurement, diffusion, is subject to uncertainty because the nature of the solid obtained by condensing a gas is not well known.

This introduces another question of significant interest in matrix studies, the exact nature of the solid obtained in these experiments. On the one hand, the solid seems to be microcrystalline, as suggested by the high scattering of light. On the other hand, the infrared spectra of pure solids prepared in this manner often indicate imperfect development of spectral features attributable to crystalline interactions. The solid thus could be partially crystalline with vitreous "pockets" or it could be a highly imperfect crystal. The calorimetric studies of DE NORDWALL and STAVELEY [7] are pertinent. They have discovered that for each of a number of solids prepared by quickly freezing a gas there is a characteristic temperature at which heat is released during warming. This temperature, T_D, is presumed to be due to a devitrification process. We have measured spectroscopically this same temperature, T_D, as revealed by diffusion processes or by development of crystal splittings. In both types of study, the ratio of T_D to the melting point is near 0·5. For three of the four compounds for which DE NORDWALL and STAVELEY found no thermal peculiarities, it seems likely that the coolant temperature was not sufficiently low to keep the sample temperature below T_D during deposition. Combining the data of DE NORDWALL and Staveley with the spectroscopic studies, it seems that the phenomenon of forming highly imperfect crystals or glasses on freezing a gas is a very general one. The examples include such extremes as argon, water, methylene chloride, and toluene. Neither type of study has, as yet, provided conclusive evidence of the precise nature of the solid, however.

In conclusion, it is amply clear that the matrix isolation method has wide and interesting applications, particularly with infrared spectral techniques. There remain certain problems of interpretation which are themselves of significant interest.

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INFRA-RED SPECTRA OF ADSORBED MOLECULES

by

N. Sheppard
University Chemical Laboratory,
Lensfield Road, Cambridge, England

SUMMARY

Progress so far achieved in the study of adsorbed molecules by means of infra-red spectroscopy is reviewed. Particularly detailed results are available from two "model" adsorption systems (a) the physical adsorption of molecules on high-area silica and (b) the chemisorption of carbon monoxide on silica-supported metals. In each case information of direct importance has been obtained on the nature of the interactions of adsorbed molecules with the surface. They point to the great potential value of the infra-red spectroscopic method for studying adsorption, particularly when spectroscopic measurements and classical adsorption measurements are made in parallel.

The principal experimental difficulty to be overcome is the loss of radiation by surface scattering and absorption by the adsorbent. High-area adsorbents are required. These scatter less radiation in the form of microporous glassy solids than as finely divided powders, but useful results can be obtained with adsorbents in the latter form. With opaque adsorbents spectra are as yet only obtainable when it is permissible to separate the adsorbent particles by a transparent "supporting" medium.

INTRODUCTION

INFRA-RED spectroscopy is unique among the spectroscopic methods of determining molecular structure in that it can be used to study compounds in all the states of matter—gas, liquid and solid—with comparable ease in each case. As a result it is the first of these methods to be used extensively to study the structure of molecules adsorbed on surfaces. A few adsorption systems have now been investigated in considerable detail and it is an appropriate time to attempt a review of the progress to date, particularly as it seems that the method may become of major importance in the future study of both physical adsorption and chemisorption. Although some of the experimental difficulties to be overcome are still formidable, the reward of progress is likely to be great.

The major part of this review will be devoted to the spectroscopic results obtained with two adsorption systems (a) the physical adsorption of various molecules on high-area silica and (b) the

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chemisorption of carbon monoxide on various metals supported on silica. Each of these systems has now been investigated spectroscopically in some detail and, although they are both somewhat favourable cases, the collected results do enable an assessement to be made of the scope of the infra-red method as applied to adsorption. A number of other isolated papers have been published which are of considerable interest and these are reviewed more briefly.

EXPERIMENTAL REQUIREMENTS

Absorption bands of measurable strength are usually obtainable from a layer of liquid from 1 to 100 μ in thickness, depending on the intrinsic strengths of the absorption bands in question. Taking 10 Å as an effective thickness of a monolayer of adsorbed molecules of moderate size it follows that about a thousand traversals of a monolayer by infra-red radiation are necessary to provide readily measurable spectra. Radiation may be lost on each surface traversal (other than by the desired absorption by the monolayer) by surface scattering and—for non-transparent materials—by absorption by the adsorbent. Although a number of adsorbents do not absorb infra-red radiation strongly, at least in certain important regions of the spectrum, the loss of radiation by scattering must always be present to some—often to a large—degree. Luckily, however, the scattering by individual particles becomes greatly reduced at particle sizes less than the wavelength (λ) of radiation used, and it is not very difficult to produce particle sizes smaller than the wavelength of typical infra-red radiation (i.e. of smaller size than 1 μ). A finely divided material of this sort has necessarily a high specific area so that, in addition to having the required property of low scattering, it also will give absorption bands of adsorbed molecules at reasonably low pathlengths. It is this fortunate conjunction of high sensitivity with low scattering that makes the spectroscopic study of adsorption feasible. At the present stage it seems that high-area adsorbents with specific surface areas of several tens or hundreds of square metres per gramme are necessary to achieve spectroscopic results of acceptable sensitivity, although this requirement may be somewhat relaxed in the future. However in practice a layer of powder, although its individual particles may be less than λ in size, still has very considerable residual scattering, perhaps because of the formation of agglomerates of effective size greater than the wavelength of the radiation. High-area adsorbents have been used which are in the form of porous glasses or gels and, from work on high-area silica to be discussed below, it seems that such a material scatters considerably less radiation than a powder of equivalent pathlength and specific area. This may be because the individual surfaces are separated from each other more often than in the case of a layer of powder.

Another advantage of working with a high-area adsorbent is that a sample of reasonable size for spectroscopic work will often adsorb measurable amounts of a gaseous adsorbate so that the spectroscopic results can be related to those of the more classical techniques for studying adsorption such as the isotherm. Such a correlation of spectroscopic work with fractional surface coverage, θ, is greatly to be desired although so far it has been attempted in only a few cases.

PHYSICAL ADSORPTION

Adsorption on high-area silica. The first successful infra-red spectroscopic experiments on adsorbed molecules were carried out in Russia in 1949 using high-area silica in the form of porous glass (YAROSLAVSKY and TERENIN (1)) and silica gel (KURBATOV and NEUIMIN (2)). The group under Professor Terenin's direction in Leningrad has since made the major contribution to the literature on the infra-red spectra of physically adsorbed molecules, although more recently workers from other parts of the world have contributed notable results.

In the early experiments work was done with layers of either porous glass or silica gel several millimetres in thickness. Under these conditions the glass itself is transparent only in the near infra-red region ($\bar{\nu} > 4000$ cm^{-1}). It is now recognized that very often so-called "oxide" surfaces have a considerable number of chemically bound OH groups. In the case of silica surfaces, the SiOH groups remain even after prolonged evacuation at temperatures in the vicinity of 400–500°C; most adsorbed water molecules are removed by such treatment. In the near infra-red region an absorption band at 7326 cm^{-1} was identified as the first overtone of the ν OH vibration of surface hydroxyls at an early stage (2). It was found that the adsorption of a variety of molecules on to the silica surface caused a shift of this OH band to lower frequencies, corresponding to the formation of hydrogen bonds of various strengths between the surface OH groups and the adsorbed molecules. These shifts varied from 10–20 cm^{-1} for non-polar adsorbates up to a more than 1000 cm^{-1} for acetone (3). At higher surface coverages new absorption bands due to CH, NH and OH groups of the adsorbed molecules could be observed (1, 2). Although much of the earlier work was done with fairly complex adsorbate molecules, some studies were made in 1950–1952 by YAROLAVSKY *et al.* with the small molecules H_2O (4), O_2 (5) and N_2 (5) adsorbed on silica. This pioneering work in the near infra-red region showed clearly the type of information obtainable from infra-red studies of such adsorption systems.

During the last few years work has been concentrated on the longer wavelength absorption bands at the fundamental vibration frequencies of the surface OH groups and adsorbed molecules. In 1953 CHEVET (6) showed that silica gel, after being heated to drive off adsorbed water, gave a sharp absorption band due to the fundamental vibration of surface OH groups which were presumed to be free of hydrogen bonding. In the same year PIMENTEL *et al.* (7) obtained an absorption band of D_2O adsorbed on silica gel for a surface coverage, θ, of less than unity; this was apparently the first paper in which an attempt was made to relate infra-red results with actual measurements of coverage. In 1954, SIDOROV (8) published spectra in the region 4000–2000 cm^{-1} of a whole series of molecules adsorbed on porous glass and confirmed the main features of the earlier work in the overtone region. In 1955 YATES *et al.* (9) demonstrated the sensitivity of the infra-red method as applied to porous glass by observing the ν OH band shifted by hydrogen bonding with adsorbed ammonia molecules at a measured value of surface coverage, $\theta \sim 0{\cdot}014$. In 1955 YOSHINO (10) observed changes in the infra-red spectra of 1:2-dichloroethane and acetylacetone caused by adsorption of these molecules on silica gel.

NIKITIN *et al.* (11) have shown that the OH groups of porous glass can be converted to OD by reaction with D_2O. They further demonstrated that the initial adsorption of H_2O on porous glass (or D_2O on the deuterated glass) caused new bands due to the adsorbed molecules but did not affect the intensity of the ν OH (ν OD) bands of the surface groups i.e. that these molecules are adsorbed on to other sites than the surface OH groups. In 1956 SIDOROV (12) made a further advance in technique by studying the adsorption of a number of small molecules both on porous glass and on methylated glass, the surface OH groups of which had been converted to OCH_3 by a repeated heat treatment with methanol. It was found that the adsorption of methanol, water, ammonia, and chloroform on porous glass occurred on two types of site. One is the surface OH group (as shown by the shifting of the ν OH band) and the other was tentatively identified as surface silica atoms. At sufficiently large amounts of adsorption the ν OH band is always shifted through hydrogen bonding, as observed in the earlier studies, but the molecules held to the surface in this fashion are rather weakly adsorbed and can be driven off by evacuation or gentle heating. When this has been done the surface OH band is reported to be restored to its original intensity, but the presence of the remaining molecules on sites of the second type is still readily shown by the persistence of their absorption bands, which usually have slightly different frequencies from those of the more weakly adsorbed molecules.

In the case of water, ammonia and methanol adsorbed on methylated glass the only absorption bands found (12) correspond to those of molecules on the second type of site on porous glass itself, confirming that the latter are not OH groups. However, in the case of methanol the strength with which these molecules are adsorbed is much less than for the unmethylated porous glass, showing that the change from OH to OCH_3 has at least a secondary effect on adsorption at the sites of the second type.

From among a considerable number of larger molecules adsorbed on porous glass SIDOROV reports that only phenol shows any sign of being adsorbed on two types of site (and the evidence here is indirect) although all of them—ranging from hydrocarbons such as benzene to polar molecules such as acetone and pyridine—are adsorbed on OH sites as shown by the shifts of the surface OH absorption bands. Shifts also occur in the frequencies of the more polar adsorbed molecules which are consistent with them being attached to the OH groups by hydrogen bonds. Attempts were made to adsorb a few of these larger molecules on to methylated glass, but only in the case of pyridine did new absorption bands due to adsorbed molecules appear in the spectrum. To the reviewer this suggests that the sites of the second type are sterically less accessible than those of the first type (OH groups), a conclusion also consistent with the fact that methylation of porous glass reduces the accessibility of the second type of site for methanol and chloroform adsorbates. If, as was suggested (12), the second type of site is a surface silicon atom this presumably interacts with the adsorbed molecule through a lone pair of electrons in the latter. It is difficult to see—on this picture—why molecules with polarizable lone pairs such as diethyl ether and benzaldehyde are not adsorbed on such sites of methylated glass unless another factor, such as a steric factor, is operative.

SIDOROV (12) also pointed out that the shifts in the absorption bands of the surface OH groups increase in the same order as the proton acceptor properties of the adsorbed molecules. More recently (1957) MCDONALD (13) has made an analogous study of adsorbed molecules on high area powdered silica. He reports exactly the same frequency (3749 cm^{-1}) for the absorption band of the surface OH groups as reported by SIDOROV for porous glass, and his results on adsorbed benzene, water and methanol are very similar indeed to those reported with porous glass. He also reports frequency shifts with small non-polar molecules such as methane, oxygen, nitrogen and the rare gases adsorbed on the OH groups at low temperatures. Combining the data from the two papers of MCDONALD and SIDOROV, direct evidence is provided for a remarkably continuous range of hydrogen bonding of the OH groups with frequency shifts from 8 cm^{-1} for adsorbed argon up to 850 cm^{-1} for adsorbed pyridine.

McDONALD also measured relative integrated intensities of the shifted OH bands and showed that there is always an increase in intensity in comparison with the value for free OH groups, as is usually the case on hydrogen bond formation (14). He further pointed out that for adsorbed nitrogen the partial pressure at which the free OH groups disappear is considerably less than that at which a monolayer is formed on such a surface as deduced from adsorption isotherms. He concludes from this (like Sidorov) that the silica surface is non-uniform in its adsorption properties.

Finally (1956) SHEPPARD and YATES (15) have also studied the adsorption of small molecules on porous glass at low temperatures, although in this work the emphasis was on the bands of the adsorbed molecules. The experiments were carried out under such conditions that the surface OH absorption bands were too strong to be measured quantitatively. These spectra were allied with estimates of the surface coverage, θ, based on measurements of the amount of gas adsorbed, the area per molecule of adsorbate, and the specific area of the glass. Absorption bands were obtained from the ν CH vibrations near 3000 cm^{-1} of methane, ethylene and acetylene. The sensitivity was such that a readily observed band was obtained from adsorbed methane at about $\theta = 0{\cdot}01$, i.e. for as little as 1/100 of a monolayer.

The forces of interaction between the surface atoms and the adsorbed molecules were reflected in the frequency shifts of the CH absorption bands. Even more direct evidence for these forces was provided by the observation of two ν CH absorption bands of adsorbed methane, one of which corresponds to the normally infrared active frequency, ν_3, and the other to the normally forbidden "breathing" frequency, ν_1. The latter is forbidden because of the tetrahedral symmetry of an isolated molecule i.e. the appearance of this band results from a distortion in shape of the molecule by the surface forces. A similar "forbidden" band was observed in the spectrum of adsorbed ethylene and, more significantly, the stretching vibration of adsorbed hydrogen was observed at the relatively low coverage of $\theta = 0{\cdot}2$. A quantitative measurement of the strength of the latter band led to a direct (if approximate) estimation of the effective electrical field gradient at the surface of porous glass.

The measurement of the spectrum of adsorbed methane under fairly high resolution also enabled an assessment to be made of the extent to which the adsorbed molecules have rotational freedom on the surface. Methane is a favourable case because (a) it is weakly adsorbed and approximately spherical in shape so that relatively free rotation might well occur and (b) its low moment of inertia would lead to fairly extensive rotational wings on the ν_3 absorption band if rotation is in fact occurring. The measured shape of the band ruled out the possibility that completely free rotation was occurring about three mutually perpendicular axes. It was, however, in close agreement with that calculated for free rotation about a single axis perpendicular to the surface, although the possibility could not be ruled out that the band width was fortuitously that of a purely vibration band (i.e. without free rotation) widened because of surface forces.

Alkali halide and other surfaces. Although the only detailed infra-red studies of physical adsorption have been concerned with silica surfaces, some results have been published which possibly correspond to the adsorption of polar molecules on polycrystalline alkali halides in the form of pressed discs. As an example of work of this type FARMER has studied the infra-red spectra of carboxylic acids in alkali halide disks (16). He finds that the spectra vary with the alkali halide chosen and differ from those of the same crystalline acids in the usual dimeric hydrogen bonded state. He concludes that the acids are in some cases directly hydrogen bonded as a monomolecular layer on to the alkali halide surface.

FRENCH *et al.* (21) have also published infra-red spectra of some surface-active agents adsorbed from solution on finely divided bentonite, and of oleic acid adsorbed on fluorite. They incorporated the adsorbent–adsorbate system in alkali halide disks to reduce the scattering of radiation by the powders.

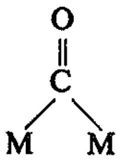
CHEMISORPTION

Carbon monoxide chemisorbed on silica supported metals. The first direct investigation of chemisorption by means of infra-red spectroscopy was apparently made by EISCHENS, FRANCIS and PLISKIN (17) in 1954. In this paper and a more detailed subsequent one (18) infra-red spectra were described of carbon monoxide chemisorbed on the metals copper, platinum, nickel and palladium.

In the form of coherent films, metals such as these are efficient reflectors of infra-red radiation, whereas in the finely divided condition (such as metal "blacks") they are good absorbers. Such adsorbents would therefore seem to be far from ideal for the observation of spectra. However, these authors obtained workable transmission through a system in which fine particles of the metal were separated from each other by deposition on small silica particles (Cab-o-sil), and they were able to obtain absorption bands of the chemisorbed substance. The metal particles were stated to have a diameter of about 70 Å in the case of platinum, and the silica particles were of diameter 150–200 Å. It seems that infra-red radiation interacts with a sufficient number of these metal particles arranged in depth such that the surface adsorbed molecules (if, like carbon monoxide, they have high extinction coefficients) cause absorption bands of measurable strength. As the conditions of preparation of surfaces are often a critical factor in adsorption studies it is pertinent to add that the metal particles were produced by drying a deposit formed by a slurry of silica particles in a solution of a metal salt, first at room temperature, and then *in vacuo* at 100–200°, followed by a reduction in hydrogen at 200–350°. The last two steps were carried out in an *in situ* absorption cell. The samples were cooled to room temperature in an atmosphere of hydrogen, the hydrogen was purged with nitrogen, and then carbon monoxide was brought into contact with the sample. Spectra were measured after excess gaseous CO had been displaced by hydrogen or nitrogen. The powdered sample rested on a horizontal fluorite plate in the absorption cell and consisted of about 8 per cent of metal in a layer of weight 0·012 g/cm^2. After combined reflection and absorption losses the transmission of the sample was 2–6 per cent near 5 μ.

In the case of copper and platinum the chemisorbed CO gave strong and sharp bands at about 2130 and 2070 cm^{-1} respectively which were clearly attributable to the presence of chemisorbed molecules linked to separate metal atoms as in (i) below. In addition much weaker and broader absorption bands in the vicinity of 1800 cm^{-1} could be attributed to chemisorbed molecules of type (ii) by analogy with the spectra of bridged CO groups of gaseous metal carbonyls. However, with these two metals it is clear that sites of type (i) greatly predominate. These latter absorption bands were only removed from platinum by pumping for many hours at 200°C, showing that the CO is strongly adsorbed. Measurements on Pt were also made at different values of the estimated surface coverage, θ, derived on the assumption that at 25°C the coverage was that of a complete monolayer as the amount of adsorbed CO did not change for a pressure range from 2 to 10^{-4} mm. The relative amounts of adsorbed CO were determined indirectly by removing it part by part by oxidation with successive measured doses of oxygen, it being assumed that oxygen is not chemisorbed

(i)

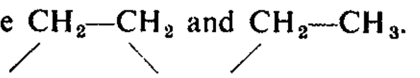


(ii)

until CO is removed. From a detailed consideration of the strengths and wavelengths of bands at different coverages obtained with an adsorbed mixture of $C^{12}O$ and $C^{13}O$ it was concluded that direct mechanical interactions occurred between adjacent adsorbed molecules for $\theta > 0{\cdot}66$. As the spectrum did not change at low coverage there was no evidence for interactions of the type expected if adsorption affects the work function of the metal. No evidence for any considerable heterogeneity of the Pt surface was obtained.

Nickel and palladium differed very considerably from copper and platinum in that the strongest absorption bands corresponded to type (ii) carbonyl groups; type (i) bands were much weaker (17, 18). The overall breadth of the bridged carbonyl band was such as to suggest that the molecules are bonded to the surface with a range of different strengths. Indeed as the relative amount of adsorbed CO was increased the maximum of this band on Pd shifted to higher frequencies in fairly discrete steps as if it consisted of three overlapping bands of frequencies about 1840, 1890 and 1930 cm^{-1}. The lower frequency component appeared at first, and the high-frequency one last. As the lowest frequency band is shifted to the greatest extent with respect to the frequency of gaseous CO ($\sim$2140 cm^{-1}), it probably corresponds to the most strongly adsorbed molecules. The authors suggest that the three overlapping component absorption bands each correspond to a fairly homogeneous set of sites, plausibly to be identified with different crystal faces. On this metal a single band due to linearly adsorbed CO of type (i) appears only at high relative coverages of the surface, suggesting that this type of adsorption only occurs on single metal atoms left by the random pairing of sites of type (ii). Such molecules are only weakly adsorbed and can be removed by pumping. The results for CO adsorbed on nickel are similar to those on palladium in so far as the bridged carbonyl bands are concerned. However, the linearly bonded CO band has two components, and is relatively stronger in this case. It was suggested that the first of these bands, which is readily removed by pumping, corresponds to molecules adsorbed as in (i) but with more than one CO to each metal atom, whereas the second corresponds to single type (i) carbonyls on nickel atoms.

Finally, in a recent review of the work of his group on chemisorption, EISCHENS (19) has reported some preliminary results with CO adsorbed on metal alloy mixtures.

Other spectroscopic studies of chemisorption. Another potentially very interesting field of adsorption on silica supported metals is the hydrocarbon one; PLISKIN and EISCHENS (19, 20) have briefly reported some interesting spectroscopic results on ethylene, propylene and acetylene adsorbed on nickel. Both ethylene and propylene showed absorption bands in the 3000 cm^{-1} region which are almost entirely due to CH bonds attached to saturated carbon atoms, i.e. the double bonds have been removed in the chemisorption process. Chemisorbed ethylene has CH_2 groups as shown by the presence of a band at about 1450 cm^{-1}, and on hydrogenation CH_3 groups are formed as shown by the band at about 1380 cm^{-1}; suggested surface species are  $\underset{/}{C}H_2—\underset{\backslash}{C}H_2$ and $\underset{/}{C}H_2—CH_3$. Hydrogen can be removed from the adsorbed groups by pumping, and some olefinic CH bands result: rehydrogenation is readily achieved. It is clear that this work is capable of much interesting development.

Some spectroscopic work has also been done on ammonia chemisorbed on a silica-alumina cracking catalyst (21, 22). In the first attempt (21) scattering losses were reduced by incorporating the catalyst + chemisorbed species in a pressed alkali halide disc, but as shown later (23) the presence of the alkali halide led to anomalous results. Work directly on a finely powdered catalyst of this type (22) showed that some ammonia was chemisorbed on Lewis type sites so that X—NH_3 groups were formed, whereas other molecules were converted to NH_4^+ on the Lowry-Brönsted type of acid sites. It remained possible however that the latter adsorbed ions were formed by reaction with small amounts of water on the catalyst despite rigid drying precautions (19).

Finally the reviewer's group at Cambridge have recently been engaged in some studies, as yet unpublished (24), of hydrocarbons chemisorbed on metals and oxides supported (so as to reduce scattering losses) on porous glass rather than powdered silica. It is hoped that some of these results will be presented at the meeting.

CONCLUSION AND PROSPECTS

In the case of molecules physically adsorbed on high area silica it has been possible to obtain from the infra-red spectroscopic results information about (a) the nature of the specific forces holding the molecules to the surface (hydrogen bonding, etc.) (b) the existence and nature of two types of site on the surface (surface heterogeneity) (c) the degree of freedom of rotational motion on the surface and (d) the effective electrical field at the surface. In addition it has been possible to make measurements at surface coverages much less than unity.

For chemisorbed carbon monoxide on silica supported metals it has been demonstrated spectroscopically that (1) CO molecules can be attached to the metal surface in linear or in bridged complexes (2) that in certain cases the surface is heterogeneous so far as both types of adsorption are concerned.

Results such as those listed above are of direct and far-reaching importance. There can be little doubt that if infra-red data were available on this scale for a wide range of adsorption systems, present-day knowledge of the chemical and physical processes involved in adsorption would be greatly extended. The main criticism that can be made of the spectroscopic work so far published is that it is rarely allied to measurements of adsorption isotherms, heats of adsorption, and other classical data on adsorption systems. It is greatly to be hoped that such parallel studies of spectroscopy and adsorption will be made in the future. The great richness of the spectroscopic data on high area silica in particular would be of much greater significance if the new facts could be correlated with data on surface coverage and heats of adsorption.

Experience so far obtained shows that if an effort is made to obtain adsorbents of moderately high area, then infra-red data can be obtained in regions of the spectrum where the adsorbent does not absorb radiation strongly. Loss of light due to surface scattering is not a serious problem when microporous glass-like adsorbents are used. However, it must be admitted that the great success so far achieved with high-area silica is in large measure due to the fact that it is available in this form. Nevertheless McDONALD (13) has shown that useful results with more limited sensitivity can be achieved also with silica in the form of a fine powder. It may be concluded with reasonable confidence that physical and chemisorption work on powders of transparent materials will be supplemented considerably by spectroscopic investigations in the near future. Those adsorbents which can be produced as a "gel" or "glass" will be particularly accessible to spectroscopic study and it would appear to be worthwhile to investigate the possibility of producing more high area adsorbents in this form.

The problem of light loss is a considerably more difficult one when the adsorbent is also a strong absorber of radiation as in the case of carbon black, graphite and the metals. However, the pioneering work of Eischens and his collaborators at the Beacon Research Laboratories of the Texas Company have shown clearly that progress can be achieved in this direction also provided that (a) the adsorbed molecules have strong absorption bands and (b) that no complication to the adsorption system accrues from the presence of a transparent substance that supports and separates the opaque particles. By using modern infra-red spectrometers near to the limit of performance it will undoubtedly be possible to achieve considerable success with this type of sample, even with fairly weak absorbers. However, the sensitivity of adsorption processes to the presence of other components is such that there will always be some doubt whether spectroscopic results obtained with a "supported" adsorbent of this type can be related directly to adsorption studies on the unsupported metals. Thus although supported catalysts are of importance, and are very well worth studying for their own sake, there remain formidable difficulties to be overcome before it can be claimed that infra-red spectroscopy is applicable to the whole field of adsorption phenomena. Nevertheless the results so far obtained are likely to stimulate a great effort in this direction in the near future.

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Attenuated total reflection*

A new principle for the production of useful infra-red reflection spectra of organic compounds

J. FAHRENFORT
Koninklijke/Shell-Laboratorium, Amsterdam
(Shell Internationale Research Maatschappij N.V.)

Abstract—Infra-red reflection spectra of exceptionally good contrast can be obtained if the interface between a dielectric of high refractive index and the sample is taken as the reflecting surface. Radiation incident from the strongly refracting dielectric on this interface at an angle somewhat larger than the critical angle will be totally reflected, but only in those frequency regions where the second medium is non-absorbing ($\kappa = 0$). In regions with $\kappa \neq 0$, reflection will not be total any more and, accordingly, a reflection spectrum of high contrast and intensity is obtained, which strongly resembles a transmission spectrum.

These spectra may, after calibration, be used as such for quantitative purposes. They may also, by graphical methods or by application of the KRAMERS–KRONIG relation, be converted into spectra of the optical constants n and κ.

Introduction

REFLECTION spectra are in general recorded for either of two reasons. The first reason is that they permit to determine the refractive and absorption indices (the optical constants); the other is that in this way data can be obtained on an otherwise intractable sample, as for instance a strongly absorbing crystal, which for transmission measurements would have to be prepared in impracticably thin layers.

The reflection technique, however, does not always lead to satisfactory results; it normally fails for substances showing weak absorption. This sets a severe limitation to the applicability of the reflection technique, as the great majority of absorption bands of organic materials are weak.

On the other hand, the numbers of cases in which organic samples are not amenable to transmission measurements is becoming increasingly important. As the development of a reflection technique suitable for weakly absorbing substances would not only extend the applicability of spectroscopic investigation but might also be expected to yield data on the optical constants of solvents and similar substances, the present investigation was undertaken.

Existing techniques and their shortcomings

Several methods [1–3] have been devised for the measurement of infra-red reflection spectra of strongly absorbing materials, and for their conversion into spectra of the optical constants. All of these methods are based on the formulae

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of Fresnel and Snellius, extended with the concept of the complex refractive index.

The formulae of Fresnel give the ratio r of the reflected amplitude to that of the incident light wave

$$r_s = -\frac{\sin(\theta - \theta_1)}{\sin(\theta + \theta_1)}; \quad r_p = \frac{\tan(\theta - \theta_1)}{\tan(\theta + \theta_1)} \tag{1}$$

where the subscript s refers to the case of light polarized perpendicularly to the plane of incidence, p to the case of parallel polarized light. θ is the angle of incidence, θ_1 the angle of refraction.

Snellius' law gives the relation between θ and θ_1

$$\sin\theta = n' \sin\theta_1 \tag{2}$$

with n' representing the refractive index which, in the case of refraction into an absorbing medium, is a complex number

$$n' = n(1 - i\kappa) \tag{3}$$

n stands for the real part of the refractive index, κ is a number called absorption index, as it is closely related to the phenomenon of absorption. Both n and κ appear in Lambert's absorption coefficient α which is given by

$$\alpha = \frac{4\pi n\kappa}{\lambda} \tag{4}$$

and hence can be calculated if n and κ are given as functions of the wavelength λ.

The complex refractive index naturally relates the angle of incidence to a complex angle of refraction. Thus we may write

$$\cos\theta_1 = (1 - \sin^2\theta_1)^{1/2} = \frac{1}{n'}(n'^2 - \sin^2\theta)^{1/2} = \frac{a - ib}{n'} \tag{5}$$

Substituting this expression in Fresnel's formulae (1), we obtain the complex reflected amplitudes

$$r_s = -\frac{a - ib - \cos\theta}{a - ib + \cos\theta}; \quad r_p = -r_s \frac{a - ib - \sin\theta\tan\theta}{a - ib + \sin\theta\tan\theta} \tag{6}$$

The reflecting powers, which will eventually be measured, are given by the squared absolute values of the complex reflected amplitudes

$$|r_s|^2 = \frac{a^2 + b^2 - 2a\cos\theta + \cos^2\theta}{a^2 + b^2 + 2a\cos\theta + \cos^2\theta} \tag{7}$$

$$|r_p|^2 = |r_s|^2 \frac{a^2 + b^2 - 2a\sin\theta\tan\theta + \sin^2\theta\tan^2\theta}{a^2 + b^2 + 2a\sin\theta\tan\theta + \sin^2\theta\tan^2\theta} \tag{8}$$

If the optical constants n and κ are to be determined from reflection measurements, evidently two simultaneous equations have to be obtained, which can be solved for n and κ. Usually these equations are found from measurements at two widely different angles θ.

From an examination of the formulae, however, it appears that the optical constants cannot always be determined accurately from the observed values of the reflecting power. If the refractive index assumes values between $n = 1$ and $n = 2$, as it usually does, reliable values for the absorption index will be derived only if its value is greater than $\kappa = 0{\cdot}2$. This may be seen from Table 1, giving the most sensitive reflecting power $|r_s|^2$ for two angles θ, constant n and a number of κ values.

Table 1. The dependence of $|r_s|^2$ on κ and θ at $n = 1{\cdot}4$

κ	$\theta = 20°$	$\theta = 70°$
0	0·030	0·255
0·1	0·032	0·263
0·2	0·040	0·309
0·3	0·053	0·369
0·4	0·070	0·432

It is seen that, though there is a considerable difference between the reflecting power at $\theta = 70°$ and that at $\theta = 20°$, the values of $|r_s|^2$ for $\kappa = 0$ and $\kappa = 0{\cdot}1$ show hardly any difference. Even the difference for $\kappa = 0$ and $\kappa = 0{\cdot}2$ is so small that it will be virtually impossible to find an accurate value of κ from this difference.

Substances whose absorption bands are accompanied by changes in κ in the region $\kappa = 0$ to $\kappa = 0{\cdot}2$ will show reflection spectra of low over-all intensity, and with insufficient contrast for a determination of the optical constants. On the other hand, absorption bands in which κ reaches a value of 0·2 are rather exceptional, at least in the spectra of organic compounds. When calculated according to (4) with $n = 1{\cdot}4$, $\lambda = 5\ \mu$ and with a sample thickness of 10 μ, a value of $\kappa = 0{\cdot}2$ results in a transmission of only 0·05 per cent. A further illustration of the κ-values normally encountered in infra-red spectroscopy is given in Table 2, which covers the most important wavelength region and the commonly used range of cell thicknesses.

Table 2. Values of κ for different combinations of sample thickness l and wavelength at $T = 0{\cdot}367$ and $n = 1{\cdot}4$

λ (μ)	l (mm)			
	0·2	0·1	0·05	0·01
2	$5{\cdot}7 \times 10^{-4}$	$1{\cdot}1 \times 10^{-3}$	$2{\cdot}3 \times 10^{-3}$	$1{\cdot}1 \times 10^{-2}$
5	$1{\cdot}4 \times 10^{-3}$	$2{\cdot}8 \times 10^{-3}$	$5{\cdot}7 \times 10^{-3}$	$2{\cdot}8 \times 10^{-2}$
10	$2{\cdot}8 \times 10^{-3}$	$5{\cdot}7 \times 10^{-3}$	$1{\cdot}1 \times 10^{-2}$	$5{\cdot}7 \times 10^{-2}$
15	$4{\cdot}2 \times 10^{-3}$	$8{\cdot}5 \times 10^{-3}$	$1{\cdot}7 \times 10^{-2}$	$8{\cdot}5 \times 10^{-2}$

Development of a new reflection technique

In the last section it was demonstrated that, from materials with optical constants in the range $\kappa < 0{\cdot}2$ and $1 < n < 2$, no useful reflection spectra can be obtained.

This situation can be improved, however, by creating the conditions required for total reflection by means of suitable choice of the refractive index n.

The refractive index is essentially only the ratio of the velocities of light in the two media adjacent to the reflecting surface.

$$n = \frac{n_2}{n_1} = \frac{v_1}{v_2} \tag{9}$$

Using, instead of the surface in air, the interface between the sample and an optically dense dielectric as the reflecting surface, it is possible to give the refractive index at the interface a greatly different value. If, furthermore, the dielectric and the angle of incidence θ are chosen in such a way than $n \leqslant \sin \theta$, reflection becomes total for samples with $\kappa = 0$, i.e. non-absorbing.

Total reflection is accompanied by a wave motion with wave fronts perpendicular to the interface in both media. If the second medium is non-absorbing, the time average of the energy transfer from one medium to the other vanishes, and all incident energy is reflected. Microscopically, however, at any moment, one finds a periodic alternation of places where energy is transferred from the first to the second medium, with places where the energy stream flows in the opposite direction.

If for the second medium $\kappa \neq 0$, it is therefore to be expected that the reflection will no longer be total, but that part of the incident radiation will be absorbed by the surface layers.

A closer consideration shows that such a reflection attenuation indeed takes place, and to such a degree that it is manifest even for small κ-values. This is apparent on inspection of Fig. 1, in which calculated values of $|r_s|^2$ for polarized and $|r|^2 = \frac{1}{2}(|r_s|^2 + |r_p|^2)$ for non-polarized light are given for angles θ slightly larger than the critical angle for total reflection. The values are calculated for the combinations $n = 0{\cdot}707$ and $\kappa = 10^{-4}$, 10^{-3}, 10^{-2}, 10^{-1} and 2×10^{-1}.

The reflection attenuation is seen to be greatest in the immediate vicinity of the critical angle, and to be appreciable for all κ-values that according to Table 2 are normally encountered in organic materials.

As in transmission spectra, a larger κ-value of the sample corresponds to a smaller intensity of the light leaving the sample. Provided we work with a well-defined angle of incidence, we may obtain

$$|r_s|^2 = 0{\cdot}97 \quad \text{for} \quad \kappa = 10^{-4}$$

$$|r_s|^2 = 0{\cdot}24 \quad \text{for} \quad \kappa = 0{\cdot}2$$

This means that the spectrum obtained will show the features of a transmission spectrum of a sample of 0·2 mm thickness in those regions where $\kappa = 10^{-4}$, and those of a sample only 0·004 mm thick for $\kappa = 0{\cdot}2$.

Experimental procedure

In the infra-red region, the measurements of reflection with $n < 1$ as described above can be carried out at the interface between the absorbing medium and a crystal of KRS 5 or AgCl. These crystals are transparent and have refractive indices of 2 or more throughout the infra-red region. The refractive index of the great majority of organic compounds is smaller.

The crystals can best be used in the shape of a hemi-cylinder. The diametrical face is used as the reflecting interface and the curved surface serves as entrance and exit window for the light beam as shown in Fig. 2(a).

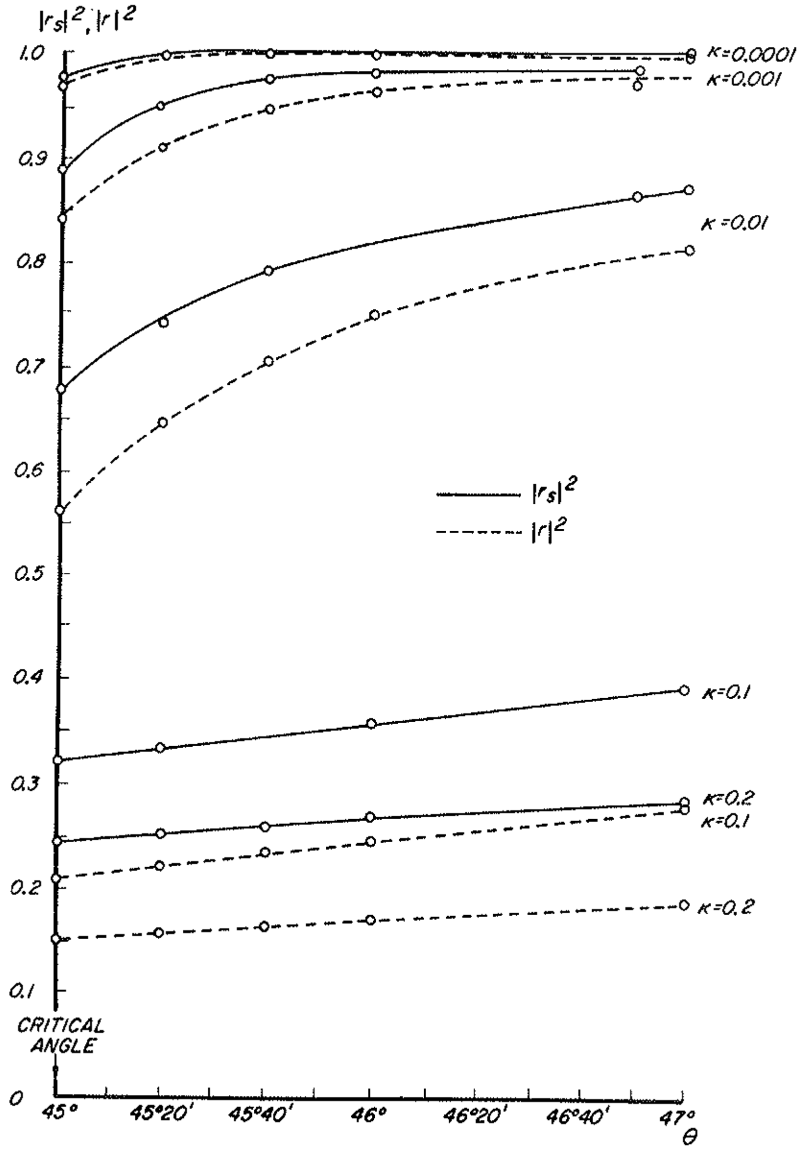
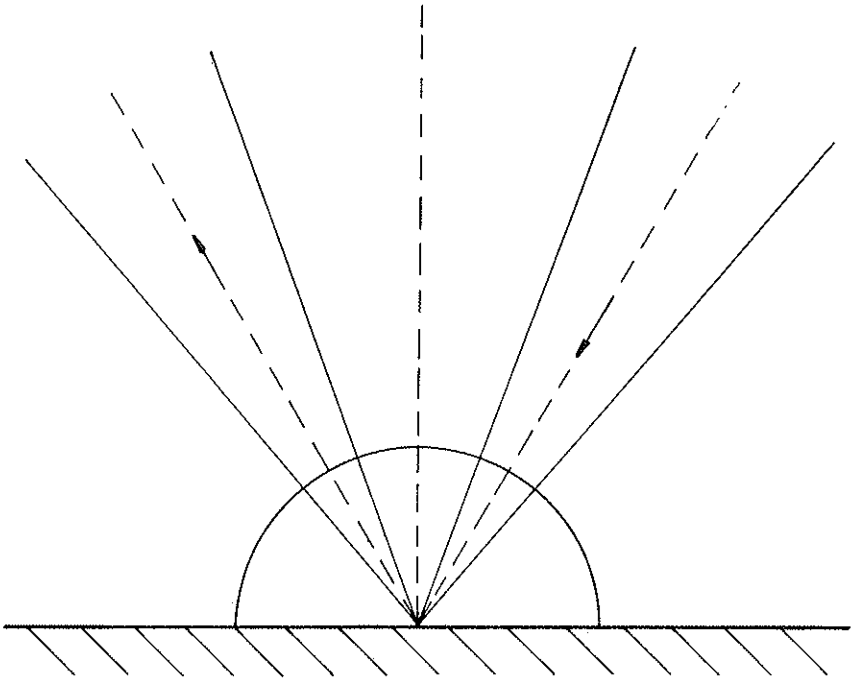


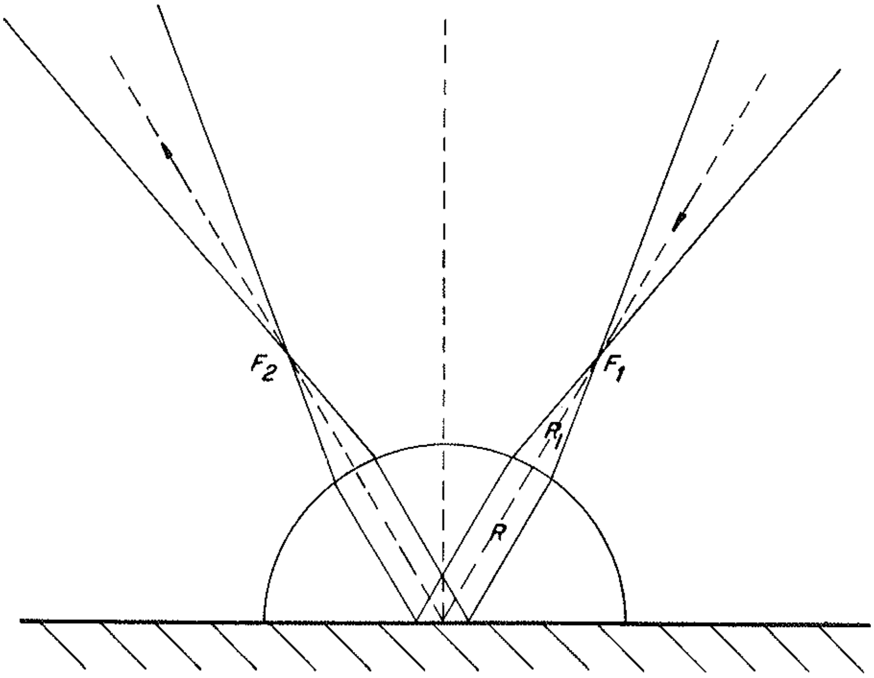
Fig. 1. Relation between reflecting power and the value of κ at angles of incidence above the critical angle for $n = 0{\cdot}707$.

When the beam has its focus in the centre of the cylinder, it passes the curved surface unrefracted, so that the angle of incidence may be given any desired value.

An improvement of this set-up is obtained if the optics are arranged so as to give a focus outside the cylinder, as shown in Fig. 2(b). If the focus is at a distance



(a) With beam focused on the reflecting interface.



(b) With a focus outside the cylinder resulting in a parallel incidence on the reflecting interface.

Fig. 2. Reflection arrangements of the hemi-cylinder.

$R_1 = R/(n-1)$ from the cylindrical surface, a fairly parallel light beam is obtained inside the crystal. The consequence is a better-defined angle of incidence.

The setting of the angle of incidence is carried out with a reflection accessory suitable for horizontal samples (Fig. 3). Radiation from the light source L passes the polarizer P and, after reflection by the spherical mirror M_1 and the plane mirror M_2, is focused on the sample S, which is covered by the hemi-cylindrical crystal. The reflected beam passes via the flat mirror M_3 and the spherical one M_4 to the flat mirror M_5 which deflects the beam over 90° and projects a 1 : 1 image of the light source on the slit of the monochromator. The position of M_3, M_4 and M_5 is fixed. In setting the angle of incidence at the desired value, L, P, M_1 and M_2 are simultaneously shifted horizontally by means of the screw T. The arms A_1 and A_2 move the sample along a circular path, keeping it at a constant distance from M_2, and in a horizontal position.

By means of two angle-dividing mechanisms, M_2 and M_3 are turned in such a way that on manipulating T the focus remains in the same position on the sample. The angle of incidence can be given any value between 15° and 85°, and may be read with an accuracy of 2′ on the scale G.

The samples are placed on a table resting on a micrometer screw which allows of exact positioning of the reflecting surface. With this accessory, liquid samples may also easily be studied.

Results

A few examples will be given here to illustrate the performance of the new attenuated total reflection (ATR) technique. In Fig. 4 recorded spectra of dibutylphthalate, an organic liquid, are presented.

A is the transmission spectrum, recorded with a light path of 0·01 mm.

B is the spectrum of the energy reflected by a bare liquid sample at $\theta = 45°$.

C is the reflection spectrum recorded with the new technique with the sample covered by an AgCl crystal.

All spectra are recorded under otherwise identical circumstances. The similarity of the transmission spectrum and the attenuated total-reflection spectrum is evident. The gain in intensity and detail present in the ATR spectrum is also well illustrated by the comparison with the normal reflection B.

In Fig. 5 the reflection spectra of an insoluble epoxy resin are given, recorded by the old and the new technique. I_0 represents the energy totally reflected by the interface KRS 5/air. Again the improvement is evident.

In Fig. 6 a comparison is given between the transmission spectrum of a KBr pellet and a reflection spectrum of a KRS 5-covered block of the same epoxy resin.

The latter spectrum was obtained from a face ground on the resin block with polishing paper. Optical contact with the cylinder was obtained by placing a thin layer of carbon disulphide between the KRS 5 crystal and the sample. It was found that in many cases the optical contact was retained after evaporation of the solvent.

Applications

As the new method bears a resemblance to transmission as well as to reflection measurements, it was examined as to its potentialities for fulfilling the specific tasks of both.

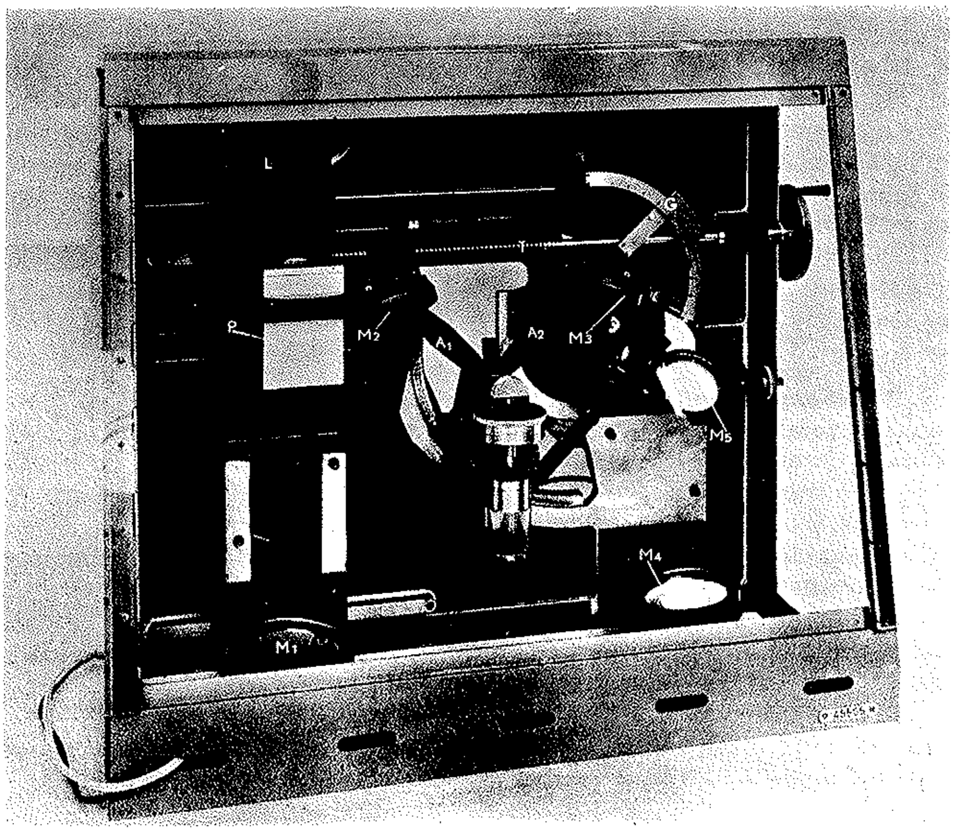


Fig. 3. Reflection accessory for measurements on horizontal samples.

Transmission spectra are used in general for purposes of identification and quantitative analysis. The similarity between the new ATR spectra and transmission spectra is so great in all cases investigated, that probably the collections of standard transmission spectra can also be used as a reference for identification by means of the reflection spectra.

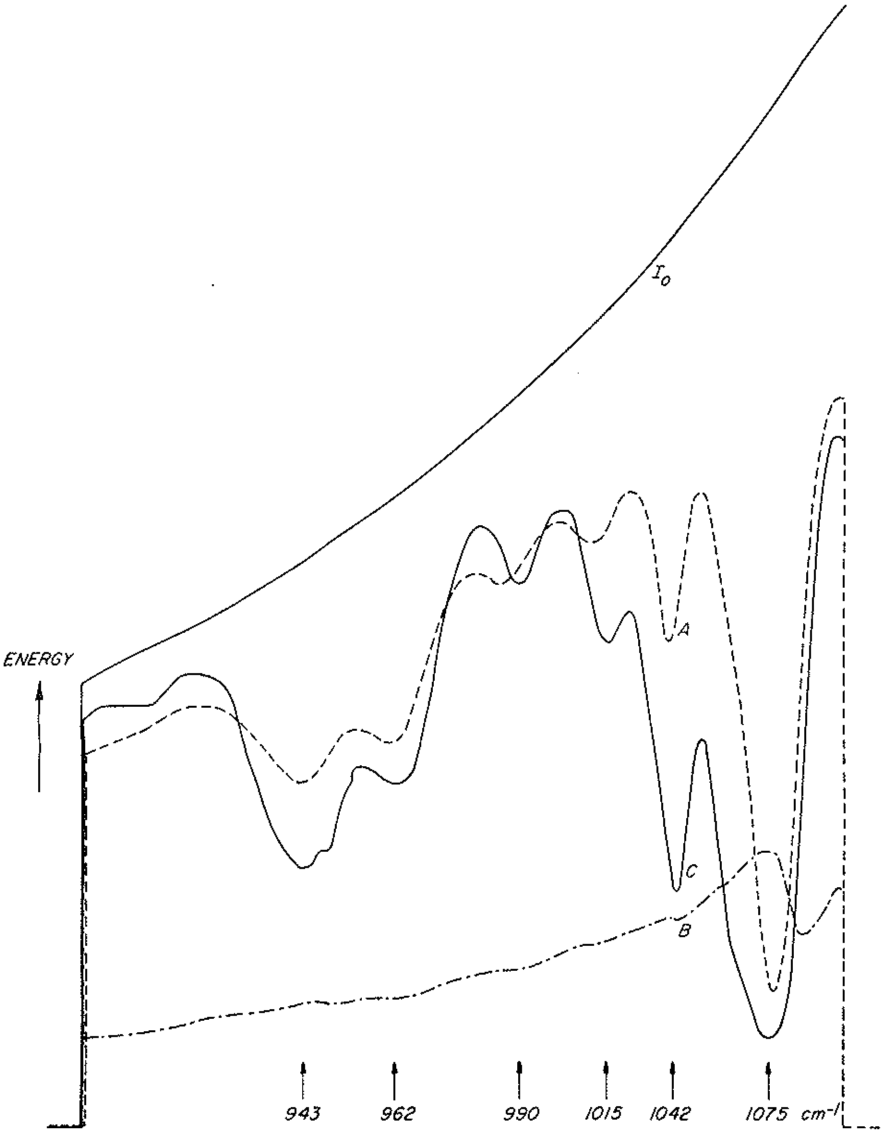


Fig. 4. Spectra of dibutylphthalate; I_0: common reference intensity for all spectra; *A*: transmission spectrum; *B*: conventional reflection spectrum; *C*: ATR spectrum using an AgCl crystal.

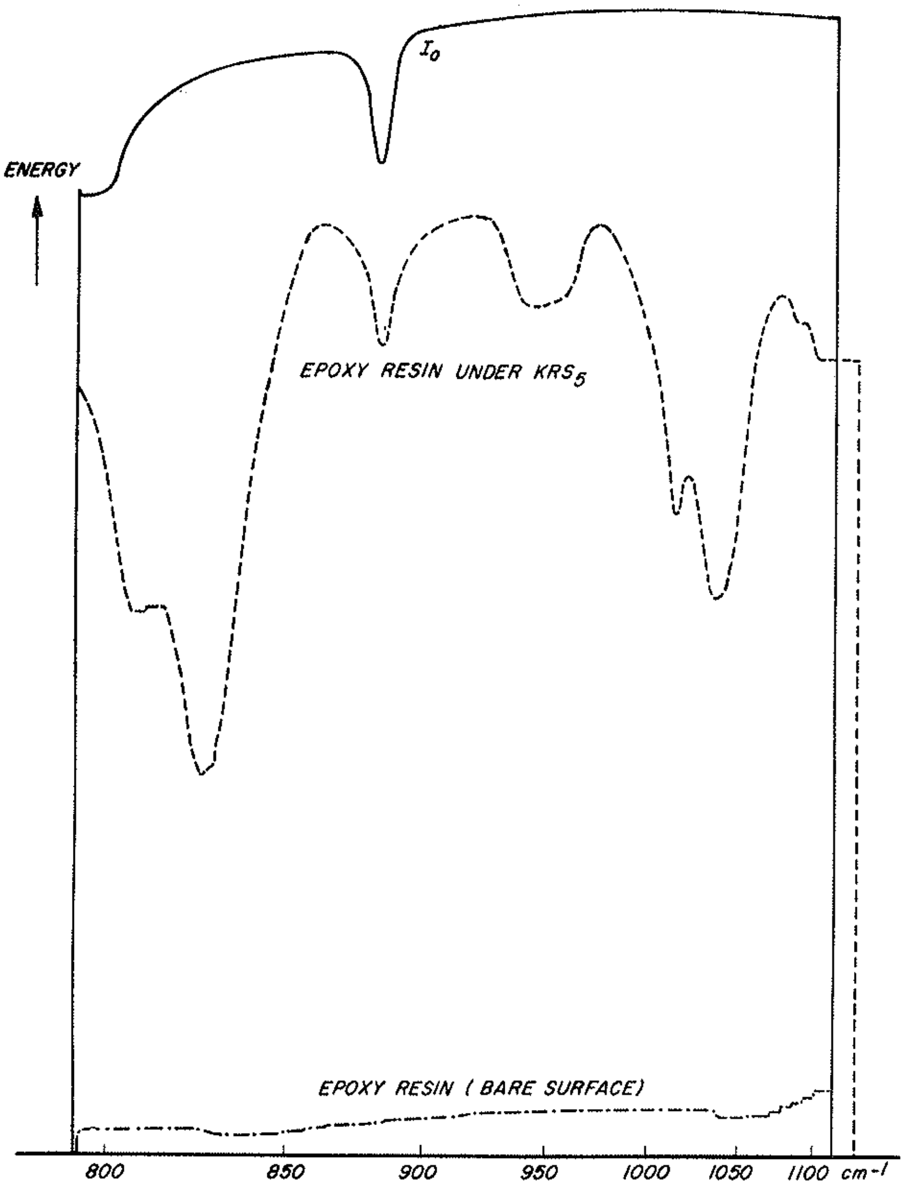


Fig. 5. Comparison between conventional reflection spectrum and ATR spectrum of a solid epoxy resin.

In view of the importance of the quantitative analytical aspect, it was ascertained how far a simple relation like that of Lambert–Beer still approximates the intensity variation of the reflection bands.

The reflection bands of a number of solutions, of decene-1 in Nujol, were measured. Taking the reflection of the pure solvent as a substitute for I_0, Beer's law was applied at the points of maximum intensity of the reflection bands. The relation between the formal "optical density" and the concentration thus obtained is given in Fig. 7. The deviation from linearity is not greater than that normally found if the optical density derived from transmission measurements is plotted as a function of concentration. We may conclude therefore, that the present ATR method could, after calibration, directly be used for quantitative purposes.

A special feature of the technique is the possibility of using a sample of arbitrary dimensions instead of a thin layer. Therefore this ATR technique may be useful for special applications, like measurement on process streams or the following of reactions in liquids, pastes or solids.

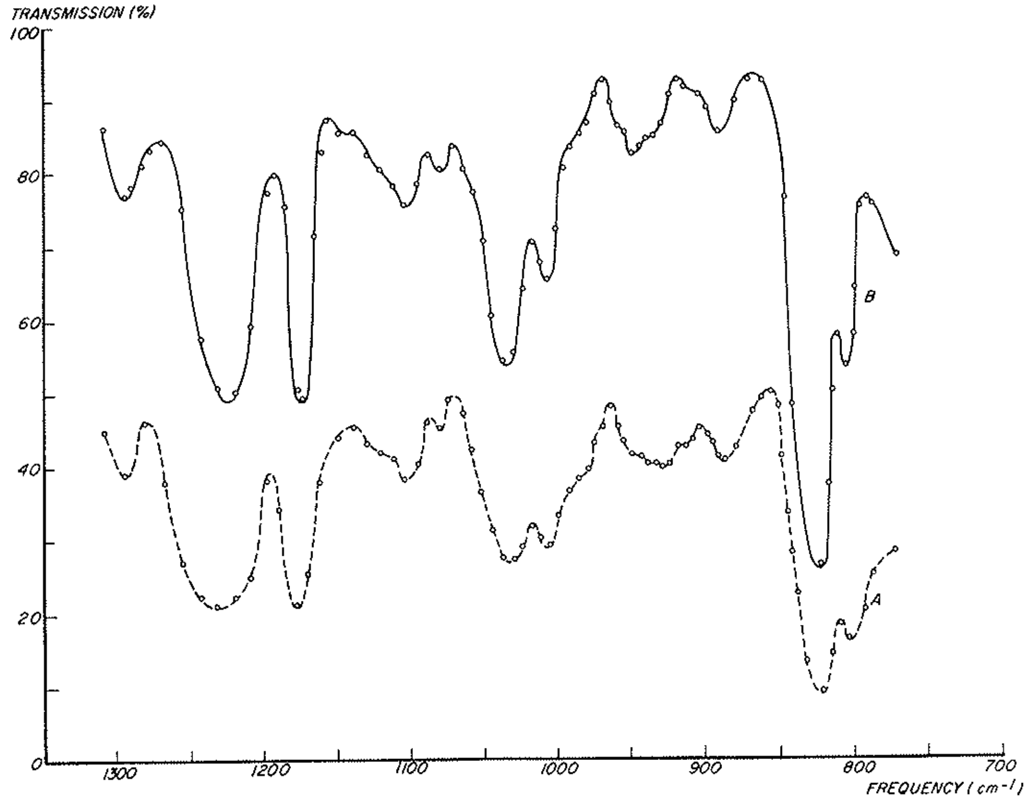


Fig. 6. Comparison between KBr-pellet transmission spectrum (A) and ATR spectrum of a solid epoxy resin (B).

While it follows from the above that in a number of cases the attenuated total-reflection spectrum can replace a transmission spectrum, it may also serve for the determination of the optical constants. As in the ATR method the angle of incidence to be used is imposed by the qualities of the sample, the usual calculating procedure which starts from measurements at two fixed angles cannot be used. Two courses could be adopted. In one procedure $|r_p|^2$ and $|r_s|^2$ are measured separately and a coincident pair of optical constants is determined by means of two families of precalculated curves presenting the intensity as a function of n and

κ similar to the curves used by SIMON [1] and by AVERY [2]. In order to apply the procedure, the families of curves must be available for any possible angle θ within a range of at least 10° and with steps no larger than 1°. An alternative to this graphical procedure is the application of the KRAMERS–KRONIG relation [3].

In this procedure the two simultaneous equations to be solved for n and κ are not obtained from two measurements, but from one measurement and subsequent application of the causality condition [4].

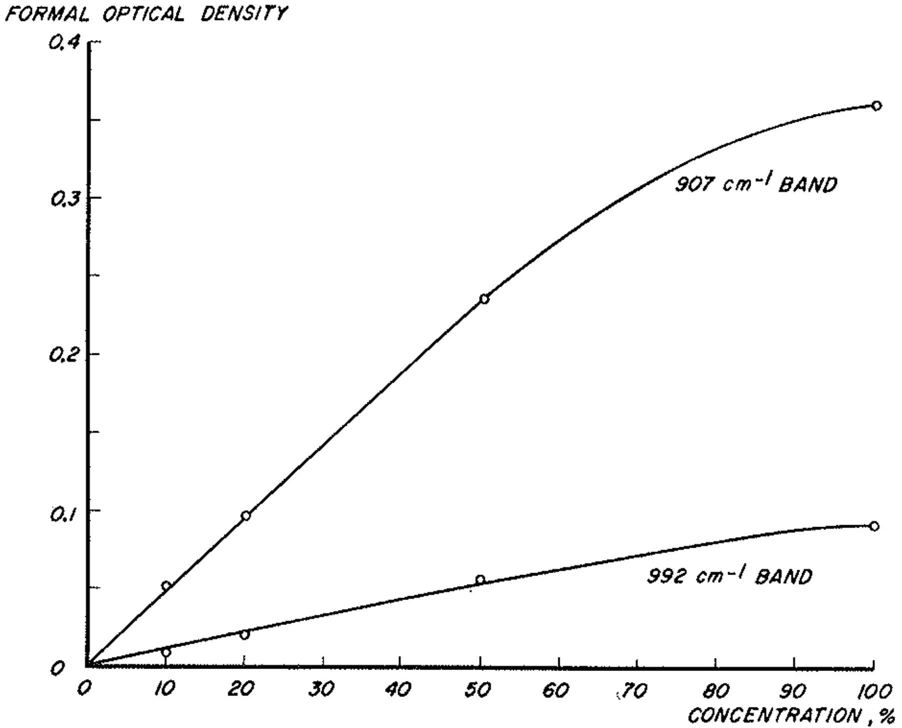


Fig. 7. Relation between formal "optical density" and concentration for two bands of decene-1 in Nujol.

The measurement in this case may be restricted to $|r_s|^2$, $|r_p|^2$ or $|r_p/r_s|^2$ (as a function of wavelength) at one angle θ. Application of the KRAMERS–KRONIG relation to the spectrum of the natural logarithm of any one of these quantities yields the phase angle ϕ of the complex reflected amplitude, e.g.

$$r_s = |r_s|\, e^{i\phi} \tag{10}$$

equivalent to (6), by means of the formula

$$\phi_c = \frac{2\nu_c}{\pi}\int_0^\infty \frac{\ln|r_s| - \ln|r_s|_c}{\nu^2 - \nu_c^2}\, d\nu \tag{11}$$

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[4] H. A. KRAMERS, *Atti congr. Fisici, Como* 545 (1927); R. de L. KRONIG, *Physik. Z.* **39**, 823 (1938); H. TAKAHASI, *Proc. Phys.-Math. Soc. Japan* **24**, 63 (1942); H. W. BODE, *Network Analysis and Feedback Amplifier Design*. Van Nostrand, New York (1945); N. G. VAN KAMPEN, *Phys. Rev.* **89**, 1072 (1953); J. S. TOLL, *Ibid.* **104**, 1760 (1956).

The suffix c denotes the point in the frequency spectrum in which the phase angle is calculated.

It is easily seen that, if r_s is known in its complex form, equation (6) yields a and b separately in terms of $|r_s|$ and ϕ. The optical constants then follow from (5). This method becomes practicable if the lengthly calculations can be made with the help of an electronic computer.

Conclusion

A new method for the production of intense and sensitive reflection spectra of weakly absorbing substances has been developed. The spectrum thus obtained shows a high degree of similarity to ordinary transmission spectra. This attenuated total reflection (ATR) technique will be useful in many cases in which normal infra-red techniques fail owing to difficulties in sample preparation.

The new reflection spectra can be used directly in combination with collections of standard transmission spectra for identification purposes.

Direct application for quantitative analysis is nearly as easy as that of transmission spectra.

Furthermore, the special features of this ATR technique might be important for application in cases where the investigation of sample layers of arbitrary thickness is unavoidable. Such circumstances are met in the spectroscopic investigation of macromolecular substances, of chemical reactions in progress and of ageing processes in surface layers, paints, etc.

In those cases where exact data on the optical constants are wanted, these may be calculated with the methods known from conventional reflection spectroscopy.

On the sensitivity of emission spectrochemical analysis

S. L. Mandelstam and V. V. Nedler
Academy of Sciences, Moscow

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Abstract—The limits of sensitivity of spectrochemical analysis are theoretically considered. The minimum amount of an element in a specimen which can be analysed is determined by that concentration which will give a signal from a spectral line which is several times greater than the average fluctuation of the signal from the radiation detector due to the background. The electronic impact excitation of the atoms is considered, and the dependence of the signal-to-noise ratio on electron concentration in the emitting region of the source, the parameters of the spectrometer and other factors, are investigated. Numerical calculations are carried out on the sensitivity of spectrochemical analysis using as sources of excitation an arc, and a hollow cathode discharge tube. The calculated sensitivity is greater by two or three orders of magnitude than the sensitivity obtained in the practical spectrochemical methods. The main loss in sensitivity occurs in the ineffective transfer of atoms contained in the specimen into the emitting region of the source, and retaining the atoms in this zone. Improvement in these ineffective parts of spectroscopic methods of analysis, and also improvements in methods of concentrating the specimens will open up a further reserve for increasing the sensitivity of spectrochemical analysis.

Recent years have brought about increasing demands on the sensitivity of spectrochemical methods of analysis. From 15 to 20 years ago a sensitivity of from 10^{-3} to 10^{-4} per cent was quite sufficient for main problems concerned with product control in industry, but with the growth of production of materials for atomic industry, methods were necessary with sensitivities of the order of 10^{-5}–10^{-6} per cent; recently, in semiconductor technology, determinations are necessary which demand sensitivities of 10^{-8}–10^{-9} per cent.

Sensitivities of 10^{-3}–10^{-4} per cent were reached by classical methods, namely, introducing the sample directly into the source for exciting the spectrum, i.e. a flame, arc or spark. An increase in the sensitivity by two or three orders of magnitude was successfully accomplished by the development of new techniques, the majority of which were based on different physical or physicochemical methods of concentrating the specimen, e.g. by using fractional vaporization, and partly by using new methods of exciting the spectrum, e.g. the hollow cathode. The greatest increase in sensitivity of spectroanalytical methods during the last few years, has been obtained by these techniques [1, 2].

It would be useful to attempt a theoretical estimation of the limits of sensitivity of spectrochemical analysis, and we present below the results of these calculations.

It is important to note the following at this point; many processes taking place in the source which have a substantial influence on the intensity of the spectral lines, are still not sufficiently understood; the values of many quantities which enter into the calculation are not exactly known. Therefore, at the present time

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[1] L. V. Lipis, *Usplch. Fiz. Nauk.* **18**, 71 (1959).
[2] L. N. Filimonov, *Zavodskaya Lab.* **25**, 936 (1959).

Reprinted from *Spectrochimica Acta*, Vol. 17, pp. 885–894, 1961. Pergamon Press Ltd.

one must not count on obtaining exact quantitative estimations of the analytical sensitivity. The aim of our calculation chiefly is to reveal the relative roles of the basic physical factors which are involved in determining the sensitivity of spectrochemical analysis. This would then permit one to establish ways of increasing the sensitivity of determinations.

Undoubtedly the majority of methods used in practical analysis nowadays have not reached the limit of their possibilities, for example the use of higher purity carbon electrodes, reagents, etc., would permit a considerable increase in the sensitivity of these methods. These ways are, however, self-evident and do not require any special treatment.

Let us choose the photoelectrical registration of the spectrum. Let T_L denote the phototube current which would be given by the analysis line from the element, and T_P the current in the absence of this element in the specimen (this is made up by the continuous background spectrum of the source and the dark current of the photomultiplier). In order to find out whether or not the analysing element is present in the sample, we must in principle carry out two series of determinations:

(1) The measurement of the intensity of the signal from the line in the spectrum of the specimen: $T_L + T_P$.

(2) The measurement of the intensity of the signal from a specimen known not to contain the element under analysis, or from a portion of the spectrum in the neighbourhood of the line.

If both of the signals T_L and T_P had a constant magnitude in the two sets of measurements, then by using a sufficiently large amplification of the photocell current, it would in principle be possible to measure any small increase in $T_L + T_P$ over T_P. This would mean that any desired sensitivity could be obtained. In fact, however, both signals fluctuate. Therefore we can establish a line in the spectrum only if

$$\overline{(T_L + T_P)} - \overline{(T_P)} > \sqrt{\Delta^2(T_L + T_P) + \Delta^2 T_P} \tag{1}$$

Knowing the magnitude of the signal fluctuations ΔT, it is possible from this to determine the minimum signal from the line T_L, and hence the limiting analytical sensitivity.

The magnitude of ΔT is made up of variations introduced by the light source errors in measuring the signal, and signal fluctuations from the phototube. Variations in the light source can in principle be eliminated, if T_P is measured simultaneously with $T_L + T_P$, for example, in the neighbourhood of the line, and having chosen the line homologous with the background. Errors in measuring the signals may not be considered in the first approximation. For the purposes of further calculations, the practical limit of analytical sensitivity, i.e. the minimum detectable concentration of an element in a sample, can be taken as that concentration which produce a signal from the spectral line of that element ten times greater than the average fluctuation, produced by the phototube, of the signal from the background:

$$T_{L\,(\mathrm{minimum})} \sim 10\Delta T_P \tag{2}$$

It may be noted that the situation is exactly similar in the case of photographic recording of the spectra. When the measurement of the density is carried out with the help of a sufficiently sensitive microphotometer over the spot on the film where the line is expected and on the adjoining portion, where there is only background, we can determine whether or not the line is present if the density in that place is greater than in an adjoining part by an amount larger than the average fluctuation of the density. This formulation of the question has been given for the first time by KAISER [3].

Let us now consider on what factors the signal to noise ratio $T_L/\Delta T_P$ depends.

The photocurrent produced by the spectral line is given by

$$T_L = \alpha\gamma F_L' \tag{3}$$

Where F_L' is the luminous flux from the line, falling on the photomultiplier, γ is the sensitivity of the multiplier expressed in amperes per lumen, and α is the mechanical equivalent of light. $\alpha = 0{\cdot}68 \times 10^{-4}$ lumens/erg sec^{-1}. The luminous flux coming from the spectral line is given by

$$F_L' = \frac{j\nu}{4\pi} lsb\,\Omega \tag{4}$$

where j_ν is the intensity of the line in the emitting volume of the source, l is the diameter of the emitting volume, s and b are the width and height, respectively, of the entrance slits of the spectrometer, and Ω is the speed of the collimator lens.

Let us now write a general expression for the intensity of lines; the electron impact mechanism is suggested for the excitation over a wide range of electron concentrations. The balance between the formation of excited atoms and the deactivation of excited atoms in the emitting region of the source can be written thus:

$$N_o N_e \langle \sigma v \rangle - N_i N_e \langle \sigma' v' \rangle - N_i A = 0 \tag{5}$$

Here N_o is the concentration of unexcited atoms of the element under observation in the emitting volume of the source, N_i is the concentration of excited atoms, and N_e is the concentration of electrons. A is the probability of spontaneous emission. σ and σ' are cross-sections for collisions of the first and second kind between atoms and electrons. v and v' are the speeds of electrons before and after collision, these are connected by the expression

$$\frac{mv^2}{2} = \chi + \frac{mv'^2}{2}$$

where χ is the energy of excitation of the analysis line. The velocity distribution of the electrons is assumed Maxwellian, corresponding to a temperature of T_e; the angular brackets denote σv averaged over the Maxwell velocity distribution.

The first term in (5) gives the rate of formation of excited atoms by collisions of the first kind with electrons, the second gives the rate of deactivation of excited atoms, due to collisions of the second kind with electrons, and the third gives the number of excited atoms which are lost due to spontaneous emission.

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[3] H. KAISER, *Spectrochim. Acta* **3**, 40 (1947).

From (5) we get

$$N_i = \frac{\langle\sigma v\rangle/\langle\sigma' v'\rangle}{1 + A/N_e\langle\sigma' v'\rangle} N_0$$

Using the Kleine–Rosseland relationship

$$\frac{\langle\sigma v\rangle}{\langle\sigma' v'\rangle} = \exp\left(-\chi/kT_e\right)$$

we have for the intensity of the spectral line

$$j_\nu = h\nu A N_i = \frac{h\nu N_0 A \exp\left(-\chi/kT_e\right)}{1 + A/N_e\langle\sigma' v'\rangle} \tag{6}$$

If the electron concentration in the emitting region of the source is large, then the second term in (5) is considerably larger than the third (the loss of excited atoms is mainly due to collisions with electrons). Under these conditions the second term in the denominator of (6) is very much smaller than 1, and so (6) simplifies to:

$$j_\nu = h\nu A N_0 \exp\left(-\chi/kT_e\right) \tag{7}$$

The second limiting case is when N_e is small, and the loss of excited atoms is due mainly to spontaneous emission. Now the second term in (5) is very much smaller than the third, and so the second term in the denominator of (6) is considerably larger than 1. Equation (6) then becomes:

$$j_\nu = h\nu N_0 N_e\langle\sigma v\rangle \tag{8}$$

Putting (6) and (4) into (3) we obtain the expression for the photocurrent, produced by the analysis line

$$T_L = \frac{\alpha\gamma l s b\Omega}{4\pi}\cdot\frac{h\nu N_0 A \exp\left(-\chi/kT_e\right)}{1 + A/N_e\langle\sigma' v'\rangle} \tag{9}$$

Let us now calculate the magnitude of ΔT_P. The current T_P is made up of the photomultiplier's dark current T_D, and that due to the continuous background of the spectrum T_C. The average variation of the background current is given by a well known equation

$$\Delta T_P = \sqrt{2eBM\tau^{-1}\left(T_D + T_C\right)} \tag{10}$$

where B is a constant $\simeq 2.5$, M is the amplification factor of the photomultiplier, and τ is the time of the measurement.

The photocurrent from the continuous spectrum is related to the luminous flux of the continuum, by the expression

$$T_C = \alpha\gamma F_C \tag{11}$$

and

$$F_C' = \frac{\varepsilon_\nu}{4\pi} l s b\,\Omega\,d\nu \tag{12}$$

where ε_ν is the intensity of the continuum, l, s, b and Ω have the meaning as before, and $d\nu$ denotes the width of the portion of the spectrum which passes through the exit slit of the spectrometer;

$$d\nu = s' \frac{c}{\lambda^2} 10^{-7} D$$

where s' is the width of the exit slit, and D is the dispersion of the instrument (in Å/mm).

In order to estimate ε_ν we assume that the continuum has a minimum value for the given source. That is to say that it depends only on the electron–ion interactions in the emitting regions of the source, i.e. recombination of electrons and ions, and radiation due to the deceleration of electrons in ionic fields (3, 2, 1, transitions). Usually there are other sources of background, for example, in an arc the background also includes the light from the ends of the electrodes, and from particles of graphite carried into the column of the arc, etc. In principle, however, these additional sources of background can be eliminated, e.g. by using diaphragms to exclude the ends of the electrodes and by using graphite which does not easily undergo sputtering and so on.

An expression of UNSOLD's [4, 5], which has been experimentally verified, is used for the intensity of the continuum produced by free–bound and free–free electron transitions:

$$\varepsilon_\nu = \frac{128\pi^3}{3\sqrt{3}} \cdot \frac{Z^2 e^6}{c^3 (2\pi m)^{3/2}} \cdot \frac{N_e N_j}{(kT_e)^{1/2}} \tag{13}$$

$$= 8 \times 10^{-46} \frac{Z^2 N_e^{\,2}}{(kT_e)^{3/2}} \text{ ergs/sec per unit frequency range}$$

where Z is the charge on the ion, which will be taken to be unity in the future, and N_j is the concentration of ions, which is taken to be equal to the electron concentration.

Equation (13) is true at high values of N_e, ($N_e \geqslant 10^{15}$) when there is a Boltzmann distribution of atoms in excited levels, so agreeing with equation (7) for the intensity of a line. In practice apparently, we would not be greatly in error if we used this expression at much lower values of N_e, especially when we take into account that at $N_e < 10^{14}$ the dark current contributes the significant amount to T_P.

Using equations (10), (11), (12) and (13) we obtain for ΔT_r the expression

$$\Delta T = \left[2eBM\tau^{-1} \left(T_D + \frac{\alpha\gamma lsb\, \Omega\, d\nu\, 8 \times 10^{-46} N_e^{\,2}}{4\pi (kT_e)^{1/2}} \right) \right]^{1/2} \tag{14}$$

We consider first the dependence of T_L, ΔT_P and $\dfrac{T_L}{\Delta T_P}$ on N_e, the concentration of electrons in the emitting region of the source.

Let us take the following numerical values. For the spectrum line, $\lambda = 3000$ Å, $\chi = 4$ eV, $A = 10^8$ sec^{-1}, $\langle \sigma v \rangle \simeq 10^{-10}$, $\langle \sigma' v' \rangle \simeq 10^{-7}$; for the emitting region of the source: $T_e = 7000$°C, $l = 1$ mm; for the spectrometer: $s = s' = 5 \times 10^{-3}$

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[4] A. UNSOLD, *Ann. Physik.* **33**, 607 (1938).
[5] W. LOCHTE-HOLTGREVEN, *Repts. Progr. in Phys.* **21**, 312 (1958).

cm, $b = 1$ cm, $\Omega = 10^{-2}$, and $D = 20$ Å/mm. The photomultiplier was given the following parameters: $\gamma = 1$ A/lumen, $M = 10^6$, $T_D = 10^{-9}$ A, $\tau = 10$ sec. Values of T_L, ΔT_P and $T_L/\Delta T_P$ were obtained, and are shown in Fig. 1 plotted on a log scale in arbitrary units.

From this graph it follows that, with chosen numerical values, the maximum analytical sensitivity (the maximum value of $T_L/\Delta T_P$), is obtained for $N_e = 10^{14}$–10^{15} electrons per cm^3. On decreasing N_e the intensity of the line is given by (8), and decreases in direct proportion to N_e, but the intensity of the background signal is determined by the dark current of the photomultiplier, and so remains practically constant. At higher values of N_e the intensity of the line reach the constant values given by (7), because the quenching collisions with electrons becoming more frequent; the intensity of the background due to electron–ion interactions rapidly increases.[*]

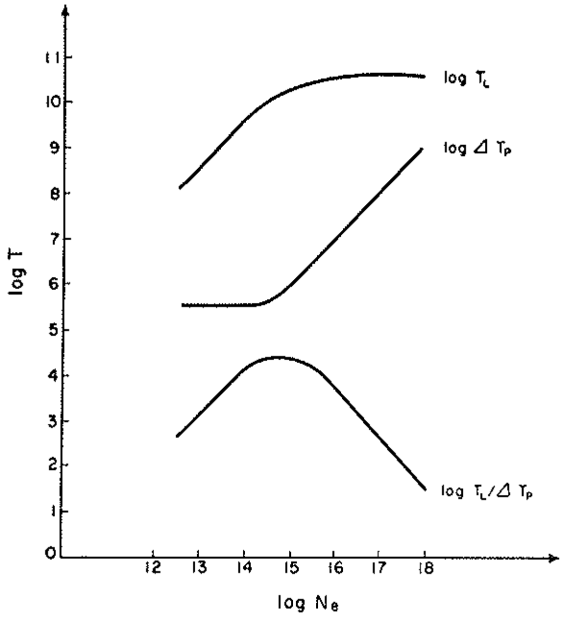

Fig. 1. The dependence of the signal from the line, the average variation of the signal from the background, and the ratio of these, on the electron concentration in the emitting region of the source.

It must be pointed out, however, that in all these calculations the electron temperature of the discharge was taken to be constant. In actual fact, of course, sources with different electron concentrations have different temperatures. The effect of source temperature on the sensitivity requires special treatment.

Another parameter which affects the analytical sensitivity, is the measurement time τ. An increase in τ decreases ΔT_P in proportion to $\tau^{\frac{1}{2}}$, but as we shall see below,

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[*] When photographic registration of the spectrum is used, the average fluctuation in the density, which was discussed above, is determined by the value of $\sqrt{(n_b + n_n)}$, where n_b is the number of granules of emulsion due to the "fogging" of the plate, and n_n is number of granules due to the continuum of the spectrum. It is that at low intensities of the continuum the sensitivity is determined by the square root of the density of "fogging" and at high intensities by the square root of the intensity of the continuum.

at the same time, the drift of atoms away from the source volume increases in proportion to τ. Thus in the sum, an increase in τ is not considered to be desirable.

Changing the parameters of the spectroscope, e.g. increasing the height and width of the slits, and the amplification factor of the photomultiplier, etc., increases the analytical sensitivity in the regions of low N_e proportional to $\gamma sb\Omega$, and in the regions of high N_e proportional to $(\gamma sb\Omega)^{1/2}$.

The use of an apparatus with a large dispersion is desirable if it is not accompanied by a decrease in the speed of it (Ω), as is usually the case.

Let us now illustrate these calculations by a numerical evaluation of the limit of sensitivity of spectrochemical analysis for two examples, choosing as the spectrum source of excitation a carbon arc and a low-pressure, hollow cathode discharge. N_e for a free burning carbon arc, in air, equals 10^{15}. In this case the expression for the line intensity is given by (7):

$$j_\nu = h\nu A N_0 \exp(-\chi/kT_e)$$

Taking the numerical values used above, we get from (4)

$$F_L' \simeq 10^{-12} N_0 \text{ erg sec}^{-1*}$$

and from (3):

$$T_L \simeq 10^{-16} N_0 \text{ A}$$

For the continuous spectrum from (12) and (13)

$$F_C' \simeq 10^{-4} \text{ erg sec}^{-1}$$

and from (11)

$$T_C \simeq 10^{-8} \text{ A}$$

The photoelectrical current from the continuum is very much greater than the dark current of the photomultiplier. Using equation (10), and putting τ equal to 10 sec, gives $\Delta T_P \simeq 10^{-11}$ A, and taking the condition as before, that $T_L \simeq 10\Delta T_P$ if a line is to be detectable, then N_0 is obtained as being approximately equal to 10^6 atoms/cm^3. If the emitting region of the source is considered to have a volume of approximately 10^{-2} cm^3, then the minimum number of atoms that must be present in this region is $N_{\min} = 10^4$ atoms. Therefore in order to detect a line, the concentration of atoms in the column of the arc must be maintained at 10^6 atoms/cm^3 during 10 sec.

Let us now attempt to estimate the smallest detectable amount M of the element in the specimen. Obviously, the minimum number of atoms is that which, during the time τ replenishes the atoms of the element lost from the column of the arc, and maintains in the column the concentration N_0. The mechanism of loss of atoms of the analysed element from the column of the arc is apparently make up of two parts:

(1) The diffusion of atoms through the gas in the arc column, from the centre to the periphery, followed by recombination of these into some or other molecules and final escape into the atmosphere.
(2) Removal of atoms by convection.

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* Here and below the results are rounded off to the nearest order of magnitude.

This last factor can be neglected, if some means or other is employed to minimize it, e.g. external stabilization of the arc column. Thus diffusion is left as the principal source of atom loss and hence determines its lowest limit.

Let us consider the column of an arc as a cylinder with diameter l and length L, and assume that all the atoms which diffuse to its surface are removed from the discharge, and hence take no further part in light emission. Then the number of atoms lost from the column in unit time is given by [6]:

$$q = S\beta\Delta N$$

where S is the surface area, $S = \pi lL$, $\beta = \mu_0{}^2 D/l^2$, $\mu_0 = 2.4$ (the first root of a Bessel function of zero order), $D =$ the diffusion coefficient and ΔN is the difference in atom concentration between the centre and the surface of the arc column. The diffusion coefficient is given by the well known equation

$$D = \frac{u\lambda_c}{3}$$

where $u = \sqrt{(8kT/\pi m)}$, $m =$ the mass of the atom under consideration, $\lambda_c =$ the mean free path, $\lambda_c = 1/\sqrt{(2)}\pi n d^2$ where n is the concentration of the carrier gas in the arc, and d is the molecular diameter for the gas. Taking $n \simeq 10^{18}$ cm^{-3}, $d^2 \simeq 10^{-15}$ cm^2, and $m \simeq 10^{-22}$ g we get $D \simeq 10$ cm^2 sec^{-1}.* For simplicity, let us assume that the atom concentration decreases uniformly from the centre outwards, so that $\Delta N/2 = N_0$ where N_0 is the average overall concentration for the arc column.

As stated above, the minimum number of atoms in the sample must be equal to the number of atoms leaving the arc in the time τ, i.e. $M = q\tau \simeq 4 \times 10^4 \times N_0 \simeq 10^{10}$ atoms. Taking the weight of one atom as $m = 10^{-22}$ g, we obtain the result that the minimum weight of an element which can be detected is $P \simeq 10^{-12}$ g. If we take a sample weighing approximately 100 mg, then for the minimum concentration which can be determined we get $C \simeq 10^{-9}$ per cent.

Let us now consider our second example. The mechanism of atom excitation in a hollow cathode discharge is still insufficiently understood. However, one can assume that the collisions between neutral atoms and electrons play the major part in the excitation of the former, and the secondary processes are absent. In this case the intensity of a line is given by (8)

$$j_\nu = h\nu N_0 N_e \langle \sigma v \rangle$$

Taking $N_e \simeq 10^{13}$ electrons/cm^3, and the values used previously for excitation cross-sections and the spectrometer parameters, we obtain from (4) the luminous flux from the line

$$F_L{}' \simeq 10^{-14}\, N_0 \text{ erg sec}^{-1}$$

and the photocurrent

$$T_L \simeq 10^{-18}\, N_0 \text{ A}$$

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* *Note added in proof:* in the recent paper by RAICHBAUM and MAYLSCH, *Optika i Spektroskopiya* **9**, 425 (1960), it was found experimentally that the diffusion coefficient of atoms from the arc column $D = 10$–20 cm^2 sec^{-1}.

[6] D. A. FRANK-KAMENETSKI, *Diffusion and Heat Transfer in Chemical Kinetics.* Akademii Nauk S.S.S.R., Moscow.

From (12) and (13) we get the luminous flux from the continuum, $F_C' \simeq 10^{-8}$ erg/sec, i.e. the intensity of the continuum is, in this case so small, that the photocurrent produced from it is smaller than the dark current of the photomultiplier. Hence the minimum measurable line intensity is determined by the average fluctuation of the dark current. Taking the measurement time as $\tau = 100$ sec, we get from (10):

$$\Delta T_P = 10^{-12}\ \mathrm{A}$$

Defining as before the minimum detectable line intensity

$$T_L = 10 \times \Delta T_P$$

we get $N_0 \simeq 10^7$ atoms/cm^3. Taking the emitting volume to be 10^{-2} cm^3

$$N_{\min} \simeq 10^5 \text{ atoms}$$

In order to evaluate the number of atoms in the specimen M to maintain the atom concentration of N_0 in the emitting region of the hollow cathode, we can assume that the concentration N_0 must be reached in the whole of the volume of the tube V (atoms settling on the walls may in principle return to the discharge area by the heating up of the walls). Putting $V = 10^2$ cm^3, we obtain $M = VN_0 \simeq 10^9$ atoms/cm^3. From this, taking $m \simeq 10^{-22}$ g the minimum weight of the element under analysis is $P \simeq 10^{-13}$ g i.e. in a 100 mg specimen, the minimum concentration C is $\approx 10^{-10}$ per cent.

The results are shown in Table 1.

Table 1

Source	Arc	Hollow cathode
The min. number of atoms in the emitting region of the source N (atoms).	10^4	10^5
Min. conc. of atoms N_0 (atoms/cm^3), etc.	10^6	10^7
Min. number of atoms in the specimen u (atoms).	10^{10}	10^9
Min. weight of the analysed element P (g).	10^{-12}	10^{-13}
Min. concentration of the analysed element in the specimen C (%)	10^{-9}	10^{-10}

So in spite of the very different spectral sources, the analytical sensitivity is obtained in both cases very closely.

The values of the limiting sensitivity given in the Table 1 are approximately two to three orders greater than those obtained in present-day practical analytical methods. It is necessary to stress again, however, the highly idealized physical picture on which the above calculations were based. The numerical values used in the calculations, e.g. transition probabilities, collision cross-sections, the conditions of vaporizing the specimen, etc., can change for different specific conditions, between very wide limits. Therefore as was already pointed out at the beginning of this article, it is not possible to attach an absolute significance to the values obtained for the sensitivities, one must consider them basically from a qualitative point of view.

The figures show that it is sufficient to have a comparatively small number of atoms of the analysed element in the emitting region of the source to obtain a line which can be measured. As is shown from a comparison of N and M, the basic loss of sensitivity is brought about by non-effective transference of the atoms contained in the specimen to the emitting region of the source, and insufficient retention of them in this zone, several orders of magnitude are lost because of this. Clearly as has been already pointed out in [1], a large reserve of sensitivity increase lies in the improvement of these parts of analytical procedures, and also in the improvement of methods of concentrating the specimen.

In order to make the calculations carried out here more accurate, it would be useful to carry out direct experimental measurements under different conditions, of factors which enter into the calculations, namely absolute intensities of lines, atom concentrations in the source region, for known concentrations of the element in the specimen, and also the intensity of the background continuum.

The analytical use of atomic absorption spectra

B. V. L'vov
Academy of Sciences, Moscow

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Abstract—A method is suggested for complete vaporization of a substance in a graphite crucible. The use of this method for quantitative analysis, using atomic absorption spectra, eliminates the effect of the composition of the sample on the analytical results. A high absolute sensitivity is reached for the determination of the majority of the elements. The apparatus and experimental procedure are described, and the dependence of the degree of absorption on experimental conditions is discussed.

Introduction

ATOMIC absorption spectra, as used in analysis, are based on the absorption of resonance lines by free atoms of a substance in the vapour phase. In comparison with emission spectroscopy, this method of analysis has several advantages:

(1) It measures directly the number of ground-state atoms, and not the number of excited ones, which depends exponentially on the temperature. At a temperature of up to 2000–3000°K the number of ground-state atoms accounts for practically the whole of the atoms in the vapour phase. The magnitude of the absorption coefficient varies only as $\sqrt{T}$, which eliminates a considerable source of error arising from temperature variation in the excitation source.

(2) The hollow-cathode discharge, which is used as a light source in this method, gives the spectrum of an element free from background, and with a small number of very intense lines. In this way the possibility of interference of lines is considerably smaller than in analytical methods using emission spectroscopy. Therefore a spectroscope with a large dispersion is not necessary for ordinary analytical work.

(3) The detection sensitivity for elements does not depend on the spectral response of the light receiver, because the absorption coefficient is determined by measuring the relative intensity of light which has passed through the absorption cell, with respect to that which has not.

The differences in the excitation potentials of resonance lines for different elements are not important, because the number of ground-state atoms are measured.

In spite of these advantages, atomic absorption spectra have not received widespread use in analytical work. This is explained by the absence of any convenient methods of vaporization of the specimen for which there is a known relationship between the concentration of the element in the specimen, and the concentration of free atoms in the gas phase.

The simplest methods of vaporization, which have been used in research in absorption spectra, are:

(1) Vaporization of the compound in a closed quartz crucible.
(2) Vaporization of the compound in a high-temperature vacuum furnace made out of graphite (King furnace).
(3) Vaporization of the compound in flames.

The use of a quartz crucible is limited for analytical purposes by the temperature of the melting point of quartz (1200°C). The use of the King furnace is also

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limited, from the analytical point of view, because the atom concentration does not depend on the quantity of the element in the specimen, but on the vapour pressure of the form in which the element under examination is introduced (salt, oxide, metal, etc.).

The most widely used of the known methods is the flame technique. A solution of the substance under analysis is sprayed into the flame, so producing a column of vapour in which the atom concentration of the element depends on its concentration in the solution. This method is becoming more and more widespread in its use in determining a number of elements by absorption [1–7].

However, even this method is not free from its disadvantages. In actual fact, the concentration of atoms in the vapour phase, under normal circumstances, is determined by the degree of dissociation of the compound, introduced or formed in the flame. The degree of dissociation of several compounds (BaO, AlO, TiO, LiOH, CsOH, etc.), in flames normally used, is extremely small [8–10]. As a result, the determination of the corresponding elements is only possible at much reduced sensitivities. The presence of foreign substances can greatly affect the degree of dissociation of many incompletely dissociated compounds. Therefore the effect of composition is not eliminated, although it is somewhat reduced in comparison with emission methods.

Method

The vaporization of a substance in the graphite crucible

The method suggested consists in complete vaporization of a substance in a graphite crucible. Diffusion of the vapour takes place through the hole for the light signal, and also because of the considerable porosity of graphite itself. Therefore complete vaporization of the specimen, and measurement of the atom concentration must be done in a time, such that it is possible to neglect atom loss due to diffusion. In order to comply with this, the substance is carried on to the cold end of a carbon electrode, this is introduced into an opening in the crucible, which is itself heated to 2000–3000°K, and the electrode is simultaneously heated from the outside by means of a d.c. arc (Fig. 1).

It is possible theoretically to estimate the diffusion of vapour through the open mouth of the crucible, and through the graphite walls [11]. It follows from such a treatment that:

(1) Since the amount of diffusion depends on the type and pressure of the surrounding gas, the loss of vapour can be decreased if the crucible is placed in an

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[1] B. J. Russel, J. P. Shelton and A. Walsh, *Spectrochim. Acta* **8,** 317 (1957).

[2] J. E. Allan, *Analyst* **83,** 466 (1958).

[3] M. E. Sikorski and P. L. Copeland, *Spectrochim. Acta* **9,** 361 (1957).

[4] A. C. Menzies, *Spectrochim. Acta* **11,** 106 (1957).

[5] D. David, *Analyst* **83,** 655 (1958).

[6] A. N. Zeidel, *Uspekhi Fiz. Nauk* **68,** 123 (1959).

[7] A. N. Zeidel, *Optika i Spectroskopiya* **4,** 701 (1958).

[8] V. G. Alexseeva and S. L. Mandelshtam, *Zhur. Tekh. Fiz.* **17,** 765 (1947).

[9] E. V. Vietz and L. V. Gurvitch, *Optika i Spectroskopiya* **1,** 22, (1956); *Doklady Akad. NaukS.S.S.R.* **108,** 659 (1956).

[10] E. Hinnov and H. Kohn, *J. Opt. Soc. Am.* **47,** 156 (1957).

[11] B. V. Lvov, *J. Engng. Phys.* **2,** No. 2, 44 (1959).

atmosphere of some gas or other (preferably a heavy one), and not in a vacuum. We filled the chamber, in which the graphite crucible was placed, with 1 atm pressure of argon.

(2) The loss of vapour by diffusion through the walls of the crucible, constructed as shown in Fig. 1, is the same order of magnitude as that through the open mouth. In order to overcome this we placed a layer of Ta foil inside the crucible.

(3) The magnitude of the loss by diffusion through the open mouth of the crucible depends only on its length. Hence in order to minimize this, it is necessary to use a long one. The loss at 2000°K for a length of 10 cm, is about 4 per cent in 0·1 sec (for Hg in an atmosphere of N_2).

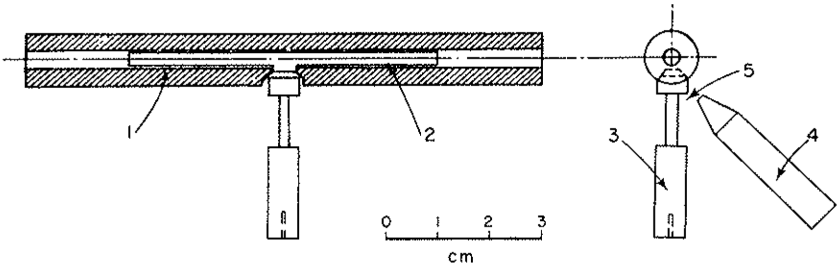

Fig. 1. The system for heating the electrodes: (1) crucible; (2) lining of tantalum foil; (3) electrode with the sample; (4) supplementary electrode; (5) arc gap.

A small quantity of a substance ($\sim$100 μg) can be vaporized by using a 40–60 A arc as supplementary heating of the electrode, in a sufficiently short time for diffusion to be neglected.

In order to determine the atom concentration in a vapour, the degree of absorption is measured for a particular portion of the absorption line contour. A resonance line for the element under analysis is used as a light signal, and is produced in a hollow cathode discharge. Photoelectric detection, with the signal continuously recorded, allows the degree of absorption to be measured at the exact moment of complete vaporization of the specimen.

Description of the apparatus

The apparatus was designed on the principles of single-beam spectrophotometry. A discharge tube equipped with changeable hollow cathodes, and without the additional circulatory system for re-cycling the argon which fills it, was used as a light source.

The graphite crucible is placed in a special chamber, as shown in Fig. 2. Brass supports for the graphite contacts between which the graphite crucible is fixed, the mechanism for changing the electrode holding the specimen, and the hinge for the setting up of the supplementary heating electrode are mounted on "Textolite" bases.

The chamber is hermetically sealed by an aluminium cover and rubber gaskets. Two holes were cut in the cover and equipped with quartz windows to allow the light signal to pass through the crucible. An additional window was cut in the front for observational purposes, and on the rear wall of the cover is fixed a radiation pyrometer for measuring the temperature of the crucible.

The electrodes are made of spectroscopically pure carbon rod 6 mm in diameter. The end of each electrode is turned down into a cone, which fits into the conical opening in the crucible. The electrodes are moved around in the chamber by means of the adjusting rod, which passes through a vac-seal. A cross is fastened on to the rod, and at each corner is fixed a tungsten wire which carries the electrode. Turning the rod allows each electrode to be brought up in turn to the opening in the crucible, without opening the chamber. The crucible itself is heated by an a.c. current supplied by a 10-kW step-down transformer.

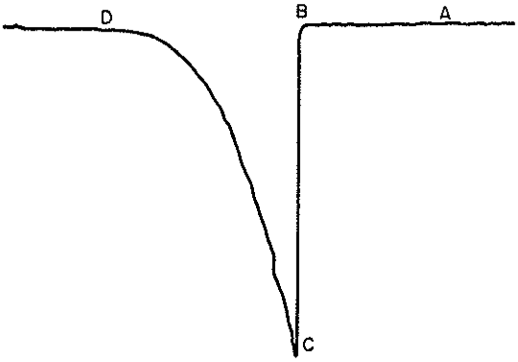

Fig. 3. Diagram of the absorption curve.

A monochromator with glass optics is used as the spectrometer, and a photomultiplier is placed against its exit slit. The signal from this is fed into a narrow-band amplifier, with an *RC* filter tuned to the modulation frequency. (In order to eliminate the background from the glowing furnace, and also the spectra of partly excited atoms in the crucible which would interfere with the line to be measured, the light from the hollow-cathode source is chopped, i.e. modulated by means of a perforated disk revolving in front of the source). The output from the amplifier is fed into an electronic recording [8] potentiometer, which has a full-scale traverse time of 1 sec.

Experimental procedure

The substance to be analysed is placed, in solution form, on the end of a carbon electrode, and then evaporated to dryness. To stop the solution from soaking into the carbon the tip of the electrode is coated with a 0·3 per cent solution of polystyrene in benzene. This is then placed on one of the wires on the metal cross, the cover closed, the chamber pumped out and then filled with argon. The crucible heaters are switched on, and the required temperature reached. The electrode, carrying the specimen is introduced into the opening in the crucible, and the d.c. arc automatically switched on. After 3–4 sec this is switched off, the electrode removed, and the following one inserted by rotating the rod.

The magnitude of the output signal is automatically recorded by the potentiometer, from the moment of switching on until the end of the measurement. A typical curve is shown in Fig. 3. *AB* corresponds to the standing signal T_0: at the

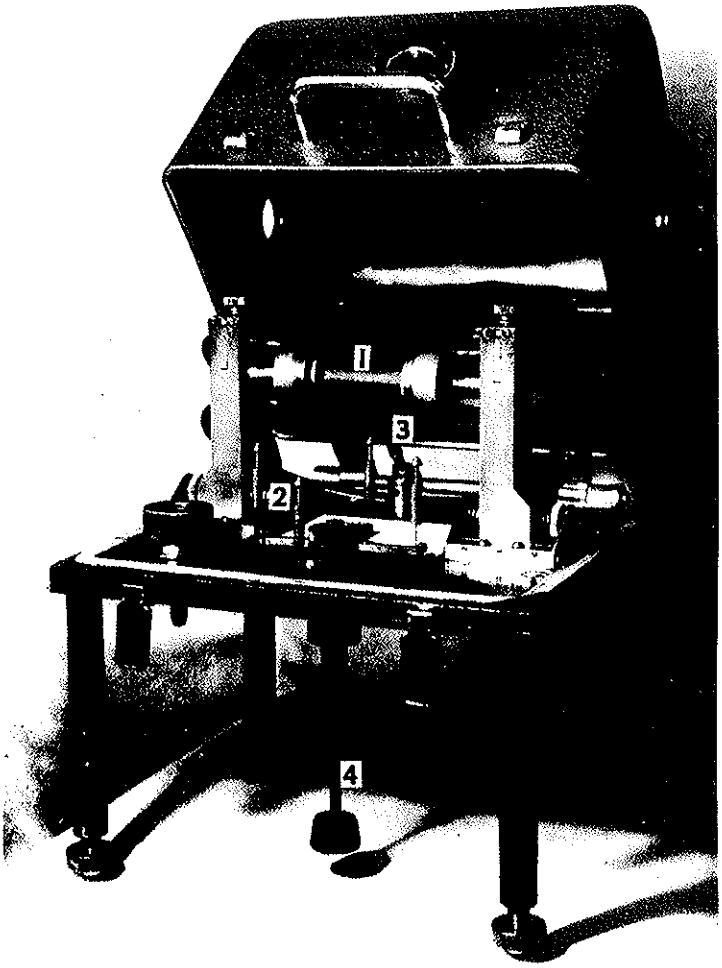

Fig. 2. The chamber: (1) crucible; (2) removable electrodes; (3) supplementary electrode; (4) adjusting rod.

point B there is a sharp decrease in the intensity of the signal, as a result of the vaporization of the specimen. C corresponds to the moment of complete vaporization of specimen, after which there is a gradual increase in the signal (CD) due to the diffusion of atoms out of the crucible. Because of this latter fact, the crucible quickly cleans itself, and can be used for the next analysis. With one crucible at 2000°C, about 100 measurements can be carried out. The optical density at the minimum in the experimental curves is taken as a measure of the degree of absorption.

Because of the time constant involved in the measurements carried out with this apparatus, we did not directly measure the time of vaporization, or the magnitude of the diffusion out of the crucible of the given dimensions and construction.

The theoretical dependence of the degree of absorption on the amount of vaporized compound present

Since the vapour in the crucible is at 1 atm, then there will be a pressure broadening (Lorentz), and also a shift $\Delta\nu_S$ in the absorption line with respect to the line at zero pressure. Therefore the line given out by the hollow-cathode source is displaced from the centre of the absorption line by $\Delta\nu_S$.

In the case when the lines given out by the source are sufficiently narrow in comparison to the absorption lines, which are pressure and temperature broadened, then the incident illumination can be taken, to all intents and purposes, to be monochromatic. The measured absorption coefficient K_S can then be expressed by the formula:

$$K_S = K_0 \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a^2 + (\omega - y^2)} \tag{1}$$

where

$$K_0 = \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\pi e^2}{mc} Nf,$$

$$\omega = \frac{2\Delta\nu_S}{\Delta\nu_D} \sqrt{\ln 2} \quad \text{and} \quad a = \frac{\Delta\nu_L}{\Delta\nu_D} \sqrt{\ln 2}$$

Here $\Delta\nu_L$ and $\Delta\nu_D$ are the Lorentz and Doppler widths of the absorption lines, f denotes the oscillator strength and N is the atom concentration [12].

The integral in (1) can be evaluated either numerically, or by means of a series. However, for the sake of simplicity it can be assigned an elementary function [13] such that (1) becomes:

$$K_S = K_0 \frac{1}{\sqrt{\pi}} \frac{a}{a^2 + \omega^2} \tag{2}$$

Substituting in (2) for ω, a and K_0 we get:

$$K_S = \frac{2e^2}{mc} \frac{\Delta\nu_L}{\Delta\nu_L{}^2 + 4\Delta\nu_S{}^2} Nf = 1{\cdot}7 \times 10^{-2} \frac{\Delta\nu_L}{\Delta\nu_L{}^2 + 4\Delta\nu_S{}^2} Nf \tag{3}$$

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[12] A. Mitchel and M. Zemanski, *Resonance Radiation and Excited Atoms*. ONTI, Moscow–Leningrad (1937).

[13] M. Born, *Optica*. ONTI, Kharkov–Kiev (1937).

Because of the highly reducing conditions existing inside the graphite crucible, the partial pressures of O and OH which can exist will be several orders lower than in a flame, hence even the most refractory of oxides (BaO, AlO, TiO, etc.) and hydroxides (LiOH, CsOH, RbOH, etc.) will dissociate almost completely. In this case the concentration of free atoms in the crucible can be related to the amount M of the element introduced (in grammes) in the following way:

$$N = \frac{6{\cdot}02 \times 10^{23} M}{ASl} \tag{4}$$

where l is the length, S the cross-sectional area of the crucible and A the atomic weight of the element.

Changing the absorption coefficient K_S and the atom concentration N in (3) for experimentally determinable quantities, i.e. optical density $D = 0{\cdot}434 K_S l$, and the amount M of substance introduced into the crucible, the following expression is obtained:

$$D = b \frac{M}{S} \tag{5}$$

where

$$b = 4{\cdot}45 \times 10^{21} \frac{\Delta\nu_L}{\Delta\nu_L{}^2 + 4\Delta\nu_S{}^2} \frac{f}{A}$$

Equation (5) is correct only for a monochromatic signal. However, because of the hyperfine structure of the lines, which is due to isotopic effects, and nuclear spins, the line width obtained in practice, in the majority of cases, is comparable with the absorption line width. Therefore the above expression is not suitable for absolute calculations in the general case.

Bearing in mind the necessary given conditions, it would appear that a quantitative analogy between oscillator strengths and magnitudes of absorption is doubtful, without taking into account the line structure and also the differences in Lorentz broadening and line shift, as was done by Russell *et al.* [1]

When such a comparison is being carried out, it must also be born in mind that, in flames, oxides and hydroxides of many elements do not completely dissociate. Therefore, even when the above conditions have been allowed for, it is possible to compare only values of αf, where α is the degree of dissociation [10].

Experimental results and discussion

We have obtained calibration curves for Li, K, Cs, Ba, Sr, Al, In, Tl, Pb, Cr, Mn and Ti (Fig. 4).

There is a marked deviation from linearity for many elements. This was also observed by Russell *et al.* [1], and Allan [2]. The fact that the lines are not monochromatic, may be due to hyperfine structure or self-absorption of the resonance lines in the source itself, leading to a considerable line broadening. This last suggestion is born out by the curvature of the graphs in cases where hyperfine splitting can be neglected (Cr, Sr, K).

The non-linearity of the concentration curves necessitates a preliminary calibration for each element.

Because of the complete dissociation of the molecules in the crucible, the effect of the composition of the sample on the analytical results is eliminated. These effects are produced by changes in the degree of dissociation of certain compounds. Since ionization at temperatures of up to 2500°K does not take place (except for the alkali metals), but vaporization of the sample is complete, there will be no effect due to fractionation. In general the quantitative results obtained by this method, do not in any way depend on the composition of the sample. This is illustrated by the determination of Mn in the presence of other substances (Table 1). On addition to the Mn of excess by weight of NaCl, $Pb(NO_3)$ and $Sr(NO_3)$, the optical density of the absorption line Mn 4030 Å remained constant within the limits of experimental error.

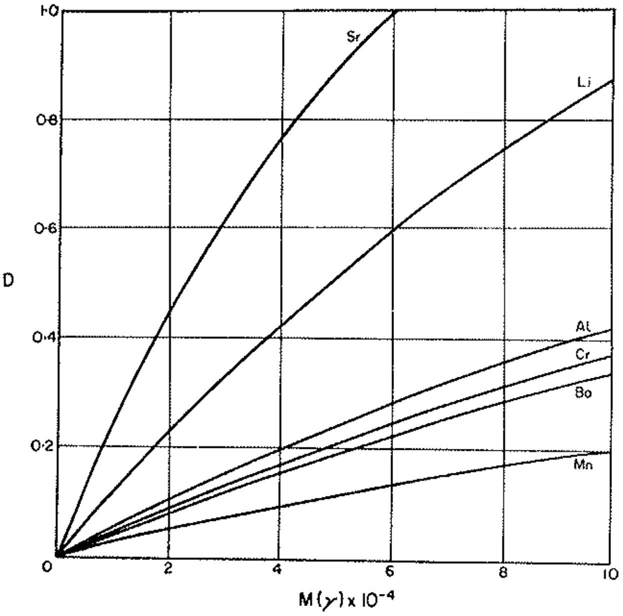

Fig. 4. Calibration curves.

Table 1. Determination of manganese in different substances

Weight ratio of Mn to the substance	Values of optical absorption density of Mn in different bases		
	NaCl	$Pb(NO_3)_2$	$Sr(NO_3)_2$
1:10	0·05	0·52	0·49
1:100	0·51	0·50	0·49
1:1000	0·50	0·50	0·50
1:10000	0·51	0·48	0·48

Let us consider another example. It is well known that in the estimation of the alkaline earths (Ca, Sr,) by flame photometry, the addition of Al to the solution markedly decreases the intensity of the Ca and Sr spectrum. A tenfold addition of

Al relative to Ca or Sr, produces a tenfold decrease in the emission of the Ca or Sr resonance line. This is explained by the formation of refractory aluminates of the corresponding metals. If the method suggested in this paper is used, then this effect is not observed. The addition of 1000 parts of Al to a specimen containing Sr did not change the absorption of the Sr 4607 Å line.

Hence, calibration and quantitative analysis can be carried out irrespective of the state of the specimen.

Although (5) is of no general use for absolute calculations, it can be used to evaluate the factors which affect the absolute sensitivity of the method. It follows from (5) that the minimum quantity of an element which can be determined to a given accuracy, i.e. the absolute sensitivity of the method, depends on the cross-sectional area of the crucible S, the accuracy with which the optical density D can be measured, and several constants on which depends b.

Experiment shows that in actual fact the sensitivity is inversely proportional to the cross-sectional area of the crucible. For technical reasons, however, it is impossible to make a furnace with an internal diameter of less than 2–3 mm.

The possibility of measuring low optical densities also increases the sensitivity. In our apparatus the limiting magnitude of the optical density which can be measured with a relative error of $\sim$50 per cent was 0·05. However, by using double-beam spectrophotometry and logarithmic amplification, it should be possible to measure 0·001–0·005 of a unit of optical density [14,15].

Finally the absolute sensitivity is determined by the choice of spectral lines, the pressure and nature of the gas, which produces greater or less broadening and shift of the absorption line, and the contour of the line given out by the source, i.e. the mode of the discharge in the hollow-cathode tube.

Values are given in Table 2 of the absolute sensitivity corresponding to an optical density of 0·05, for vaporizing compounds in a 3-mm diameter crucible, with a Ta lining, at a temperature of 2200°C, and 1 atm pressure (argon).

Increasing the accuracy of measurement, and using more sensitive resonance lines (Table 2) the absolute sensitivity could be increased still further.

For a given absolute sensitivity, the relative sensitivity is determined by the amount of substance existing in the vapour phase. Increasing the amount of specimen is limited by the fact that, in the end, the volume of vapour becomes comparable with the internal volume of the crucible. Because of this, some of the vapour will escape from the crucible, due to the increase in pressure, and hence will introduce an error in the determination of a concentration. Increasing the internal volume of the crucible will allow a greater quantity of a substance to be vaporized. However, increasing the volume, whilst maintaining a constant absolute sensitivity, is only possible by increasing the length. Hence, the relative sensitivity of this method depends on the length, and not on the cross-sectional area of the crucible.

One must also take into account the fact that the volume of vapour is not determined by weight but by the number of molecules. Therefore the relative sensitivities must depend on the type of compound: for light ones (Al_2O_3, SiO_2, BeO, etc.) this will be lower than for heavier ones (U_3O_8, Pb, SrO, etc.). If we take

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[14] P. Hariharan and M. S. Bhalla, *J. Opt. Soc. Am.* **47**, 378 (1957).
[15] C. C. Yang and V. Legallais, *Rev. Sci. Instr.* **25**, 801 (1954).

as a limit that amount of a substance which will give on vaporization at 2500°K, a volume equal to the internal volume of a crucible 10 mm long by 3 mm diameter, then for an average molecular weight of 30, up to 100 μg of a substance can be vaporized. The choice of such criteria specifies that only half of the total amount of vaporized substance will remain in the crucible, the remainder escaping due to the pressure increase. The relative sensitivities for the majority of elements, based on the data given in Table 2 for absolute sensitivities, are about $n \times 10^{-5}$–$n \times 10^{-3}$ per cent.

Table 2. Absolute sensitivity

Line measured (Å)	Transition	Absolute sensitivity (μg)	Most sensitive line	Transition
Li 6707	$2^2S_{1/2}$–$2^2P_{3/2}$	5×10^{-5}	Li 6707	$2^2S_{1/2}$–$2^2P_{3/2}$
K 4044	$4^2S_{1/2}$–$5^2P_{3/2}$	1×10^{-3}	K 7667	$4^2S_{1/2}$–$4^2P_{3/2}$
Cs 4555	$6^2S_{1/2}$–$7^2P_{3/2}$	7×10^{-3}	Cs 8521	$6^2S_{1/2}$–$6^2P_{3/2}$
Sr 4607	5^1S_0–5^1P_1	2×10^{-5}	Sr 4607	5^1S_0–5^1P_1
Ba 5535	6^1S_0–6^1P_1	1×10^{-4}	Ba 5535	6^1S_0–6^1P_1
Al 3961	$3^2P_{3/2}$–$4^2S_{1/2}$	1×10^{-4}	Al 3093	$3^2P_{3/2}$–$3^2D_{3/2\ 5/2}$
In 4101	$5^2P_{1/2}$–$6^2S_{1/2}$	4×10^{-4}	In 3039	$5^2P_{1/2}$–$5^2D_{3/2}$
Tl 5350	$6^2P_{3/2}$–$7^2S_{1/2}$	5×10^{-4}	Tl 2768	$6^2P_{1/2}$–$6^2D_{3/2}$
Pb 4057	6^3P_2–7^3P_1	1×10^{-2}	Pb 2833	6^3P_0–7^3P_1
Ti 4981	a^5F_5–y^5G_6	5×10^{-3}	Ti 3653	a^3F_4–y^3G_5
Mn 4030	$a^6S_{5/2}$–$z^6P_{7/2}$	2×10^{-4}	Mn 2794	$a^6S_{5/2}$–$y^6P_{7/2}$
Cr 4254	a_7S_3–z_7P_4	1×10^{-4}	Cr 3578	a_7S_3–y_7P_4

The following fact must be borne in mind when large amounts of a substance are being vaporized. As the vapour leaves through the open mouth of the heated crucible, a region of condensation is set up causing a "fog" to develop, hence scattering the incident light beam and producing a spurious measurement of absorption. For example, vaporization in a crucible 20 mm long by 3 mm diameter of 50 μg of NaCl produces a scattering which corresponds to an optical density of 0·2.

To overcome this phenomenon, we used a crucible with slits cut in the end. The vapour escapes through these slits and considerably reduces the amount which escapes along the axis of the beam. Slits 5 mm long and 3 mm broad practically completely stopped the scattering from 100 μg NaCl.

Incidental analytical errors of the method described are as follows:

(1) Errors in measuring the dosage of the specimen.
(2) Errors in measuring the optical density.
(3) Errors arising out of the change in experimental conditions. (Temperature change of the crucible, change in the mode of the discharge.)

Errors in dosage can be limited to 1 or 2 per cent by use of a micropipette. Errors in measuring the optical density can be made very small by using double-beam spectrophotometers and logarithmic amplification. A more persistent error is that arising out of changes in sensitivities due to changes in the mode of discharge in the hollow-cathode source. Care must therefore be taken in designing the discharge tube.

The speed with which measurements can be made is sufficiently high. We carried out about twenty determinations per hour. Improving the separate steps of the process should make still further reductions in the analysis times.

The use of absorption methods for quantitative analysis is limited by the following difficulties, which are independent of the way in which vaporization is brought about:

(1) The determination of a series of elements (halogens, gases, sulphur, carbon) whose resonance lines lie in the vacuum region of the spectrum, is impossible without the necessary technical complications to the apparatus.

(2) The determinations of a few refractory elements (U, Th, Zr, etc.) is apparently also impossible, because their resonance lines are too weak, and the vapour pressures are exceedingly small, even at the maximum temperatures which can be reached in flames and graphite furnaces (3000°C).

A specific disadvantage of the suggested method lies in the fact that the dosing of small quantities requires the preliminary solution of the substance.

Torsional frequencies in the far infrared—I

Molecules with a single methyl rotor*

W. G. Fateley and Foil A. Miller
Mellon Institute, Pittsburgh 13, Pa.

(*Received* 20 *February* 1961)

Abstract—Transitions between torsional levels have been observed in the far infrared for nine compounds. The results are:

Compound	cm^{-1}	$v'' \rightarrow v'$	Potential barrier (cal/mole)
CH_3CHO	150	$0 \rightarrow 1$ (A)	1180
	262	$0 \rightarrow 2$ (A)	1186
	276	$0 \rightarrow 2$ (E)	1179
CH_3CH_2Cl	243	$0 \rightarrow 1$ (A)	3580
CH_3CHF_2	222	$0 \rightarrow 1$ (A)	3210
$HCOOCH_3$	130	$0 \rightarrow 1$ (A)	1165
CH_3N_3	126	?	?
CD_3N_3	90	?	?
CH_3NCO	143	?	?
CH_3NCS	128	?	?
CH_3SCN	131	?	?

The potential barriers for the first four compounds are in excellent agreement with microwave results. For the remaining five substances there are questions about which torsional transition is being observed, and there are no good microwave results for comparison.

Introduction

The rotation of a methyl group relative to a reference framework such as —CHO, —NCO, or —CH_2Cl is opposed by a threefold potential barrier (Fig. 1). If the barrier is sufficiently high the rotation reduces to a torsional oscillation. The torsional energy levels would be triply degenerate if it were not for the tunneling effect; this, however, splits them into two sublevels, one of which is non-degenerate (symmetry species A of the C_3-group) and the other doubly degenerate (species E). As shown in Fig. 1, the A-sublevel is alternately lower and higher than the corresponding E-level. The splitting becomes greater as the levels approach the top of the barrier, and finally well above the barrier the levels go over into those for a freely-rotating methyl group.

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There is almost no published work describing the direct observation of transitions between torsional levels of *methyl groups* [1]. For some molecules (e.g. ethane) these transitions are forbidden in both the infrared and Raman spectra. Even when allowed in the Raman effect, they seem to be so weak that they are seldom observed. For example we have tried hard to find the torsional transition in the Raman spectrum of methyl isothiocyanate, knowing just where to look, but with no success [2]. We have now observed such transitions in the far infrared for several compounds. They occur in the range 90–280 cm^{-1}.

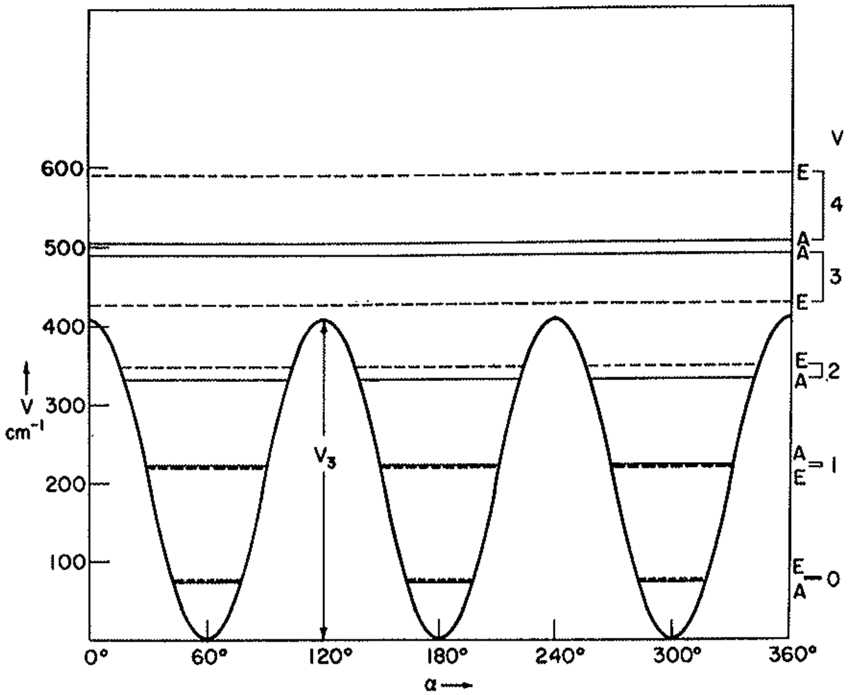

Fig. 1. Potential function and energy levels for hindered rotation. $V(\alpha) = V_3(1 + \cos 3\alpha)/2$. Drawn to scale for acetaldehyde, with $V_3 = 412{\cdot}7$ cm^{-1} = 1180 cal/mole.

This paper discusses the results for molecules in which a single methyl group is attached to a "rigid" framework, and in which there are three identical potential minima. Examples are CH_3CHO, CH_3NCO, and CH_3CH_2Cl. The reason for this restriction is that the theory has been developed particularly well for such molecules, especially by Prof. E. B. Wilson, Jr. and his students. This same group has

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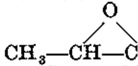
[1] The only earlier work of which we are aware is: (a) CH_3NH_2: A. Hadni, *J. phys. radium* **15**, 375 (1954); (b) CH_3CH_2F: E. Catalano and K. S. Pitzer, *J. Phys. Chem.* **62**, 873 (1958);


(c) $\mathrm{CH_3{-}\overbrace{CH{-}CH_2}^{O}}$: O. Ballaus and J. Wagner, *Z. physik. Chem. Leipzig* B**45**, 272 (1939); M. C. Tobin, *Spectrochim. Acta* **16**, 1108 (1960). (d) Some work on CD_3NH_2, CD_3ND_2, $CH_3CH{=}CH_2$ and CH_3OCH_3 by Prof. R. C. Lord of Mass. Inst. of Tech. which has appeared only as WADC technical report 59–498, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio (February, 1960). There are of course other papers where torsional frequencies have been inferred from combination tones.

[2] F. A. Miller and W. B. White, *Z. Elektrochem.* **64**, 701 (1960).

made careful and thorough microwave studies of several such compounds, and by that means has determined the heights of the potential barriers. The theory and many results have been well summarized in a recent excellent review by Lin and Swalen [3]. Infrared spectroscopy provides completely independent data from which to calculate these barriers, so the two techniques provide a mutual check on each other. It is particularly valuable to us in starting this work to be able to confirm our assignments from the microwave results.

Hindered rotation in molecules with more than one methyl rotor (e.g. CH_3OCH_3), or involving non-equivalent minima (CH_2Cl—CH_2Cl), are deferred for another paper. Molecules in which methyl groups rotate relative to a *symmetrical planar* framework (CH_3NO_2, toluene) are also not considered here; they have a sixfold potential barrier which apparently is very small.

Experimental

A. *Spectroscopic procedures*

The infrared spectrometer used for the range 80–350 cm^{-1} has been described elsewhere [4]. Wavenumbers of sharp bands should certainly be accurate to better than ± 1 cm^{-1}, but for broad bands the uncertainty may be ± 2–3 cm^{-1}. For the present work the calculated spectral slit width varied between 3 and 9 cm^{-1}, with 5 cm^{-1} being a typical value. (The transmission of the spectrometer fluctuates through the spectrum, being governed largely by the efficiency of the reststrahlen reflections. Naturally, the signal-to-noise ratio is most favorable near the reststrahlen peaks, and is poorest in regions between them.) Strenuous efforts were made to remove false energy, and nowhere did it amount to more than 5 per cent of the total signal.

Gaseous samples were measured in a standard 1-m folded-path cell with polyethylene windows. The pressures used are given in Table 1. Several of the compounds had too little vapor pressure to give a satisfactory gas spectrum. These were examined as solids by depositing them from the vapor onto a cold polyethylene support at liquid nitrogen temperature in a conventional low-temperature cell.

Because vapor phase frequencies are preferred, it is desirable to know the frequency shift between the solid and vapor states. To test this, gas and solid state frequencies have been compared for acetaldehyde. An absorption was observed in each at 150 ± 1 cm^{-1}. Hence in this case the torsional frequencies are remarkably independent of physical state. Various experimental difficulties have prevented us from obtaining any other comparisons, but we suspect that solid phase frequencies can be used without great error for the molecules considered here.

The low-temperature solid deposits usually appear to be glassy. If they were well crystallized, there would be a possibility of added complications in the spectra due to lattice vibrations and crystal field splittings. To see whether this was likely,

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[3] C. C. Lin and J. D. Swalen, *Revs. Mod. Phys.* **31,** 841 (1959).
[4] F. A. Miller, G. L. Carlson and W. B. White, *Spectrochim. Acta* **15,** 709 (1959).

two of the compounds (CH_3NCO and CH_3N_3) were also deposited as dilute suspensions in a matrix of cyclohexane. It was hoped that this would destroy the crystallinity of the sample and eliminate any unwanted complications. No change was produced in the far infrared spectrum.

B. *Origin of the samples*

Because acetaldehyde usually contains enough water to present serious interference in the far infrared, some care was taken to purify the sample. After a preliminary distillation, it was vacuum transferred from a glass vessel at 148°K through four traps at 148°K to a collection trap at 77°K. (The 148°K temperature was obtained by using an equilibrium mixture of solid and liquid ethanol.) The normally strong bands of water vapor were then no longer observed.

Chloroethane and 1 : 1-difluoroethane gases were obtained from the Matheson Chemical Co. and dried with Linde type 4A molecular sieves. Commercial methyl formate proved to have about 3·5 per cent of CH_3OH impurity in the vapor which caused serious interference. It was finally removed after distilling through a fifteen-plate column, passing the vapor over silica gel to remove the remaining methanol, and then over molecular sieves to remove any water.

Methyl azide, methyl azide-d_3, and methyl isocyanate were provided through the kindness of Dr. D. E. MILLIGAN of Mellon Institute, who had prepared them for another purpose. Because their spectra showed no infrared bands not previously reported, it was assumed that they were sufficiently pure. Methyl thiocyanate and methyl isothiocyanate were commercial products, and were used without further treatment.

Theory

It will be helpful to summarize the theory briefly before discussing the results. HERSCHBACH's formulation and notation will be used [5]. The model is that of a rigid symmetric top (i.e. a CH_3 group) attached to a rigid framework which may be completely asymmetrical. Since the top has a threefold symmetry axis, the potential energy hindering rotation may be expressed in a Fourier series as

$$V(\alpha) = \frac{V_3}{2}(1 + \cos 3\alpha) + \frac{V_6}{2}(1 + \cos 6\alpha) + \ldots \qquad (1)$$

where V_3 is the height of the threefold potential barrier, V_6 of the sixfold one, and so on.

It is assumed here that all terms after the first may be dropped; there is good evidence for this.* When this potential is put in the wave equation for the torsional motion, Mathieu's equation is obtained. The energy solutions for each torsional quantum number v give two sublevels; one is non-degenerate (A) and the other is doubly degenerate (E). The torsional energy is:

$$E_{v\sigma} = 2{\cdot}25 F b_{v\sigma} \qquad (2)$$

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* V_6 is probably $\leqslant 0{\cdot}01\ V_3$ (see [3], p. 844).

[5] D. R. HERSCHBACH, *J. Chem. Phys.* **31**, 91 (1959).

where v = principal torsional quantum number.
σ = an index designating either the A- or E-levels
$b_{v\sigma}$ = an eigenvalue of the Mathieu equation;
$$F = h^2/8\pi^2 rI_\alpha; \tag{3}$$
rI_α = reduced moment of inertia for internal rotation,
$$= I_\alpha[1 - I_\alpha \sum_g (\lambda_g{}^2/I_g)]; \tag{4}$$
I_α = moment of inertia of the internal top (i.e. CH_3) about its symmetry axis;
λ_g = cosine of the angle between the axis of the internal top and the gth principal axis of inertia of the entire molecule;
I_g = gth principal moment of inertia of the entire molecule.

The observed infrared frequency gives the *difference* between two of the energy levels which, according to (2), is

$$\Delta E_{v\sigma} = 2{\cdot}25F(\Delta b_{v\sigma}) \tag{5}$$

Thus if the absorption frequency is known, and there is enough structural information to determine F, $\Delta b_{v\sigma}$ can be calculated. From this $\Delta b_{v\sigma}$ a dimensionless parameter s can be obtained from tables of solutions for the Mathieu equation. The barrier height can then be calculated from s by using:

$$V_3 = 2{\cdot}25Fs \tag{6}$$

One problem is to know *which* torsional levels are involved in an observed transition. It is here that the microwave-determined barriers have provided an invaluable guide to us.

Tables of $b_{v\sigma}$ vs. s are given in HERSCHBACH's paper [5]. HERSCHBACH has prepared another set of tables [6] which are easier to use for the present purposes than those in [5], and which include many more values of v. He has kindly provided us with a set, and all the results in this paper were obtained from these rather than from [5].

A sample calculation is given in the discussion of acetaldehyde.

Discussion of results

The results are summarized in Table 1. Table 2 gives the source of the structural data, and lists the values of F and s used. In the discussion of the results, the compounds are divided into two groups depending upon whether their spectra were measured in the gaseous or solid state. The results are generally much more reliable for the former group.

A. *Molecules measured in the gaseous state*

1. *Acetaldehyde* (CH_3CHO). We begin with acetaldehyde because it is the most favorable case. It has been studied very carefully by microwave spectroscopy [7],

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[6] D. R. HERSCHBACH, *Tables for the Internal Rotation Problem.* Department of Chemistry, Harvard University. These tables are described in *J. Chem. Phys.* **27**, 975 (1957).

[7] R. W. KILB, C. C. LIN and E. B. WILSON, JR., *J. Chem. Phys.* **26**, 1695 (1957).

Table 1. Infrared bands and potential barriers

Compound	Observed (cm^{-1})*	Intensity†	Pressure in 1-m cell (cm Hg)	Assignment of CH_3 torsion	V_3 (cal/mole)	
					Infrared‡	Microwave
A. *Gas phase measurements*						
(1) CH_3CHO	150 ± 1	vw	(solid)	0 → 1 (*A*)		
	143	s				
	150	m	8	0 → 1 (*A*)	1180	1168 ± 30 [5]
	158	m				
	~257	vw				
	262	w	40	0 → 2 (*A*)	1186	
	268	w				
	273	w				
	276	w	40	0 → 2 (*E*)	1179	
	280?	vw				
(2) CH_3CH_2Cl	235·5	s				
	243 ± 1	w	74	0 → 1 (*A*)	3580	3560 ± ? [11]
	251·5	s				
(3) CH_3CHF_2	222 ± 2	m	74	0 → 1 (*A*)	3210	3180 ± 20 [14]
(4) $HCOOCH_3$	130	w	50	0 → 1 (*A*)	1165	1190 ± 40 [15]
B. *Solid phase measurements*						
(5) CH_3N_3	126 ± 1	w, b		0 → 1 (*A*)	980	
				0 → 2 (*E*)	300	
(6) CD_3N_3	90 ± 1	w, b		0 → 1 (*A*)	830	
				0 → 2 (*E*)	290	
(7) CH_3NCO	143 ± 1	m, b		0 → 1 (*A*)	1200	
				0 → 2 (*A*)	560	
				0 → 2 (*E*)	400	
(8) CH_3NCS	128 ± 1	m, b		0 → 1 (*A*)	700	275 ± 150 [18]
				0 → 2 (*A*)	380	
				0 → 2 (*E*)	<50	
(9) CH_3SCN	131 ± 1	m, b		0 → 1 (*A*)	1000	
				0 → 2 (*A*)	500	
				0 → 2 (*E*)	300	

* All cm^{-1}'s are ±0·5 cm^{-1} unless otherwise stated.
† w, m, s = weak, medium, strong. v = very, b = broad.
‡ All V_3 values are at least ±15 cal/mole.

and HERSCHBACH has applied his theory to it as a specific example [5]. Likewise we feel that our infrared results are more complete and reliable for it than for any other molecule we have studied.

In the solid only a very weak band at 150 cm^{-1} was found. In the gas nine peaks were observed: three at 143, 150, and 158 cm^{-1}, and six at 257, 262, 268, 273, 276, and 280 cm^{-1} (Fig. 2). We are not sure of the proper explanation for these. Acetaldehyde is approximately a symmetric top, since $I_A = 8{\cdot}933$, $I_B = 49{\cdot}741$, and $I_C = 55{\cdot}553$ a.m.u. Å^2 [7]. The average spacing between the subbands of a $\perp$ band of such a top is expected to be about 3 cm^{-1} [8]. However, the strong coupling between internal and overall rotation will destroy the regularity of the pattern. The observed spacings are 7 and 8 cm^{-1} at 150 cm^{-1}, where the spectral

Table 2. Parameters used in the calculations

Compound	F (cm^{-1})	Transition $v'' \rightarrow v'$	s	Structural data Reference	Structural data Completeness
1. CH_3CHO	7·696	$0 \rightarrow 1\ (A)$	23·835	[5]	Very good
		$0 \rightarrow 2\ (A)$	23·973		
		$0 \rightarrow 2\ (E)$	23·830		
2. CH_3CH_2Cl	5·858	$0 \rightarrow 1\ (A)$	95·065	[10]	Fair
3. CH_3CHF_2	5·468	$0 \rightarrow 1\ (A)$	91·262	[13]	Very poor
4. $HCOOCH_3$	5·680	$0 \rightarrow 1\ (A)$	31·861	[15]	Very good
5. CH_3N_3	6·543	$0 \rightarrow 1\ (A)$	23·314	[16]	Good
		$0 \rightarrow 2\ (E)$	7·192		
6. CD_3N_3	3·772	$0 \rightarrow 1\ (A)$	34·305	—	Good
		$0 \rightarrow 2\ (E)$	11·899		
7. CH_3NCO	6·727	$0 \rightarrow 1\ (A)$	27·779	[17]	Fair
		$0 \rightarrow 2\ (A)$	13·020		
		$0 \rightarrow 2\ (E)$	9·330		
8. CH_3NCS	9·505	$0 \rightarrow 1\ (A)$	11·472	[18]	Very poor
		$0 \rightarrow 2\ (A)$	6·293		
9. CH_3SCN	6·921	$0 \rightarrow 1\ (A)$	22·578	[19]	Very poor
		$0 \rightarrow 2\ (A)$	11·163		
		$0 \rightarrow 2\ (E)$	6·819		

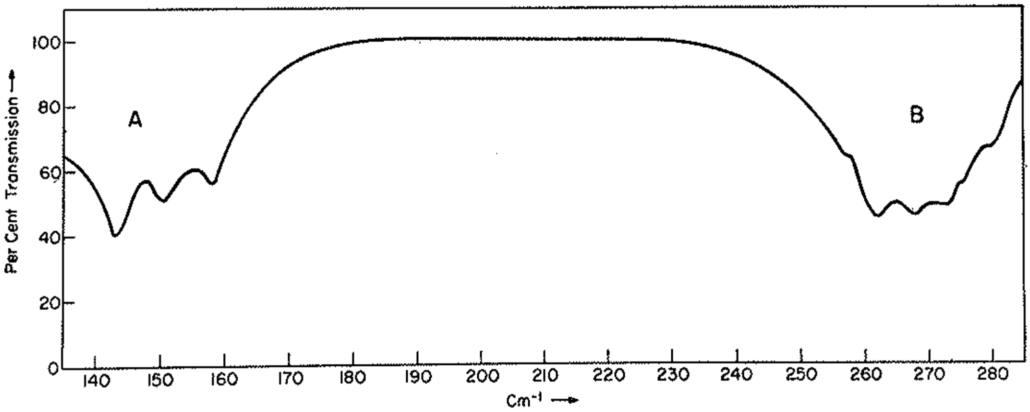

Fig. 2. Infrared absorption of acetaldehyde vapor at low frequencies. Path length = 1 m. A. 8 cm pressure; slit width = 8·5 cm^{-1}. B. 40 cm pressure; slit width 3·5 cm^{-1}. There was no other absorption between 80 and 350 cm^{-1}.

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[8] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* p. 424. Van Nostrand, New York (1945).

slit width was calculated to be 8·5 cm^{-1}. They are from 3 to 6 cm^{-1} at 270 cm^{-1}, where the spectral slit width was about 3·5 cm^{-1}. Hence considerably more detail would be observed with higher resolution, and we could not expect to find the predicted 3 cm^{-1} spacing in this experiment.

Let us assume that 150 cm^{-1} is the $0 \rightarrow 1$ transition for the methyl torsional mode. Furthermore let us assume that the A- and E-levels for both $v = 0$ and $v = 1$ are so close together that the separate infrared transitions are not resolved. (This will be confirmed later.) We shall carry through a sample calculation of the barrier height V_3, using the A-levels. From equation (5) one has:

$$\Delta E_{v\sigma} = E_{1A} - E_{0A} = 150\ \text{cm}^{-1} = 2{\cdot}25F(\Delta b_{v\sigma})$$

The value of F for acetaldehyde is given explicitly in [5] as 230·7 kMc, which is 7·696 cm^{-1}.[*] Hence

$$\Delta b_{v\sigma} = b_{1A} - b_{0A} = 8{\cdot}663$$

One now goes to HERSCHBACH's tables [6] to find the value of s which gives this Δb_{vA}. One finds:

	$s = 20$	$s = 28$
$(v = 1)\ b_{1A}$	12·10	14·52
$(v = 0)\ b_{0A}$	4·20	5·03
Δb_{vA}	7·90	9·49

Interpolation gives $s = 23{\cdot}84$.[†] Substituting this in equation (6) leads to $V_3 =$ 413 cm^{-1} or 1180 cal/mole. This value should be compared with the microwave result of 1168 ± 30 cal/mole [5]. The latter value is based on the same theory for the energy levels, but on a completely different set of transitions. The agreement is very satisfactory.

By reversing the calculations, the value for the barrier can now be used to determine the energies of the A- and E-sublevels for various torsional quantum numbers. The results are given in Table 3. They are also shown on Fig. 1, which is drawn to scale for acetaldehyde. It will be seen from Table 3 that the splitting for $v = 0$ is only 0·09 cm^{-1}, and for $v = 1$ is 2·2 cm^{-1}. We could therefore not expect to resolve the transition $0 \rightarrow 1$ (A) from $0 \rightarrow 1$ (E) because the spectral slit width was always greater than 3 cm^{-1} at 150 cm^{-1}. Our earlier assumption is thus justified. It is also interesting to note that the levels for $v = 3$ and higher lie above the barrier.

The collection of weak peaks between 257 and 280 cm^{-1} is attributed to the $0 \rightarrow 2$ transition, for which the absorption is expected to be complex because of the following reasons. The $v = 2$ level is split into A- and E-sublevels about 15

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[*] In [3], Table VI, F is erroneously given as 17·77 cm^{-1}. This is really 2·25 F.

[†] If reference [5] is used rather than the more extensive tables [6], the desired data are found in Appendix D, p. 107. The $b_{vA} = \sum_i w_i$. Thus for $s = 20$, b_{1A} is $11{\cdot}976 + 0{\cdot}121 + 0{\cdot}003 = 12{\cdot}100$. The $b_{vE} = \omega_0 - \frac{1}{2}\omega_1 - \frac{1}{2}\omega_2 + \omega_3 - \frac{1}{2}\omega_4 - \cdots\cdots$. Thus for $s = 20$, b_{1E} is $11{\cdot}9761 - 0{\cdot}1205/2 - 0{\cdot}0027/2 + 0{\cdot}0001 = 11{\cdot}9146$.

cm^{-1} apart. Associated with each of the resulting torsional transitions $0 \rightarrow 2$ (A) and $0 \rightarrow 2$ (E) is rotational structure, which in turn will be complex because of the coupling between internal and overall rotation. These two bands will overlap seriously. The net result is a complicated absorption for which only the crude contour has been observed. Because it is not possible to locate the band centers with confidence from the appearance of the band, they have been determined from the energy levels of Table 3. This gives $0 \rightarrow 2$ (A) = 261 cm^{-1}, $0 \rightarrow 2(E)$ = 276 cm^{-1}. The observed absorption maxima at 262 and 276 cm^{-1} have therefore been taken as the band centers. Possibly the agreement is fortuitous, for the observed maxima may be the result of accidental build-up of intensity from the overlapping lines of the two bands. The other four peaks are arbitrarily considered to be rotational branches flanking these two band centers (see Table 1). Similarly 143 and 158 cm^{-1} are taken to be branches of the fundamental at 150 cm^{-1}.

Table 3. Energy levels for acetaldehyde
(V_3 = 412·7 cm^{-1} = 1180 cal/mole)

v	Sublevel	Energy (cm^{-1})	Δ (cm^{-1})
0	A	79·58	0·09
	E	79·67	
1	E	227·4	2·2
	A	229·6	
2	A	340·6	15·3
	E	355·9	
(Barrier)		(412·7)	
3	E	435·8	62·0
	A	497·8	
4	A	513·3	86·1
	E	599·4	

The agreement between the infrared and microwave results, and the internal consistency of the $0 \rightarrow 1$ and $0 \rightarrow 2$ infrared transitions, is very good. This is particularly pleasing because acetaldehyde is the molecule whose internal rotation has been most thoroughly studied by both methods. However, it should be mentioned that MÖLLER has reported infrared absorption in acetaldehyde at 175 cm^{-1} which he attributed to the torsional fundamental [9]. We found no absorption whatever in this range, and believe him to be in error.

There is an arbitrary feature in our treatment which should be noted. It has been assumed that the 150 cm^{-1} absorption is due to the $0 \rightarrow 1(A)$ absorption. What if it were $0 \rightarrow 1(E)$? This would give a barrier of 423 cm^{-1}, or 1210 cal/mole,

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[9] K. D. MÖLLER, *Compt. rend.* **250**, 3977 (1960).

which is in less good agreement with the microwave result. Or, since we could not resolve the 2 cm^{-1} separation of the two $0 \rightarrow 1$ transitions, perhaps 150 cm^{-1} is the resultant of both. Then V_3 would be approximately the average of the two previous values, or about 1195 cal/mole. This is just within the uncertainty range of the microwave results. We have arbitrarily used 1180 cal/mole for the barrier in deriving Table 3.

Finally, from the energy levels of Table 3 we find that the transition $1(A \text{ or } E) \rightarrow 2(A)$ is expected near 112 cm^{-1}, and $1(A \text{ or } E) \rightarrow 2(E)$ near 127 cm^{-1}. No absorption was observed at either place, but the bands are expected to be weak because they start from an excited state.

General remarks on accuracy. The heights of the potential barriers are quite sensitive to the exact value of the infrared frequency. For example lowering the observed frequency for acetaldehyde by 1 cm^{-1} lowers the barrier by 15 cal/mole. For this molecule the frequency is believed to be accurate to better than 1 cm^{-1}, so that the transition 150 ± 1 cm^{-1}, assumed to be $0 \rightarrow 1(A)$, gives a barrier of 1180 ± 15 cal/mole.

The barrier heights also depend on the structural parameter F, although they are not as sensitive to this as to the frequency. For example changing F for acetaldehyde from 7·696 to 7·896 cm^{-1} (2·6 per cent) changes V_3 from 1180 to 1154 cal/mole (2·5 per cent). For most of the molecules considered in this paper, really good structural information is not available and it has been necessary to make guesses at bond distances and angles. Clearly, the barriers should be recalculated when more accurate data become available. In Table 2 we have given the source of the structural data and an estimate of its quality.

2. *Ethyl chloride* (CH_3CH_2Cl). Structural data on this molecule are of fair quality [10], and a microwave study has given a value of 3560 cal/mole for the barrier [11]. Infrared absorption in the gas phase was found at 235·5, 243 ± 1, and 251·5 cm^{-1}, with 243 being much weaker than the other two (Fig. 3a). We believe that these are rotational branches. The 7·5 and 8·5 cm^{-1} separations are within the range of values observed for other infrared bands of ethyl chloride [12]. Attributing 243 cm^{-1} to the $0 \rightarrow 1(A)$ transition leads to a barrier of 3582 cal/mole, in excellent agreement with the microwave value of 3560 cal/mole. Because the barrier is relatively high, the splittings between the A- and E-sublevels are much too small for us to resolve. Even for $v = 2$ it is only 2 cm^{-1}.

We were unable to find this absorption in a solid film. Similarly we were unable to find the $0 \rightarrow 2$ transition, which is calculated from the barrier value to be at 471 cm^{-1}. Weak bands were observed at 461 and 496 cm^{-1} which presumably have other origins.

3. 1:1-*Difluoroethane* (CH_3CHF_2). Structural data for this molecule are very incomplete [13]. The vapor spectrum has absorption at 222 ± 2 cm^{-1}. The sample could not be condensed onto the cold plate, so the solid spectrum is not available. Assignment of 222 cm^{-1} to $0 \rightarrow 1(A)$ gives a barrier of 1123 cm^{-1} or 3210 cal/mole,

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[10] R. S. WAGNER and B. P. DAILEY, *J. Chem. Phys.* **26**, 1588 (1957).
[11] D. R. LIDE, *J. Chem. Phys.* **30**, 37 (1959).
[12] L. W. DAASCH, C. Y. LIANG and J. R. NIELSEN, *J. Chem. Phys.* **22**, 1293 (1954).
[13] N. SOLIMENE and B. P. DAILEY, *J. Chem. Phys.* **22**, 2042 (1954).

in very good agreement with the microwave value of 3180 ± 20 cal/mole [14]. Because the A–E splittings are small in both levels, essentially the same result would be obtained for $0 \rightarrow 1(E)$. No $0 \rightarrow 2$ nor $1 \rightarrow 2$ transition was observed. (They are expected at 430 and 203 cm^{-1}, respectively.)

4. *Methyl formate* ($HCOOCH_3$). CURL has made a thorough microwave study of the structure and potential barrier of this compound [15]; his value for the latter is 1190 ± 40 cal/mole. Infrared absorption was found at 130 cm^{-1} (Fig. 3b). Assigning this to $0 \rightarrow 1(A)$ gives a barrier of 1164 cal/mole, in good agreement with CURL's result.

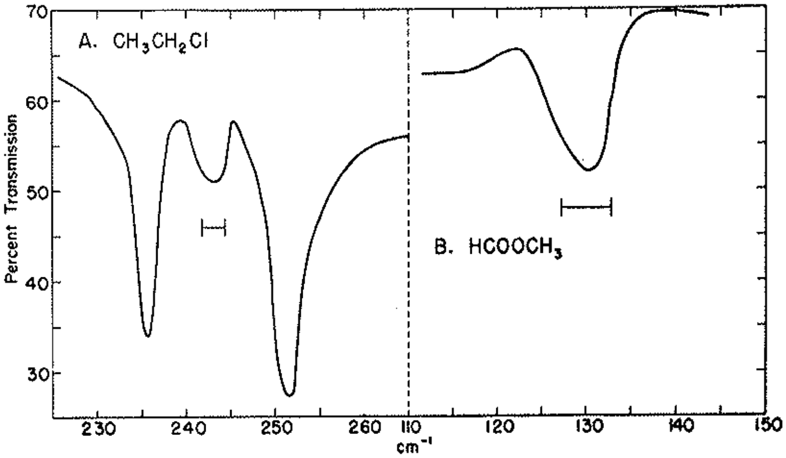

Fig. 3. A. Infrared band of chloroethane. Slit width ≃ 2·5 cm^{-1}. One-meter cell, 74 cm Hg pressure. B. Methyl formate. Slit width ≃ 5·3 cm^{-1}. One-meter cell, 50 cm Hg pressure. No bands of water or methanol were present.

B. *Molecules measured in the solid state*

The remaining compounds were studied only as solids at about 77°K. The results are generally less reliable or complete than for the previous ones. There is a question about the change of frequency with state. Also there is a microwave determination of the barrier for only one of these compounds (CH_3NCS), and it is quite inaccurate. Consequently the results presented here are only tentative.

5 *and* 6. *Methyl azide and methyl azide-d_3* (CH_3N_3 *and* CD_3N_3). These substances were studied as solids because there was insufficient sample for gas phase work. Frequencies were observed at 126 for CH_3N_3 and 90 cm^{-1} for CD_3N_3. Their ratio is 1·40. This is surprising because it is very close to the ratio for harmonic vibrations, whereas the assumed potential function is far from harmonic. If these are arbitrarily assumed to be the $0 \rightarrow 1(A)$ transitions, the barrier height is calculated to be 981 cal/mole for CH_3N_3, and 832 cal/mole for CD_3N_3. The agreement is not satisfactory. If they are taken to be the $0 \rightarrow 2(E)$ transitions, the barriers are 303 and 289 cal/mole. The $0 \rightarrow 2(A)$ transition for CH_3N_3 would then be about 100 cm^{-1}, where it could easily have been missed. For CD_3N_3, it would be beyond

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[14] D. R. HERSCHBACH, *J. Chem. Phys.* **25**, 358 (1956).
[15] R. F. CURL, JR., *J. Chem. Phys.* **30**, 1529 (1959).

our range. There is no microwave value for comparison. We leave the problem in this unsatisfactory state. Structural data for CH_3N_3 are from LIVINGSTON and RAO [16], and are good. The same dimensions were assumed for CD_3N_3.

7. *Methylisocyanate* (CH_3NCO). Again the solid state was used because of insufficient sample, and again there are no microwave results for comparison. The structural information is from EYSTER *et al.* [17]. Absorption was observed at 143 cm^{-1}. If this is $0 \rightarrow 1(A)$, the barrier is 1202 cal/mole. Results for two other assignments are given in Table 1.

8. *Methylisothiocyanate* (CH_3NCS). An unpublished microwave study has been made of this molecule which gives the F-value and a barrier of 275 ± 150 cal/mole [18]. Infrared absorption was found at 128 cm^{-1} in the solid. If this is due to the $0 \rightarrow 1(A)$ transition, the calculated barrier is 701 cal/mole, which is incompatible with the tentative microwave results. Assuming that 128 cm^{-1} is the $0 \rightarrow 2(A)$ transition gives $V_3 = 384$ cal/mole, but this then requires $0 \rightarrow 2(E)$ at 152 cm^{-1} where nothing was observed. If 128 cm^{-1} is attributed to the $0 \rightarrow 2(E)$ transition, the barrier is less than 50 cal/mole which again is incompatible with the microwave results. Consequently only the second assignment, giving $V_3 = 384$ cal/mole, seems acceptable, but we are not confident that it is correct.

9. *Methylthiocyanate* (CH_3SCN). The vapor pressure of this compound is too small to give a gas-phase spectrum in the meter cell. In the liquid there is very broad absorption around 131 cm^{-1}, but it was impossible to find the band center accurately. In the solid at 77°K there is a strong, broad absorption at 131 ± 1 cm^{-1}. Unfortunately the structural data are very poor [19], and there is no microwave-determined barrier.

Attributing 131 cm^{-1} to $0 \rightarrow 1(A)$ gives a barrier of 1005 cal/mole. Assigning it to $0 \rightarrow 2(A)$ gives 497 cal/mole, but predicts $0 \rightarrow 2(E)$ at 160 cm^{-1} where nothing was observed. Finally assigning it to $0 \rightarrow 2(E)$ gives 304 cal/mole, and predicts $0 \rightarrow 2(A)$ at 95 cm^{-1}. Nothing was observed there, but a weak band could easily be missed.

Concluding remarks. The infrared and microwave results agree well for the four molecules studied in the gas phase. For the five examined as solids, the results must be regarded as tentative and unsatisfactory. It would be especially helpful to have higher resolution for the infrared work.

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[16] R. L. LIVINGSTON and C. N. R. RAO, *J. Phys. Chem.* **64**, 756 (1960).

[17] E. H. EYSTER, R. H. GILLETTE and L. O. BROCKWAY, *J. Am. Chem. Soc.* **62**, 3236 (1940).

[18] S. SIEGEL. Thesis, Harvard University (1959). Private communication from Prof. E. B. WILSON, JR.

[19] C. I. BEARD and B. P. DAILEY, *J. Am. Chem. Soc.* **71**, 929 (1949).

The C=S stretching frequency and the "—N—C=S bands" in the infrared*

C. N. R. Rao and R. Venkataraghavan
Department of Inorganic and Physical Chemistry,
Department of Organic Chemistry,
Indian Institute of Science, Bangalore-12, India

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Abstract—A correlation of the infrared spectra of thiocarbonyl derivatives based on the literature data has been carried out. Assignments have also been made in some new systems. Since simple alkyl thioketones are unstable, we have prepared thiofenchone in order to obtain a reference C=S stretching frequency. The C=S stretching frequency in thiofenchone has been found around 1180 cm^{-1} which is in fair agreement with the value calculated for thioformaldehyde. In the case of the thiocarbonyl derivatives where the C=S group is linked to elements other than nitrogen, the stretching frequency is generally found in the region 1025–1225 cm^{-1}. Strong vibrational coupling is operative in the case of the nitrogen containing thiocarbonyl derivatives and three bands seem to consistently appear in the regions 1395–1570 cm^{-1}, 1260–1420 cm^{-1}, 940–1140 cm^{-1} due to the mixed vibrations. These bands, which may be tentatively designated as the "—N—C=S I, II and III bands", could be useful in qualitative analysis.

INTRODUCTION

Frequencies ranging from 850 to 1550 cm^{-1} have been attributed to the C=S stretching frequency in the literature and there seems to be no adequate correlation of the literature data [1]. A careful examination of the data reveals that the assignments of very high or low frequencies are always in the nitrogen-containing thiocarbonyl compounds. It therefore becomes necessary to distinguish two groups of thiocarbonyl derivatives: the first group, where the thiocarbonyl group is linked to atoms such as carbon, sulphur, oxygen and chlorine and the second group, where the thiocarbonyl group is linked to one or two nitrogen atoms. An unambiguous assignment of the C=S stretching frequency seems to be possible only when the C=S group is attached to atoms other than nitrogen. In this communication we have carried out a correlation of the infrared spectra of thiocarbonyl derivatives based on the literature data and have also reported assignments in some new systems. There was, however, need for a reference C=S stretching frequency in a simple saturated thioketone. Since simple alkyl thioketones are unstable, we have prepared thiofenchone for this purpose.

EXPERIMENTAL

Thiofenchone was prepared by refluxing fenchone with phosphorous pentasulphide in heptane. The other compounds investigated are dithio-oxamide,

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* Material taken from the Ph.D. thesis of R. Venkataraghavan to be submitted to the Indian Institute of Science under the guidance of C. N. R. Rao.

[1] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London (1958).

Reprinted from *Spectrochimica Acta*, Vol. 18, pp. 541 – 547, 1962. Pergamon Press Ltd.

2-mercapto 3,4-dimethylthiazole, thiozolidine-2-thione, 2-mercaptobenzthiazole, thiosemicarbazides, tetrazolinethiones and guanylthioureas, of which the last two series of compounds were prepared in connection with other studies [2, 3]. The others were commercially available.

Infrared spectra were recorded employing Perkin–Elmer spectrometers, models 21 and 137B. The samples were in the form of solutions in CCl_4 or $CHCl_3$ or solids dispersed in Nujol mulls or KBr pellets.

RESULTS AND DISCUSSION

Thiocarbonyl derivatives where the C=S *group is linked to elements other than nitrogen*

The C=S stretching frequency in thiofenchone is found around 1180 cm^{-1}. This is in fair agreement with the calculated frequency in thioformaldehyde [4]. The various thiocarbonyl derivatives for which the infrared data are available are ethylenetrithiocarbonate [5, 6], alkyl and perfluoroalkyl trithiocarbonates [7], dithioesters [8], 2,4-dihydroxy dithiobenzoic acid [9], thiobenzophenones [10], pyr-4-thione, 2,6-dimethyl pyr-4-thione and thiopyr-4-thione [11], pyrid-4-thione [12], γ-mercaptoaza compounds [13], alkyl and perfluoroalkyl chloroformates [7], thiophosgene [9] and dianthogens and xanthates [14, 15]. The assignments in these derivatives have been shown in the form of a correlation diagram in Fig. 1. In the case of the xanthate compounds, the assignment in the range 1020–1070 cm^{-1} [14] has been preferred. The assignment in the region 1140–1265 cm^{-1} [15] probably corresponds to the C—O stretching vibration. The correlation clearly shows that the C=S stretching frequency in these derivatives falls within the range 1125 ± 100 cm^{-1}.

No simple correlation of the C=S stretching frequency with electronegativities of the atoms directly linked to the group is apparent. The linear relationship found by DAASCH [16] is not considered to be generally valid. In substituted phenyl thiocarbonyl derivatives [8, 10] the C=S stretching frequency does not show any simple relationship with the Hammett σ or σ^+ constants of the substituents [17]. The thiocarbonyl group is not at all similar to the carbonyl group

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[2] E. LIEBER, C. N. R. RAO, C. N. PILLAI, J. RAMACHANDRAN and R. D. HITES, *Can. J. Chem.* **36**, 801 (1958).

[3] K. S. SURESH, J. RAMACHANDRAN and C. N. R. RAO, *J. Sci. Ind. Res. (India)* **20**B, 203 (1961).

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[6] L. J. BELLAMY and P. E. ROGASCH, *J. Chem. Soc.* 2218 (1960).

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[9] J. I. JONES, W. KYNASTON and L. J. HALES, *J. Chem. Soc.* 614 (1957).

[10] N. LOZACH and G. GUILLOUZO, *Bull. soc. chim. France* 1221 (1957).

[11] A. R. KATRITZKY and R. A. JONES, *Spectrochim. Acta* **17**, 64 (1961).

[12] A. R. KATRITZKY and R. A. JONES, *J. Chem. Soc.* 2947 (1960).

[13] E. SPINNER, *J. Chem. Soc.* 1237 (1960).

[14] L. H. LITTLE, G. W. POLING and J. LEJA, *Can. J. Chem.* **39**, 745 (1961).

[15] M. L. SHANKARANARAYANA and C. C. PATEL, *Can. J. Chem.* **39**, 1633 (1961).

[16] L. W. DAASCH, *Spectrochim. Acta* **13**, 257 (1958).

[17] C. N. R. RAO and R. VENKATARAGHAVAN, *Can. J. Chem.* **39**, 1757 (1961).

with regard to bond polarity and electrical effects of substituents [6]. The insensitivity of the thiocarbonyl stretching frequency to electrical effects is further confirmed by the fact that the calculated frequency of 1120 ± 40 cm^{-1} for thioformaldehyde is not very different from the observed frequency of 1140 cm^{-1} for thiophosgene [4] and 1180 cm^{-1} for thiofenchone.

The only cases where the C=S frequency falls outside the limits of this correlation are xanthione, thioxanthione and N-methyl thioacridone, all of which are heteroaromatic ketones. The C=S stretching frequency in these systems is found at 1330 ± 30 cm^{-1} [18].

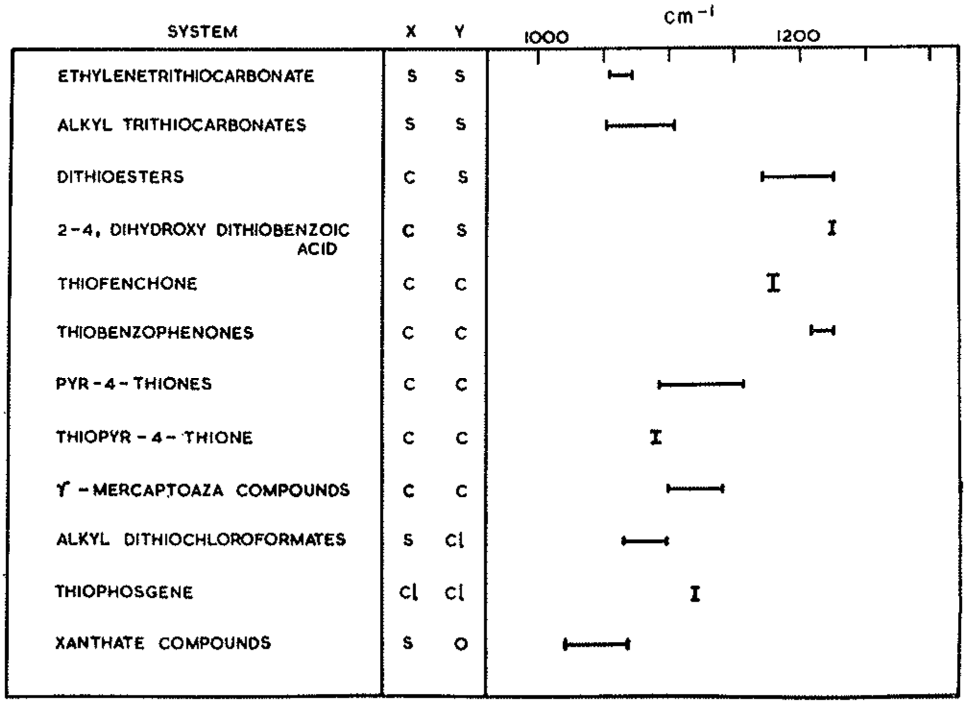

Fig. 1. The C=S stretching frequencies in thiocarbonyl derivatives where the group is linked to elements other than nitrogen. X and Y refer to the elements directly linked to the thiocarbonyl group.

Thiocarbonyl derivatives where the C=S *group is linked to one or two nitrogen atoms*

There has been great indefiniteness with regard to the assignment of the C=S stretching frequency in nitrogen containing compounds. The assignment in these compounds varies in the wide range of 850 to 1570 cm^{-1}. Randall *et al.* [19] first observed that a strong band is present in the region 1471–1613 cm^{-1} in compounds where the N—C=S unit is present. Several authors [1, 2, 20, 21] have made a

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[18] T. Bergmann, *J. Am. Chem. Soc.* **77**, 1549 (1955).

[19] H. M. Randall, R. G. Fowler, N. Fuson, J. R. Dangl, *Infrared Determination of Organic Structures.* D. Van Nostrand, New York (1949).

[20] J. Mann, *Trans Inst. Rubber Ind.* **27**, 232 (1951).

[21] J. Chatt, L. A. Duncanson and L. M. Venanzi, *Suomen Kemistilehti* **29**B, 75 (1956).

similar assignment in a number of such systems. Subsequently it has been shown by Elmore [22] that this thioureide band results from the coupling of the C—N stretching vibration and the NH deformation vibration. The extreme variations in the assignment of the C=S stretching frequency in nitrogen-containing thiocarbonyl derivatives is undoubtedly due to vibrational coupling effects. In most of these systems the C=S stretching vibration is not localized. The vibrations that interact will naturally vary with the system. Thus in thiourea the vibrations due to C—N stretching, C=S stretching and NH_2 rocking can interact to give the observed infrared frequencies [4, 23]. In the thioamide system, coupling can take place among C—N stretching, C=S stretching and NH deformation vibrations. The observed infrared bands in nitrogen-containing thiocarbonyl compounds are therefore due to mixed vibrations and an estimate of the mixing effects will only be possible by normal co-ordinate analysis similar to that reported for N-methyl acetamide by Miyazawa *et al.* [24]. Many of the earlier assignments of the C=S frequencies in compounds such as thioamides [6], dithio-oxamides [25], thiadiazoles [26], tetramethylthiurammonosulphide [27], thiosemicarbazides and tetrozolinethiones [2], thiobenzanilide [28] and thiohydantoins [22] appear to be partial in the sense that these might have had some contribution from the C=S stretching. The assignments of the C=S stretching frequencies in thioacetamide and tetramethylthiurammonosulphide in the region 960–980 cm^{-1} by Bellamy and Rogasii [6], based on solvent effects, are also considered to be partial assignments. The observed solvent effects are small and such effects may not be conclusive in establishing assignments. It is however possible that the 960–980 cm^{-1} band in these compounds has appreciable contribution from C=S stretching and therefore show solvent shifts similar to other simpler thiocarbonyl derivatives. Although it appears impossible at first sight to obtain any kind of correlation of the infrared spectra of nitrogen-containing thiocarbonyl derivatives, a critical survey of the existing data indicates that some generalizations are possible. In such a correlation one should only consider molecules with similar structural units. Thus, a strict comparison of the spectra of thiourea and thioacetamide cannot be made since the interacting vibrations would be different.

In the case of thiourea, the bands at 1472, 1415 and 1086 cm^{-1} may be considered as composite bands of NH_2 bending, C—N stretching and C=S stretching. The band at 730 cm^{-1} may have some contribution from the NCS bending vibration. In thioacetamide [4, 6, 29], the frequencies at 1393, 1303 and 974 cm^{-1} are probably due to the mixing of NH bending, C—N stretching and C=S stretching vibrations, the band at 715 cm^{-1} having some contribution from NCS bending. A similar

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[22] D. T. Elmore, *J. Chem. Soc.* 3489 (1958).

[23] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano *J. Am. Chem. Soc.* **80**, 527 (1958).

[24] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.* **29**, 611 (1958).

[25] T. A. Scott Jr. and E. L. Wagner, *J. Chem. Phys.* **30**, 465 (1959).

[26] G. D. Thorn, *Can. J. Chem.* **38**, 1439 (1960).

[27] G. D. Thorn, *Can. J. Chem.* **38**, 2349 (1960).

[28] D. Hadzi, *J. Chem. Soc.* 847 (1957).

[29] W. Kutzelnigg and R. Mecke, *Spectrochim. Acta* **17**, 530 (1961).

assignment has been made in the case of thioformamide by DAVIES and JONES [30] for the bands at 1432 and 1287 cm^{-1}, who have rightly called them the asymmetric and symmetric NCS stretching vibration frequencies. The absorption bands reported by MARVEL *et al.* [31] for N-substituted thioamides may similarly be reassigned to the various mixed vibrations. In N-n butyl thioacetamide the bands at 1336, 1305, 1181, 1110 and 930 cm^{-1} are likely to be due to composite vibrations of NH bending, C—N stretching, C═S stretching, C—C stretching and CH_3—C stretching. In N-thioacetylpiperidine where there is no contribution from NH bending the spectrum seems to be slightly different [31]. In this molecule the highest composite vibration frequency occurs at 1284 cm^{-1} which probably has the greatest contribution from C—N stretching. The infrared bands of dithiooxamide [9, 25] may also be reinterpreted in terms of coupled vibrations [32]. The NH in-plane bending in the range 1503–1534 cm^{-1} assigned by MILLIGAN *et al.* [32] in substituted dithiooxamides is likely to have considerable contribution from C—N stretching. The recent assignments for the absorption bands of 2,5-dimercapto-1, 3,4-thiadiazole derivatives by THORN [26] should also be interpreted in terms of coupled vibrations. Similar assignments are possible for the recent infrared data on thiosemicarbazones [33].

The frequencies commonly found in a number of thioamides and similar derivatives have been presented in the form of a correlation diagram in Fig. 2. The systems included in the correlation are thioformamide [30], thioacetamide [4,29], dithiooxamides [9, 25, 32], 2,5-dimercapto-1,3,4-thiadiazoles [26], 2-mercapto-3,4-dimethylthiazole, thiozolidine-2-thione, tetramethylthiurammonosulphide [27], thiourea [4], thiosemicarbazides [2], thiohydantoins [22], tetrazolinethiones [2], guanylthioureas [3], 2-mercaptobenzthiazole [3] and thiosemicarbazones [33]. The correlation clearly shows that the three bands in the regions 940–1140 cm^{-1}, 1260–1420 cm^{-1} and 1395–1570 cm^{-1} are common to most of the systems.

MECKE *et al.* [5] assigned the C═S stretching frequency to the region 1050–1200 cm^{-1} in some cyclic thioamides. An examination of the charts reveals that there are several other strong bands in the 1300–1400 cm^{-1} region which may also be assigned to some coupled vibrations. SPINNER [13, 34] seems to feel that there is no vibrational mixing in the case of pyridthiones and related compounds and assigns the C═S stretching frequency in the vicinity of 1140 cm^{-1}, on the basis that it is the only strong band in the spectrum. An examination of his data* seems to indicate fairly strong bands in the three regions obtained in the correlation in Fig. 2 and it is felt that an exclusive assignment of the frequency for the localized C═S vibrations in these compounds is not clear cut.

CONCLUSIONS

As a result of these correlations it is possible to assign the range 1025–1225 cm^{-1}

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* Ref. 13 Appendix. Personal communication.

[30] M. DAVIES and W. J. JONES, *J. Chem. Soc.* 955 (1958).

[31] C. S. MARVEL, P. DE RADZITSKY and J. J. BRADER, *J. Am. Chem. Soc.* **77**, 5997 (1955).

[32] B. MILLIGAN, E. SPINNER and J. M. SWAN, *J. Chem. Soc.* 1919 (1961).

[33] P. W. SADLER, *J. Chem. Soc.* 957 (1961).

[34] E. SPINNER, *J. Org. Chem.* **23**, 2037 (1958).

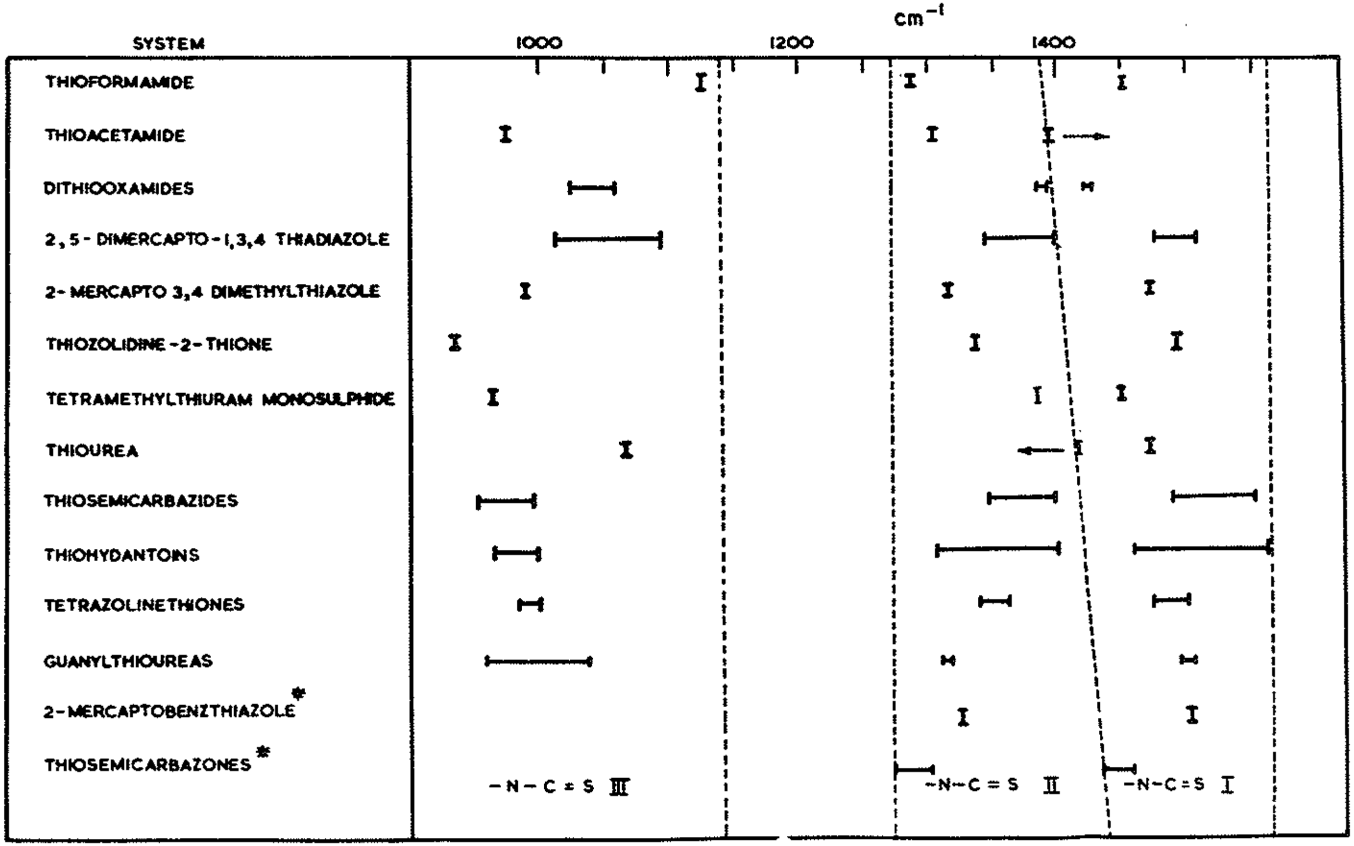

Fig. 2. The C═S stretching frequency in thiocarbonyl derivatives where the group is linked to one or two nitrogen atoms. The dotted lines represent the three distinct regions of the "—N—C═S absorptions".

* Data in the region 940–1140 cm^{-1} are not available for thiosemicarbazones, and it is difficult to make any specific assignment in the case of 2-mercaptobenzthiazole.

to the C=S stretching vibration in simple derivatives where there are no appreciable coupling effects (i.e. the thiocarbonyl group is linked to elements other than nitrogen). In compounds where the thiocarbonyl group is linked to one or two nitrogen atoms strong vibrational coupling effects are possible and the C=S vibration is not localized. However three bands seem to consistently appear in the regions 1395–1570 cm^{-1}, 1260–1420 cm^{-1} and 940–1140 cm^{-1} in these nitrogen-containing derivatives due to the mixed vibrations. These bands which may be tentatively designated as the "—N—C=S I, II and III bands" could be useful in qualitative analysis.

Acknowledgement—The authors are most grateful to Professor D. K. BANERJEE and Professor M. R. A. RAO for their keen interest in the work and to Dr. J. RAMACHANDRAN for his assistance in the early stages of the work.

Vibrational analysis of the n-paraffins—II. Normal co-ordinate calculations

J. H. SCHACHTSCHNEIDER and R. G. SNYDER
Shell Development Company, Emeryville, California

(*Received* 31 *May* 1962)

Abstract—Extensive normal co-ordinate calculations on the extended n-paraffins C_2H_6 through n-$C_{14}H_{30}$ and polyethylene have been carried out using a perturbation method programmed for the IBM 7090 which adjusts force constants for any number of molecules simultaneously. Our ability to fit some 270 fundamental frequencies to their observed values with an average error of 0·25 per cent lends strong support to our interpretation of the vibrational spectra of the n-paraffins. Our confidence in the correctness of our interpretation for the n-paraffins extends to polyethylene, whose spectrum we believe is now correctly assigned. These calculations have also led to normal co-ordinates and a thirty-five parameter valence force field for the n-paraffins. The valence force field has been compared to a Urey–Bradley force field derived from the same molecules, and some shortcomings of the Urey–Bradley field are apparent. Transferability of the force constants among the n-paraffins is excellent. The success of a calculation in which isobutane and neopentane were included with the n-paraffins suggests that this transferability may also extend to branched hydrocarbons.

INTRODUCTION

THIS is the second of two papers concerning the interpretation of the vibrational spectra of the n-paraffins and polyethylene and the evaluation of an intramolecular force field for them. In the first paper [1] we presented new infrared data and made vibrational assignments for the n-paraffins C_3H_8 through n-$C_{19}H_{40}$. In this paper we report on computer-programmed vibrational calculations on the n-paraffins, leading to confirmation of our earlier assignments [1], to normal coordinates and to force constants. Our computer program, devised for adjusting a set of force constants common to a group of related molecules to give simultaneously a least squares fit between observed and calculated frequencies for all molecules, allows us to take advantage of the large number of frequency data available for the n-paraffins and in consequence to compare the Urey–Bradley and the valence force fields, which are the ones currently most in use. To explore the question of force constant transferability between the n-paraffins and the branched paraffins, we included in some of the calculations isobutane and neopentane along with the n-paraffins.

A limited number of calculations on n-paraffins have appeared in the past. Valence force constants and normal co-ordinates for ethane have been evaluated by HANSEN and DENNISON [2] and the Urey–Bradley force field has been applied to ethane and polyethylene by SHIMANOUCHI and MIZUSHIMA [3,4]. In the present work we obtained the force constants by simultaneously fitting observed frequencies of C_2H_6, C_2D_6, C_3H_8, C_3D_8, n-C_4H_{10} through n-$C_{10}H_{22}$ polyethylene, iso-C_4H_{10}, iso-C_4D_{10},

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[1] R. G. SNYDER and J. H. SCHACHTSCHNEIDER, *Spectrochim. Acta* **19**, 85 (1963).
[2] G. E. HANSEN and D. M. DENNISON, *J. Chem. Phys.* **20**, 313 (1952).
[3] T. SIMANOUTI, *J. Chem. Phys.* **17**, 734 (1949).
[4] T. SIMANOUTI and S. MIZUSHIMA, *J. Chem. Phys.* **17**, 1102 (1949).

Reprinted, in part, from *Spectrochimica Acta*, Vol. 19, pp. 117 – 168, 1963. Pergamon Press Ltd.

neo-C_5H_{12} and neo-C_5D_{12}. Vibrational frequencies and assignments for C_3H_8 and the normal paraffins were taken from the previous paper [1]. In some cases the assignments reported there are a result of these calculations. Other frequencies and assignments are from the literature.

Computer Methods

Solution of the secular equation

The vibrational problem was set up in internal valence co-ordinates, R, using Wilson's [5,6] G-matrix method. The kinetic energy is given by

$$2T = \dot{R}'G^{-1}\dot{R} \tag{1}$$

and the potential energy by

$$2V = R'FR \tag{2}$$

In these co-ordinates the vibrational secular equation takes the familiar form

$$L^{-1}GFL = \Lambda$$

or

$$GFL = L\Lambda \tag{3}$$

where Λ is a diagonal matrix of the frequency parameters and L is the transformation from normal co-ordinates, Q, to internal co-ordinates

$$R = LQ \tag{4}$$

For the solution of the secular equation on a digital computer, we found it convenient to use a method previously suggested by Miyazawa [7]. Although the product GF is not symmetric, it can be diagonalized by diagonalizing two symmetric matrices. Consider the solution of

$$GA = A\Gamma \tag{5}$$

where A is the eigenvector matrix of G, and Γ is the diagonal matrix of the eigenvalues of G. Then we define a transformation

$$W = A\Gamma^{1/2} \tag{6}$$

and apply it to the F matrix; thus,

$$H = W'FW. \tag{7}$$

H is symmetric since A is orthogonal and Γ is diagonal. If we then diagonalize H, i.e. solve the secular equation

$$HC = C\Lambda \tag{8}$$

we can write

$$W'FWC = C\Lambda. \tag{9}$$

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[5] E. B. Wilson, Jr., *J. Chem. Phys.* **7**, 1047 (1939).

[6] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York (1955).

[7] T. Miyazawa, *J. Chem. Phys.* **29**, 246 (1958).

Multiplying equation (9) on the left by W we obtain

$$WW'FWC = WC\Lambda \tag{10}$$

and since

$$WW' = G \tag{11}$$

we have

$$GFWC = WC\Lambda \tag{12}$$

and comparing equations (3) and (12) we conclude that

$$L = WC. \tag{13}$$

This method of solving the secular equation has several advantages:

(1) The L matrix given by equation (13) is properly normalized.

(2) We can use the very fast machine methods, such as Jacobi's method, for diagonalizing the symmetric matrices G and H.

(3) Redundant co-ordinates need not be removed before diagonalizing G.

(4) The G matrix can be diagonalized by a separate program and the kinetic energy may be introduced into the molecular vibrational problem by means of equation (11).

(5) L^{-1} is easily obtained as

$$L^{-1} = C'\Gamma^{-1}W' \tag{14}$$

since

$$\Gamma^{-1}W' = \Gamma^{-\frac{1}{2}}A' = W^{-1}. \tag{15}$$

Evaluation of force constants

Force constants were evaluated using an iterative method described by King [8]. We have programmed this method for the IBM 7090 computer. Similar programs have been described by Curtis [9] and by Overend and Scherer [10], and we shall adopt the notation introduced by Overend and Scherer. By this method an initial set of force constants is refined to give a least-squares fit of the calculated frequencies to the observed frequencies. Corrections to the initial F_0 matrix are related to the frequency errors by

$$\Delta\lambda_i = \sum_k\sum_l (L_0)_{ki}(L_0)_{li}\Delta F_{kl} \tag{16}$$

where the $(L_0)_{ki}$ are the elements of the normal co-ordinate transformation for the zero-th order secular equation

$$GF_0L_0 = L_0\Lambda_0 \tag{17}$$

and $\Delta\lambda_i$ is the difference between the observed and calculated frequency parameter. The elements of the F matrix are not independent and a transformation [10] Z is defined such that

$$F_{kl} = \sum_j Z_{kl}{}^j\Phi_j{}^* \tag{18}$$

where the Φ_j are the independent valence force or Urey–Bradley force constants.

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* The coefficients $Z_{kl}{}^j$ can be defined so that the F_{kl} are the elements of the F matrix or the elements of the symmetrized F matrix.

[8] W. T. King. Dissertation, University of Minnesota (1956).

[9] E. C. Curtis. Dissertation, University of Minnesota (1959).

[10] J. Overend and J. R. Scherer, *J. Chem. Phys.* **32**, 1289 (1960).

Equations (16) and (18) are combined to give

$$\Delta\lambda_i = \sum_k \sum_l \sum_j (L_0)_{ki}(L_0)_{li} Z_{kl}{}^j \Delta\Phi_j. \tag{19}$$

The terms $\sum_k \sum_l (L_0)_{ki}(L_0)_{li} Z_{kl}{}^j$ may be considered as the elements, $(JZ)_{ij}$, of a matrix JZ of dimension $n \times m$ where n is the number of vibrational frequencies and m is the number of independent force constants in the assumed potential function. Equation (19) can then be written in matrix form as

$$\Delta\Lambda = JZ\Delta\Phi \tag{20}$$

where $\Delta\Lambda$ is a column matrix of the $\Delta\lambda_i$ and $\Delta\Phi$ is a column of the $\Delta\Phi_j$. If $n > m$ the weighted least-squares solution is given by

$$(JZ)'P\Delta\Lambda = (JZ)'P(JZ)\Delta\Phi \tag{21}$$

where P is a diagonal weighting matrix, usually taken as Λ^{-1}.

In the evaluation of a set of force constants for a series of molecules, it is desirable to combine the perturbation equations (20) for all of the molecules in the series. The size of the combined equations in addition to the space needed to store W, L and Z for each molecule put impossible demands on the amount of high-speed storage of even the largest digital computers. We have developed a technique by which only one molecule or factored block of a molecule need be considered at any one time in core storage.* This is accomplished by partitioning equation (20) thus

$$\begin{bmatrix} \Delta\Lambda_1 \\ \hdashline \Delta\Lambda_2 \\ \hdashline \cdot \\ \cdot \\ \cdot \\ \hdashline \Delta\Lambda_i \\ \hdashline \cdot \\ \cdot \\ \cdot \\ \hdashline \Delta\Lambda_v \end{bmatrix} = \begin{bmatrix} (J_1Z_1) \\ \hdashline (J_2Z_2) \\ \hdashline \cdot \\ \cdot \\ \cdot \\ \hdashline (J_iZ_i) \\ \hdashline \cdot \\ \cdot \\ \cdot \\ \hdashline (J_vZ_v) \end{bmatrix} \Delta\Phi \tag{22}$$

where $\Delta\Lambda_i$ and J_iZ_i are the matrices for a single molecule (or factored block). It can be shown that the normal equations for the combined molecules are given by

$$\sum_{i=1}^{v} (J_iZ_i)'P_i\Delta\Lambda_i = \sum_{i=1}^{v} (J_iZ_i)'P_i(J_iZ_i)\ \Delta\Phi. \tag{23}$$

By this means it is possible to consider a single molecule (or block) at a time in high-speed storage and to use magnetic tape for intermediate storage.

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* This method has also been suggested by OVEREND [11].

[11] J. OVEREND, *Ohio State Sympo. Molecular Structure Spectrosc., June* **1961**.

In the remaining 45 pages of this article, the authors set up the internal coordinates for normal paraffins, compare the valence force fields and Urey–Bradley force fields for these systems, and present the detailed assignments of the normal-mode frequencies. The paper concludes with the following summary:

SUMMARY

On the basis of almost complete vibrational assignments of fundamentals in the infrared spectra of the extended n-paraffins, C_3H_8 through n-$C_{19}H_{40}$, presented in the previous paper [1], computer-programmed normal co-ordinate calculations have been carried out. Some 270 fundamental frequencies of C_2H_6 through n-$C_{14}H_{30}$ together with polyethylene have been calculated simultaneously, with an average error of 0·25 per cent of the observed frequency, by a single thirty-five parameter valence force field. In addition, frequencies of C_2D_6 and C_3D_8 and the branched hydrocarbons, isobutane and neopentane together with the frequencies of the n-paraffins and polyethylene, for a total of 240 frequencies, were calculated with an average error of 0·7 per cent by a thirty-eight parameter force field. Thus the first calculation demonstrates the transferability of force constants among the n-paraffins and the second calculation suggests that this transferability extends as well to the branched hydrocarbons, especially since the larger error in this calculation is due primarily to the inclusion of the deuterated molecules. The larger errors in the calculated frequencies of the deuterated molecules reflect the fact that our force constants are weighted heavily in favor of the undeuterated molecules whose vibrational modes are known in general to be the more anharmonic and we are reminded again that our force constants have not been derived from harmonic frequencies.

Calculations on these same molecules using a Urey–Bradley force field were also carried out. A simple sixteen parameter Urey–Bradley force field failed badly to reproduce frequencies, though when this field was modified by including interactions between nearest neighbor and next-nearest neighbor methyl and methylene groups to give a total of thirty-one parameters, the average error became 1·4 per cent, to be compared with an average error of 0·7 per cent using the valence force field. A comparison of the thirty-eight parameter valence force field and the thirty-one parameter modified Urey–Bradley force field indicates that the deficiency in the latter is among the valence-angle-bending interaction constants centered on a methylene carbon atom; more precisely the introduction of these interactions in terms of a single parameter, the intermolecular tension, is too restrictive. We find that in order to achieve as good a frequency fit as with the valence force field it is necessary to include essentially as many parameters in the Urey–Bradley field as were used in the valence force field.

Our analysis of the vibrational spectra of the n-paraffins has led us to a virtually complete interpretation of their fundamental vibrations and to an understanding of the nature of normal modes themselves. The fact that we can calculate about 350 frequencies with an average error of about ½ per cent gives us considerable confidence that our interpretation is correct. This confidence extends to polyethylene whose spectrum we now believe to be assigned correctly.

Use of high-temperature pre-mixed flames in atomic absorption spectroscopy

M. D. Amos* and J. B. Willis†

(*Received* 12 *October* 1965)

Abstract—Pre-mixed flames having temperatures of about 2900°C may be produced by burning acetylene either with nitrous oxide or with oxygen–nitrogen mixtures. The performance of both types of flame in the atomization of metals for atomic absorption spectroscopy is fairly similar, though the acetylene–nitrous oxide mixture is more convenient and can be burned with greater safety at a long burner.

The new flames allow the addition of some 25 metals to the list of those that can be determined by atomic absorption spectroscopy. They possess the further advantage that they permit the determination of metals such as calcium, strontium, barium and molybdenum, which are only partially atomized in cooler flames, with higher sensitivity and greater freedom from chemical interference.

1. INTRODUCTION

IN DESCRIBING their work on the first application of atomic absorption spectroscopy to the determination of metals in solution RUSSELL *et al.* [1] wrote:

"At the present state of its development, by far the most serious difficulty in the absorption method is due to the difficulty in atomizing various elements. For example, highly oxidizable elements such as aluminium, silicon, hafnium, etc. are not atomized in the air–coal gas flame used in this work and are thus not detectable in absorption. Similarly, many other elements will not be completely atomized, thus decreasing the sensitivity and providing a serious obstacle to accurate absolute analysis".

In the intervening nine years the air–coal gas flame has been supplemented by the air–propane and air–acetylene flames and satisfactory methods of analysis have been worked out for some thirty metals. It is well recognized however that several elements, notably the alkaline earths, molybdenum and tin are only incompletely atomized‡ in these flames, while a number of others, such as aluminium, beryllium, titanium and vanadium are not atomized at all.

Apart from the work of ROBINSON [2], who atomized aluminium by spraying a solution into a spark discharge, efforts to atomize this latter group of metals

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* Sulphide Corporation Pty. Ltd., Boolaroo, N.S.W., Australia. Present address: Technical Representative, Techtron Pty. Ltd., Heathrow House, Bath Road, Cranford, Middlesex, England.

† Division of Chemical Physics, Commonwealth Scientific and Industrial Research Organization, Box 4331, G.P.O. Melbourne, Australia.

‡ Throughout this paper the word "atomization" will be used in its exact sense to mean "production of atoms" rather than in the colloquial sense meaning "production of a fine spray". The device used for spraying a solution into a flame will be referred to as a "nebulizer" rather than by the more usual term "atomizer".

[1] B. J. RUSSELL, J. P. SHELTON and A. WALSH, *Spectrochim. Acta* **8**, 317 (1957).

[2] J. W. ROBINSON, *Anal. Chim. Acta* **27**, 465 (1962).

Reprinted from *Spectrochimica Acta*, Vol. 22, pp. 1325 – 1343, 1966. Pergamon Press Ltd.

have mostly involved the use of direct-injection burners to aspirate solutions in organic solvents into an oxy-hydrogen or oxy-acetylene flame, and some success has been achieved in this direction, notably by FASSEL and MOSSOTTI [3], SLAVIN and MANNING [4], and DOWLING *et al.* [5]. However, since direct-injection burners are unpleasantly noisy in operation and in any case give tall narrow flames which are difficult to use efficiently in absorption work without the introduction of multipass optics, it is clearly desirable to develop pre-mixed flames having reasonably long light paths and using burners which can be fitted directly to the spray-chamber of a simple atomic absorption spectrophotometer.

The present paper describes the use of two types of flame meeting these requirements. Experiments on the determination of aluminium in the oxygen–nitrogen–acetylene flame have already been reported [6], and a preliminary account of the nitrous oxide–acetylene flame has recently appeared [7]. At the Third Australian Spectroscopy Conference (Sydney, 1961) [8] Mr. J. E. Allan reported that he was experimenting with the nitrous oxide–acetylene flame, but his experiments were abandoned because of the poor sensitivities obtained [9].

This paper does not give full details for the determination of each metal in practical types of sample, but it gives an idea of the sensitivities obtainable and discusses some of the phenomena observed during the use of these flames. For reasons of convenience the metals studied are classified into two groups: "refractory" metals, which form such stable oxides that they cannot be determined in the air–acetylene flame; and "borderline" metals, which can be determined in such a flame but are known to be incompletely atomized in it.

2. CHOICE OF FLAME

The chief difficulty in working with high-temperature pre-mixed flames, such as oxygen–hydrogen or oxygen–acetylene, is that they usually have high burning-velocities. This means that to prevent flash-back a high rate of gas flow through the burner port must be maintained, which in turn requires that the total area of the burner port must be small. Table 1 shows the characteristics of some high-temperature flames together with those of the low-temperature flames commonly used in atomic absorption work.

Although the oxygen–cyanogen flame appears attractive on account of its high temperature and relatively low burning-velocity, ROBINSON [13], using a direct-injection burner, was unable to detect absorption in it with aluminium, tantalum, or tungsten solutions. The difficulty of obtaining supplies of cyanogen, together with the hazards associated with the toxic and explosive nature of this gas, prevented any continuation of ROBINSON's work in the authors' laboratories.

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[3] V. A. FASSEL and V. G. MOSSOTTI, *Anal. Chem.* **35**, 252 (1963).

[4] W. SLAVIN and D. C. MANNING, *Anal. Chem.* **35**, 253 (1963).

[5] F. B. DOWLING, C. L. CHAKRABARTI and G. R. LYLES, *Anal. Chim. Acta* **28**, 392; **29**, 489 (1963).

[6] M. D. AMOS and P. E. THOMAS, *Anal. Chim. Acta* **32**, 139 (1965).

[7] J. B. WILLIS, *Nature* **207**, 715 (1965).

[8[R. A. DURIE, *Nature* **192**, 927 (1961).

[9] J. E. ALLAN, personal communication.

Table 1. Characteristics of flames suitable for atomic absorption spectroscopy

Gas mixture	Maximum flame speed, (cm sec^{-1})	Maximum temperature (°C)	References
Air–coal gas	*ca.* 55	1840	[10]
Air–propane	82	1925	[10]
Air–hydrogen	320	2050	[10, 11]
Air–acetylene	160	2300	[10, 11]
50% oxygen + 50% nitrogen–acetylene	640	2815	[11]
Oxygen–acetylene	1130	3060	[11]
Oxygen–cyanogen	140	4640	[10]
Nitrous oxide–acetylene	180	2955	[12]
Nitric oxide–acetylene	90	3095	[12]
Nitrogen dioxide–acetylene	160	?	[12]

Experiments with mixtures of pure oxygen and acetylene were carried out using a burner consisting of a single row of 25 holes of 0·61 mm internal diameter made by push-fitting lengths of hypodermic needle at 3 mm centres into a water-cooled brass block 8 mm thick, and fitted to an all-metal spray-chamber. Using a nebulizer consuming about 6 l/min oxygen and 5·5 l/min acetylene to give a fairly luminous flame, the absorbance obtained for an aqueous aluminium solution was only about 40 per cent of that obtained by AMOS and THOMAS [6] with a 30 × 0·46 mm slot burner and a flame produced by burning acetylene with a nitrogen–oxygen mixture containing 60 per cent oxygen. The risk of flash-back if the acetylene flow was reduced too far and the tendency of the burner holes to become clogged with particles of soot and salt caused this approach to be abandoned.

Supplies of nitric oxide and nitrogen dioxide were not readily available, but MANNING [14] has since found that the sensitivity for aluminium is about 60 per cent greater in the nitric oxide–acetylene than in the nitrous oxide–acetylene flame, so that further investigation of the use of nitric oxide may be worthwhile.

Thermodynamically the combustion process in the stoicheometric nitrous oxide–acetylene flame may be considered as

$$5N_2O \rightarrow 5N_2 + 5/2O_2 \; H_{298} = 101{\cdot}5 \text{ kcal}$$
$$C_2H_2 + 5/2O_2 \rightarrow 2CO_2 + H_2O(g) \; H_{298} = 300{\cdot}1 \text{ kcal},$$

i.e. the nitrous oxide decomposes to give a mixture of 33·3 per cent oxygen and 66·7 per cent nitrogen, with which the acetylene burns, the temperature of the flame being increased by absorption of the energy liberated by this decomposition.

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[10] R. MAVRODINEANU and H. BOITEUX, *Flame Spectroscopy*, Wiley, New York (1965).

[11] E. BARTHOLOMÉ, *Z. Elektrochem.* **54**, 169 (1950).

[12] W. G. PARKER and H. G. WOLFHARD, *Proc. Fourth Internat. Symp. Combustion*, 420 (1952); *Proc. Fifth Internat. Symp. Combustion*, 718 (1954).

[13] J. W. ROBINSON, *Anal. Chem.* **33**, 1067 (1961).

[14] D. C. MANNING, *Perkin–Elmer Atomic Absorption Newsletter* **4**, No. 4, p. 267 (1965), and personal communication.

3. EXPERIMENTAL

In each laboratory a Techtron AA-3 atomic absorption spectrophotometer* was used. The hollow-cathode tubes† were fed with stabilized current modulated at 100 c/s and the amplifier was modified by increasing the capacitor in the damping circuit from 150 to 500 μF. The level of fluctuation in the measurement of absorption was usually ±0·5 per cent or less. The Sirospec grating monochromator had a linear dispersion of 33 Å/mm at the exit slit, at which an R106 photomultiplier‡ tube was placed. The modifications to the atomizer and burner system in the two instruments are described below.

3.1 *The oxygen–nitrogen–acetylene flame*

The nebulizer, spray-chamber and burner were essentially similar to those described by Amos and Thomas and shown in Fig. 1 of their paper [6], the solid stainless steel burner having a slot of 30 × 0·46 mm. Cylinders of compressed oxygen–nitrogen mixtures were made up to order by a commercial supplier.

In operation the acetylene was turned on first and the flame lit, the flow of acetylene being increased to an amount found by experience to be somewhat in excess of that needed for final optimum operation with the oxygen–nitrogen mixture used. The oxygen–nitrogen mixture was then gradually turned on until the pressure at the nebulizer reached 14–15 psi and the acetylene flow was reduced until the desired flame was obtained. This was generally a somewhat fuel-rich flame with a blue cone about 3 mm high and a luminous incandescent "feather" 20–35 mm high, as shown in Fig. 1(a), though, as will be seen later, small variations are advantageous for certain elements. The operating pressure of gas in the spray-chamber was 15–20 cm of water so that the drain tube from the spray-chamber had to be immersed in water to at least this depth.

In turning off the flame the oxygen–nitrogen mixture was turned off first, and then the acetylene.

A safety screen was used to protect the operator in case of flash-back, but it should be noted that the equipment described was used for several months without misadventure.

3.2 *The nitrous oxide–acetylene flame*

The nebulizer was the adjustable one described by Davies *et al.* [15], though the standard Techtron nebulizer was also found suitable. The optimum rate of liquid uptake was usually between 2 and 4 ml/min. The Techtron spray-chamber, complete with the glass bead which breaks up the flow of the spray, was retained, but the tubular burner normally supplied with the AA-3 instrument was found unsuitable as it tended to warp with the heat generated by the high-temperature flame. It was replaced by a solid stainless-steel burner of the design shown in Fig. 2 and having a slot either 100 × 0·38 mm or 50 × 0·46 mm.

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* Techtron Pty. Ltd., 271 Huntingdale Road, East Oakleigh, Victoria, Australia.

† Atomic Spectral Lamps Pty. Ltd., 25 Islington Street, Collingwood, Victoria, Australia.

‡ Hamamatsu Television Co., Ltd., Hamamatsu City, Shizuoka Prefecture, Japan.

[15] D. A. Davies, R. Venn and J. B. Willis, *J. Sci. Inst.* **42**, 816 (1965).

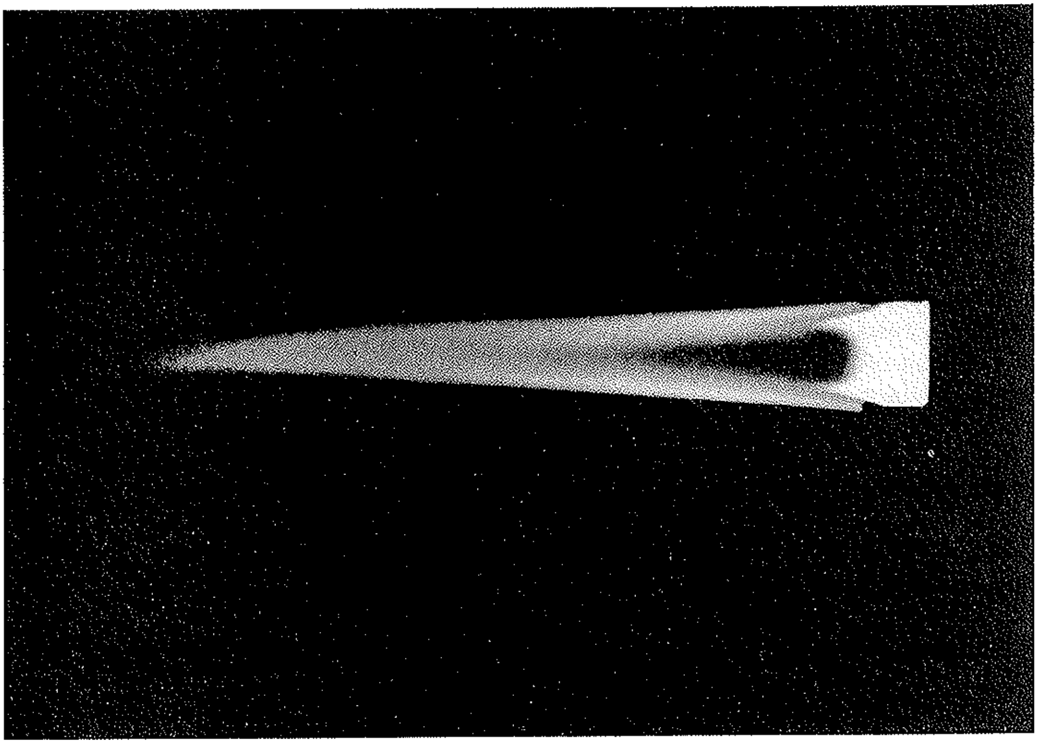

Fig. 1(a). Oxygen–nitrogen–acetylene flame.

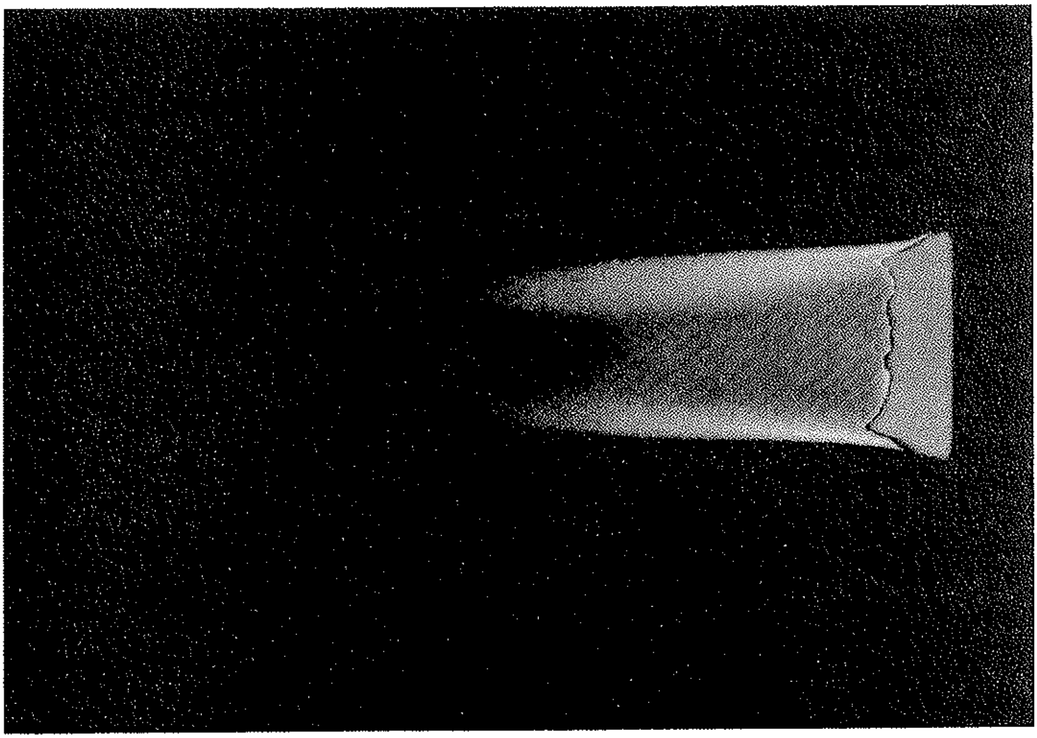

Fig. 1(b). Nitrous oxide–acetylene flame.

The cylinder of nitrous oxide* was fitted with a reducing valve to give a constant pressure of 50 psi, at which pressure the gas was fed to the Techtron gas control unit where it was regulated by the valve normally used for controlling the air-pressure.

In operation the acetylene was lit first and the flow adjusted to about 4 l/min after which the nitrous oxide was set to give a pressure of 15–20 psi at the nebulizer, corresponding to a flow of 6–7 l/min at atmospheric pressure. The acetylene flow was then adjusted to give the desired flame, which was generally somewhat fuel-rich, with a blue-grey cone 2–3 mm high and a 10–25 mm red "feather", as shown in Fig. 1(b). For some elements the flow of acetylene was best increased until the flame was appreciably luminous, while for a few it was reduced until the red "feather" almost disappeared. The temperature of the burner-top rose over the course of about 25 min to 190°C and remained steady at this temperature.

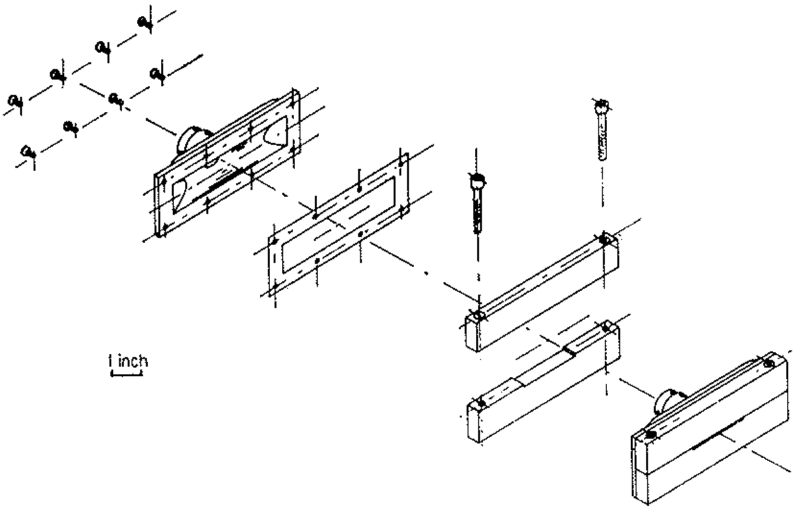

Fig. 2. Burner used for nitrous oxide–acetylene flame.

The operating pressure of gas in the spray-chamber was 3–5 cm water and so the drain tube from the spray-chamber was immersed to a depth of at least 5 cm in a beaker of water.

In extinguishing the flame either gas could safely be turned off first, though if an atomizer with a smaller nitrous oxide consumption were used it might be advisable always to turn off the nitrous oxide before the acetylene.

A mask having a 6 mm diameter circular opening was placed over the lens which focussed the flame on to the entrance slit of the monochromator, as restriction of the light beam to a limited area of the flame was found to increase the sensitivity slightly for many metals.

With most resonance lines lying above about 3000 Å the emission from the metal atoms in the flame gave rise to a small signal on the output meter. This

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* Liquid nitrous oxide was supplied in cylinders described as containing 1800 gal and costing in Melbourne $A20, i.e. £8 sterling. One cylinder lasted for 12–14 hr running.

noise signal was "backed-off" where necessary, but could be reduced or eliminated in most cases by increasing the hollow-cathode current. Since the resonance lines of most of the metals studied show little self-reversal, much higher currents than those used here could be employed without loss of sensitivity. Replacement of the broad-band amplifier with a tuned amplifier virtually eliminated this noise component of the flame emission.

4. EFFECT OF FLAME LENGTH

With low-temperature flames it is generally found that for a given nebulizer and spray-chamber lengthening the flame improves the absorption, at any rate up to a flame length of about 100 mm. With the high-temperature flames used in the present work this is not always true, and in fact for most metals the optimum flame length is relatively short. The oxygen–nitrogen–acetylene flame is difficult to burn safely at a long burner on account of its high burning-velocity, but with the nitrous oxide–acetylene flame, as mentioned earlier, a burner having a slot as large as 100 × 0·38 mm can be used. Table 2 shows the effect of burner length on the absorption of aqueous solutions of a number of metals in the nitrous oxide–acetylene flame. It will be seen that for tin, magnesium and chromium, all of which can be atomized fairly well in the air–acetylene flame, the two burners have roughly equivalent performance, but that for beryllium, which gives barely detectable absorption in the air–acetylene flame [16, 17], the absorbance is significantly greater with the shorter burner. For the remaining metals, which require a flame much hotter than air–acetylene to bring about any atomization at all, use of the shorter burner becomes increasingly advantageous. This is probably due to the excessive cooling at the edges of the long, thin flame produced by the 100 mm burner.† Experiments with aluminium solutions showed that reducing the length below 50 mm led to some loss of sensitivity, so all subsequent work using the nitrous oxide–acetylene flame was carried out with the 50 × 0·46 mm slot burner.

Table 2. Effect of burner length on absorption using the nitrous oxide–acetylene flame

			Absorbance*		
Metal	Concentration (μg/ml)	Resonance line (Å)	100 × 0·38 mm burner	50 × 0·46 mm burner	Ratio of absorbances
Sn	100	2246·1	0·201	0·187	1·07
Mg	1	2852·1	0·229	0·229	1·00
Cr	10	3578·7	0·237	0·240	0·99
Be	2	2348·6	0·315	0·360	0·87
Al	100	3092·7	0·155	0·432	0·36
Ti	100	3642·7	0·034	0·125	0·27
V	100	3184·0	0·073	0·273	0·27

* Light beam restricted by masking lens.

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† The experiments by Mr. J. E. ALLAN, mentioned earlier, were carried out with a burner having a slot of 120 × 0·25 mm.

[16] B. M. GATEHOUSE and J. B. WILLIS, *Spectrochim. Acta* **17**, 710 (1961).

[17] J. E. ALLAN, *Spectrochim. Acta* **18**, 259 (1962).

5. SENSITIVITIES FOR "REFRACTORY" METALS

5.1 *Method of investigation*

Several of the elements investigated have very complex emission (and absorption) spectra, and in general only those lines emitted fairly strongly by the hollow-cathode lamp were investigated. As found by ALLAN [18] for iron and manganese, the strongest lines in emission are not always the most sensitive in absorption, and it is quite possible, in any case, that the relative sensitivities of certain lines may vary a little from lamp to lamp.

With the oxygen–nitrogen–acetylene flame the optimum flame conditions, burner height, and lamp currents were determined for each metal, and using these optimum settings a re-appraisal was made of the most sensitive absorption lines. The sensitivity (concentration giving 1 per cent absorption) was then calculated from measurements on solutions producing an absorption of 10–20 per cent. This method, while not ideal, does provide a basis for comparison and is reasonably valid provided there are no excessive deviations from linearity in the absorbance-concentration curve.

With the nitrous oxide–acetylene flame essentially the same procedure was followed, but for each element a calibration curve was prepared, and the sensitivity was read from this.

Table 3 shows the sensitivities for metals forming refractory oxides, which cannot be atomized with the air–coal gas, air–propane or air–acetylene flames. It will be seen that in most cases the sensitivities obtained with the two high-temperature flames are fairly similar, and the difference may be largely due to differences in the nebulizers and spray-chambers of the two instruments. Using the same atomizer and burner (30 × 46 mm slot) very similar absorbances were obtained for aluminium with both flames.

The lines for study were chosen with the help of the tables of spectral lines and energy levels published by CORLISS and BOZMAN [19] and by MOORE [20]. For the rare earth metals the qualitative measurements of MOSSOTTI and FASSEL [21] were taken as a guide in the choice of lines. In general only those lines emanating from the ground state or from states close to it were investigated.

5.2 *Notes on individual elements*

5.2.1 *Beryllium.* With the air–acetylene flame this element is barely detectable [16, 17] but use of a high-temperature flame enables its determination with a sensitivity approaching that for magnesium. The beryllium resonance line, like that of magnesium, becomes appreciably self-absorbed as the hollow-cathode current is increased. It will be seen from Table 3 that with the oxygen–nitrogen–acetylene flame the use of 45 per cent rather than 60 per cent oxygen is advantageous, and in fact even 30 per cent oxygen allows the measurement of beryllium with good sensitivity. The effect of potentially interfering materials is discussed later.

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[18] J. E. ALLAN, *Spectrochim. Acta* 800 (1959).

[19] C. H. CORLISS and W. R. BOZMAN, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, N.B.S. Monograph No. 53 (1962).

[20] C. E. MOORE, *Atomic Energy Levels*, N.B.S. Circular No. 467 Vol. 3 (1958).

[21] V. G. MOSSOTTI and V. A. FASSEL, *Spectrochim. Acta* **20**, 1117 (1964).

5.2.2 *Aluminium.* Amos and Thomas [6] found that the presence of iron or of chloride ion partially suppressed aluminium absorption in the oxygen–nitrogen–acetylene flame, 20,000 μg/ml iron lowering the aluminium absorbance by 21 per cent and 0·5 N hydrochloric acid by 11 per cent. With the nitrous oxide–acetylene flame no effect could be detected with 0·5 N hydrochloric acid, while iron, added either as the chloride or sulphate, had a slight enhancing effect at the 10,000–30,000 μg/ml level. Similar results were found when using the same nebulizer and spray-chamber with both the oxygen–nitrogen–acetylene and nitrous oxide–acetylene flames, so that the discrepancy with the results of Amos and Thomas is obviously due to differences in the atomizing systems rather than in the nature of the flames.

5.2.3 *Cerium and thorium.* Mossotti and Fassel [21], using three passages of light from a continuous source through a row of three oxygen–acetylene flames burning at direct-injection burners, were unable to detect atomic absorption by ethanolic solutions of cerium salts. The spectrum of $\mathrm{Ce^{I}}$ does not seem to have been analysed in full, so it is not possible to identify with certainty those lines emanating from the ground state which might be expected to show absorption, but 25 of the stronger lines attributed to $\mathrm{Ce^{I}}$ and $\mathrm{Ce^{II}}$ were measured in the present work without any success. The only line showing detectable absorption was the unresolved triplet at 5200 Å, which showed about 1 per cent absorption with a solution containing 1000 μg/ml cerium.

No absorption was detected at any of the lines of $\mathrm{Th^{I}}$ emanating from the ground state for aqueous solutions of 1000 μg/ml in the oxygen–nitrogen–acetylene flame.

5.2.4 *The rare earths.* The rare-earth metals show partial ionization in the nitrous oxide–acetylene flame, and the sensitivities quoted in Table 3 can be improved somewhat by suppression of this ionization, as will be discussed later.

It is interesting that the sensitivities for the heavy rare-earths are considerably better than for the light ones, and this is fortunate, since the heavier earths are the more difficult to determine spectrophotometrically on account of the overlapping of absorption bands [22]. The atomic absorption technique should prove very valuable in the analysis of rare-earth mixtures, since no mutual interference is expected. Unfortunately, hollow-cathode lamps were not available for terbium or thulium, but there is evidence that both of these metals should show useful sensitivity in atomic absorption.

Skogerboe and Woodriff [23], using an oxygen–hydrogen flame as source and an oxygen–acetylene flame as the atomizing medium, found in ethanol solution a sensitivity for 1 per cent absorption of 2·3, 7, and 2 μg/ml for europium, thulium and ytterbium respectively. In the present work the sensitivities for europium and ytterbium in aqueous solution were found to be 1·8 and 0·25 μg/ml respectively (0·6 and 0·2 μg/ml if ionization was suppressed).

Ytterbium in the air–acetylene flame shows about half the absorption it does in the nitrous oxide–acetylene one, but the absorption in the former flame is almost completely suppressed by the addition of 1000 μg/ml potassium as chloride.

The only study made of possible chemical interference with the determination of the rare-earth metals was the measurement of dysprosium in solutions containing

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[22] D. C. Stewart and D. Kato, *Anal. Chem.* **30,** 164 (1958).

[23] R. G. Skogerboe and R. A. Woodriff, *Anal. Chem.* **35,** 1977 (1963).

Table 3. Sensitivities (μg/ml in aqueous solution) for 1% absorption

Metal	Wavelength Å	Oxygen–nitrogen–acetylene Lamp current (mA)	Spectral slit width (Å)	Sensitivity 45% oxygen	Sensitivity 60% oxygen	Notes	Nitrous oxide–acetylene Lamp current, (mA)	Spectral slit width (Å)	Sensitivity	Notes
Be	2348·6	10	1·7	0·033	0·035	*a*	6	3·3	0·024	*d, f*
B	2497·7	10	3·3	200	90	*b*	20	0·8	50	*c, g*
	2496·8			350	150				100	*c, g*
Al	3092·7	10	1·7	1·0	0·7	*a*	11	3·3	1·0	*d, f*
	3961·5			1·3	0·9				1·2	*d, f*
	3082·2			1·4	1·0					
	3944·0			2·0	1·4					
	2373·4			3·3	2·3					
	2367·1			4·0	2·8					
	2575·4			8·8	6·1					
Sc	3911·8						10	2·5	0·8	*d, f*
	3907·5								1·1	*d, f*
	4023·7								1·2	*d, f*
	4020·4								1·7	*d, f*
	3269·9								2·8	*d, f*
Y	4102·4						16	3·3	5·0	*d, h*
	4128·3								5·4	*d, h*
	4077·4								5·7	*d, h*
	4142·9								11	*d*
La	3574·4						33	1·7	110	
	3927·6								280	
	4037·2								280	
Pr	4951·4						40	1·7	72	*c, h*
	5133·4								92	*c, h*
	4736·7								140	*c*
Nd	4634·2						40	1·7	35	*c, h*
	4896·9								48	*c, h*
	4719·0								72	*c, h*
Sm	4296·7						40	1·7	21	*d, h*
	4760·3								29	*d, h*
Eu	4594·0						9	3·3	1·8	*e, h, m*
							14		2·4	*e, i, m*
	4627·2								3·0	*e, i, m*
	4661·9								3·0	*e, i, m*
	3111·4								16	*e, i, m*

Gd	3684·1						40	0·8	38	*d, i*
	4078·7								42	*d, h*
	3783·1								46	*d, h*
	4058·2							1·7	51	*d, h*
Dy	4211·7						13	1·7	1·5	*d, h*
							30		1·7	*d, i*
	4194·9						30		3·4	*d, i*
Ho	4103·8						17	3·3	2·2	*c, i*
	4053·9								2·8	*c, i*
	4163·0								3·5	*c, i*
	4254·4								85	*c*
Er	4008·0						12	1·7	1·4	*d, i*
	3862·8						35		2·3	*d, i*
	3892·7						12		4·5	*d, h*
Yb	3988·0						10	3·3	0·25	*e, i*
	3464·4								0·8	*e, h*
	2464·5								1·6	*e, i*
	2672·0								10	
Lu	3359·6						16	1·7	12	*d, i, k, n*
	3312·1							3·3	21	*d, i, k*
	3567·8							1·7	27	*d, i, k*
Si	2516·1	15	3·3	33	10	*b*	12	1·3	2·5	*f, g, l*
	2514·3			40	12					
	2519·2			50	15					
	2506·9			80	25					
	2528·5			80	25					
	2524·1			120	35					
Ge	2651·6	15	3·3	5·5	6·5	*a*	10	3·3	1·5	*c, f*
	2592·5			12	15					
	2754·6			16	20					
	2709·6			18	22					
	2691·3			35	40					
Ti	3642·7	15	3·3	3·3	3·0	*b, j, k*	20	3·3	3·5	*c, f, j*
	3653·5			3·3	3·0				3·5	
	3354·6			3·5	3·2					
	3199·9			3·8	3·5					
	3635·5			4·1	3·7				4·8	
	3998·6			5·0	4·6				6·5	
	3341·9			5·3	4·8				6·7	
	3753·6			6·4	5·8					
	3752·9			6·4	5·8					
	3741·1			6·8	6·2					
	3371·5								7·2	

Table 3 (Cont.)

Metal	Wavelength (Å)	Oxygen–nitrogen–acetylene Lamp current (mA)	Oxygen–nitrogen–acetylene Spectral slit width (Å)	Oxygen–nitrogen–acetylene Sensitivity 45% oxygen	Oxygen–nitrogen–acetylene Sensitivity 60% oxygen	Oxygen–nitrogen–acetylene Notes	Nitrous oxide–acetylene Lamp current, (mA)	Nitrous oxide–acetylene Spectral slit width (Å)	Nitrous oxide–acetylene Sensitivity	Nitrous oxide–acetylene Notes
Zr	3601·2	15	3·3	20	18	*b, j, k*	15	3·3	15	*c, f, j*
	3519·6			22	20					
	3011·8			34	30					
	3863·9			44	39					
	3547·7			50	43					
	3623·9			50	45					
	3029·5			65	58					
	2985·4			72	65					
	3890·3			72	65					
	3509·3			87	78					
Hf	3072·9	15	3·3	33	25	*b, j, k*	15	3·3	14	*c, g, j*
	2866·4			40	30					
	2898·3			95	70					
	2964·9			105	80					
	3682·2			105	80					
	2950·7			130	100					
	3020·5			145	110					
	2904·8			200	150					
	2940·8			200	150					
	3777·6			200	150					
V	3184·0	16	3·3	4	2	*b, k*	20	6·6	1·5	*c, f*
	3185·4			5	2·5					
	3183·4			5	2·5					
	3066·4			15	8				4·0	*c, f*
	3703·6			17	9					
	3840·8			25	12					
	4379·2			35	18					
	3855·8			35	18					
	4384·7			50	25					
	4390·0			50	25					
Nb	3580·3	20	1·7	30	27	*b, k*	11	1·7		
	3349·1			30	27				24	*c, i*
	4079·7			36	32					
	4058·9			41	36					
	4123·8			44	40					
	4100·9			47	42					
	3358·4			47	42					
	3726·2			60	55					
	3791·2			73	66					
	3342·0			73	66					

Ta	2714·0	16	3·3	36	30	*b, j, k*	15	3·3	11	*c, f, j*
	2608·6			70	58					
	2775·9			70	58					
	2559·4			80	70					
	2647·5			110	90					
	2661·3			140	120					
	2758·3			140	120					
W	2551·4	15	3·3	19	17	*b, k*	33	0·8	5·3	*c, i*
	2681·4			22	19					
	2724·4			30	26					
	4008·8			31	28					
	2947·4			33	30				18	*c, f*
	2831·4			38	35					
	2896·0			48	44					
	2656·5			52	47					
	2718·9			55	49					
	4074·4			74	66					
	2944·4								12	*c, i*
U	3584·9						30	0·8	120	*d, i, k*
	3514·6								300	*d, i, k*
	3489·4								325	*d, i, k*
	3466·3								800	*d, i, k*
Re	3460·5						10	3·3	12	*c*
	3464·7								20	
	3451·9								33	

a Fuel-rich flame, feather 25–40 mm high, light beam 4–8 mm above burner top.
b Slightly fuel-rich flame, feather 20–30 mm high, light beam 4 mm above burner top.
c Fuel-rich flame, feather approximately 30 mm high and becoming luminous.
d Slightly fuel-rich flame, feather approximately 20 mm high.
e Fairly lean flame, feather approximately 5 mm high.
f Calibration curve straight.
g Calibration curve flattens somewhat at high concentrations.
h Calibration curve bends upwards at high concentrations.
i Calibration curve slightly sigmoid.
j Measured in 2% HF solution.
k Only the most sensitive lines listed.
m Addition of potassium (1000 μg/ml) increases the sensitivity about three-fold and straightens the calibration curve.
n Strong flame emission at this wavelength makes use of a tuned amplifier desirable.

sulphuric or phosphoric acids. In these solutions an enhancement of the dysprosium absorption was found relative to the value in solutions containing dysprosium chloride alone, and amounted to about 12 per cent in the presence of 0·1 N sulphuric or 0·07 N phosphoric acid.

5.2.5 *Germanium.* Though this element shows slight absorption in a rich air–acetylene flame (sensitivity *ca.* 120 μg/ml for 1 per cent absorption) and somewhat greater sensitivity in the air–hydrogen one, use of a high-temperature flame is necessary to achieve adequate sensitivity for analytical purposes.

5.2.6 *Titanium, zirconium, hafnium and tantalum.* These metals show interferences in the presence of hydrofluoric acid and iron which are of importance from both theoretical and practical points of view, and are typified by the figures for titanium shown in Table 4.

Table 4. Effect of hydrofluoric acid and iron on titanium absorption in the oxygen–nitrogen–acetylene flame (60% oxygen)

Solution	Sensitivity for 1% absorption at 3642·7 Å (μg/ml)
Ti in 0·02% HF	4·5
Ti in 2% HF	3·0
Ti in 4% HF	2·9
Ti in 6% HF	2·9
Ti in 2% HF + 0·2% Fe^{3+}	1·4
Ti in 2% HF + 0·4% Fe^{3+}	1·3
Ti in 2% HF + 1% Fe^{3+}	1·3
Ti in 4% HF + 1% Fe^{3+}	1·3
Ti in 6% HF + 1% Fe^{3+}	1·3

Zirconium, hafnium and tantalum show the same type of behaviour, the sensitivity increasing two-fold by addition of 1 per cent iron to a solution of the metal in 2 per cent hydrofluoric acid. Since these metals are normally brought into solution by use of hydrofluoric acid, their sensitivities are quoted in Table 3 as those found in 2 per cent solutions of this acid.

Enhancement of the absorption of these four metals by hydrofluoric acid and iron is also found with the nitrous oxide–acetylene flame, though its magnitude is considerably less.

The explanation for this behaviour is probably as follows: A solution of a simple salt of, say, titanium, when sprayed into the flame, is very quickly decomposed to form TiO molecules, which in the high temperature environment react with atomic carbon to produce titanium atoms through the reaction $TiO + C \rightleftharpoons Ti + CO$. In the presence of fluoride it may well be that the titanium forms a stable complex fluoroacid which inhibits the formation of TiO but is more readily decomposed at high temperatures to yield a higher population of atoms in the flame. Further, when both fluoride ions and a second cation are present the formation of an even more stable double fluoride may increase this effect. The differences in magnitude of these enhancements in the two types of high-temperature flame used may reflect differences in both the atomization conditions and the chemical reactions proceeding in the flames.

The enhancements are controllable, as they reach limiting values at practically useable concentrations and consequently represent a useful method of improving the detection limits for these four metals. However, much more extensive investigation is required before the practising analytical chemist can determine these elements in a routine fashion by atomic absorption methods.

6. "BORDERLINE" ELEMENTS

There are several metals which can be determined in the air–acetylene flame, but which are obviously far from being completely atomized under these conditions. The degree of absorption is critically dependent on the exact composition of the air–acetylene mixture and on the region of the flame in which the absorption is measured [16, 24], and there is a marked tendency for the metal to undergo chemical interferences. Magnesium, though suffering from interference by aluminium, is normally well atomized in the air–acetylene flame, and the sensitivity is actually greater than in hotter flames. The other elements in this group, however, show improved absorption in the oxygen–nitrogen–acetylene or the nitrous oxide–acetylene flame, and the absorption is no longer so dependent on flame conditions. Table 5 shows the sensitivities for these metals in the air–acetylene and nitrous oxide–acetylene flames.

Table 5. Sensitivities (μg/ml in aqueous solution for 1% absorption) for "borderline" metals

Metal	Wavelength (Å)	Air–acetylene 50 × 0·46 mm burner	Nitrous oxide–acetylene 50 × 0·46 mm burner	Air–hydrogen 100 × 0·51 mm burner
Mg	2852·1	0·01	0·02	
Ca	4226·7	0·13	0·03*	
Sr	4607·3	0·2*	0·06*	
Ba	5535·5	10	0·4*	
Mo	3132·6	0·7	0·4	
Sn	2246·1	4†	2·5	1
	2354·8	4†	2	1·5
	2863·3	4†	2·5	1

* Ionization suppressed by addition of KCl.
† 100 × 0·51 mm slot burner used.

ALLAN [9] has found the air–hydrogen flame, in spite of its lower temperature, to be more effective than the air–acetylene one in atomizing tin, and for purposes of comparison sensitivities measured with this flame are included in Table 5. Air–hydrogen mixtures can safely be burned at a solid stainless steel burner with a 100 × 0·51 mm slot; indeed a slot as wide as 0·76 mm can be used if an auxiliary air supply to the spray-chamber is provided while lighting and shutting off the

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[24] C. S. RANN and A. N. HAMBLY, *Anal. Chem.* **37**, 879 (1965).

flame. In the air–hydrogen flame, however, tin is subject to interferences: the absorbance of a 100 μg/ml solution of tin was reduced about 15 per cent by the presence of 5000 μg/ml sodium (as sodium hydroxide), whereas no interference was observed for the same solution in the air–acetylene flame.

It will be observed from Table 5 that for tin the relative sensitivities of the different lines vary with the type of flame. This has also been noticed by Allan [9] and is attributable to the fact that the population of tin atoms in the $^3P_1$ energy level 1692 cm^{-1}, from which the 2354·8 Å line arises, relative to that in the $^3P_0$ ground state, from which the other two lines arise, is significantly greater at 2900°C than at 2300°C. The values of N_{1692}/N_0 for 2050°, 2300° and 2955°C are calculated to be 1·05, 1·16 and 1·40 respectively.

6.1 *Ionization in the flame*

Calcium, strontium, barium, yttrium, the rare-earth metals and uranium measured in the nitrous oxide–acetylene flame give calibration curves showing a distinct curvature *away* from the concentration axis. This curvature can usually be removed by addition of excess of a potassium or caesium salt, and Fig. 3 shows this effect for calcium. Figure 4 shows the calibration curve for ytterbium, which is slightly sigmoid, owing to the superposition of the curvature just mentioned with the curvature in the opposite sense due to self-absorption of the resonance line in the hollow-cathode discharge.

This behaviour suggests that at the temperature of the nitrous oxide–acetylene flame the alkaline earth and rare-earth metals are appreciably ionized, and that this ionization can be suppressed by addition of an excess of the salt of a more easily ionized metal such as potassium (ionization potential 4·3 eV) or caesium

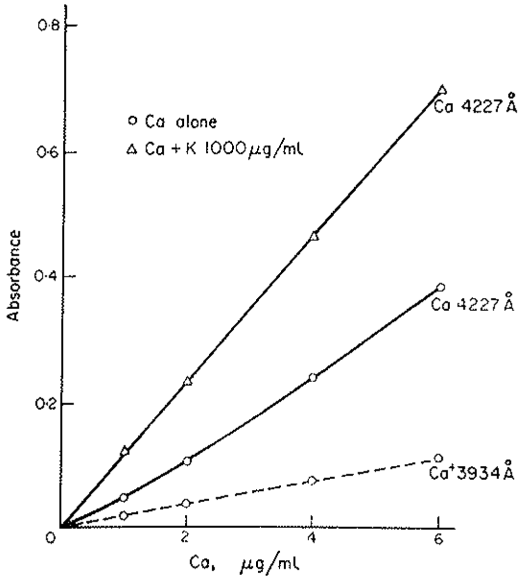

Fig. 3. Ionization of calcium in the nitrous oxide–acetylene flame.

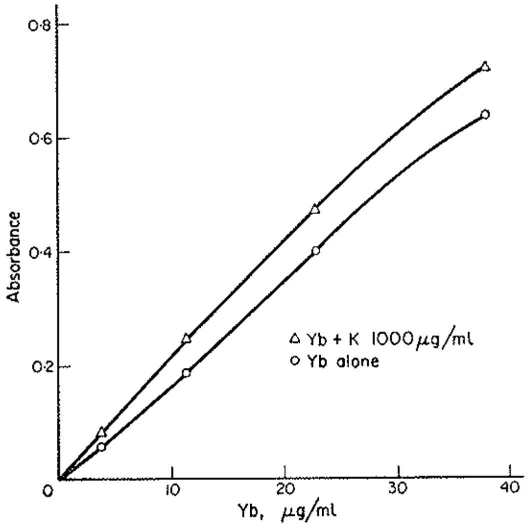

Fig. 4. Ionization of ytterbium in the nitrous oxide–acetylene flame.

(3·9 eV), the high concentration of electrons formed in the reaction

$$K \rightarrow K^+ + e^-$$

tending to reverse the reation

$$Ca \rightarrow Ca^+ + e^-.$$

The presence of metal ions in the flame and their removal by addition of a potassium or caesium salt can be demonstrated by measurement of the absorption of the resonance line of the ion, as shown in Fig. 5. It will also be seen that as the extent of the ionization increases its suppression by a given concentration of potassium becomes less complete. Strontium is already known [25] to undergo appreciable

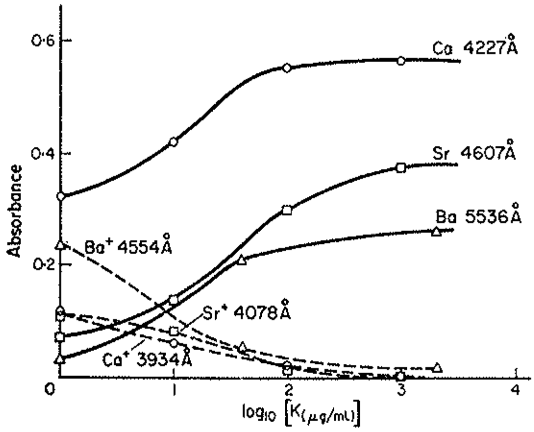

Fig. 5. Effect of increasing amounts of potassium on the absorption of calcium (5 µg/ml), strontium (5·5 µg/ml) and barium (30 µg/ml) in the nitrous oxide–acetylene flame.

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[25] D. Trent and W. Slavin, *Perkin-Elmer Atomic Absorption Newsletter* No. 22, July (1964).

Table 6. Approximate extent of ionization in flames, (%)

Metal	Ionization potential, (eV)	Concentration, (μg/ml)	Air–acetylene flame	Nitrous oxide–acetylene flame
Be	9·32	2	*	0
Mg	7·64	2	0	6
Ca	6·11	5	3	43
Sr	5·69	5·5	13	84
Ba	5·21	30	0†	88
Yb	6·2	15	‡	20

* No appreciable atomization.
† Atomization very inefficient.
‡ Potassium chloride suppresses absorption almost completely.

ionization in the air–acetylene flame, and the present work shows that the ionization of the alkaline earth-metals is of major importance when determining them with a high-temperature flame. Table 6 shows the approximate extent of ionization of several metals in air–acetylene and nitrous oxide–acetylene flames.

6.2 *Interferences*

Apart from increasing the sensitivity for "borderline" metals, use of a high-temperature flame diminishes or completely removes many of the well-known chemical interferences associated with the determination of these metals by atomic absorption spectroscopy.

Preliminary investigations with the oxygen–nitrogen–acetylene flame, using both 45 per cent and 60 per cent oxygen, were carried out on solutions of beryllium (2 μg/ml), magnesium (2 μg/ml), calcium (5 μg/ml), strontium (5 μg/ml) and barium (50 μg/ml) in the presence of 100 μg/ml each of silicon, phosphorus and aluminium. The results indicated that:

(1) In all parts of the oxygen–nitrogen–acetylene flame interferences are considerably less than in the air–acetylene flame.

(2) To obtain complete freedom from interference the light path must be 5–15 mm higher in the flame than the position in which optimum sensitivity is found. This suggests that the formation of free atoms in the flame is a more complicated process than the mere dissociation of a refractory compound.

Some of these effects were studied in greater detail using the nitrous oxide–acetylene flame. The absorption of 2 μg/ml of beryllium was found to be completely unaffected by the presence of 2·5 N sulphuric acid, while 1000 μg/ml of phosphorus, added as phosphoric acid, produced a very slight (*ca.* 2 per cent) enhancement of the absorption. Aluminium, in concentrations up to about 50 μg/ml had no effect, but a concentration of 500 μg/ml produced a 10 per cent depression of the absorbance.

Figure 6 shows that aluminium, added as the sulphate, while suppressing magnesium absorption very strongly in the air–acetylene flame actually *enhances* it by 10–20 per cent in the nitrous oxide–acetylene one. This effect is not specific for aluminium, however, as corresponding concentrations of potassium chloride cause a similar, though smaller, enhancement.

Figure 7 shows likewise that phosphorus, added as phosphoric acid, at high concentrations enhances calcium absorption in the nitrous oxide–acetylene flame.

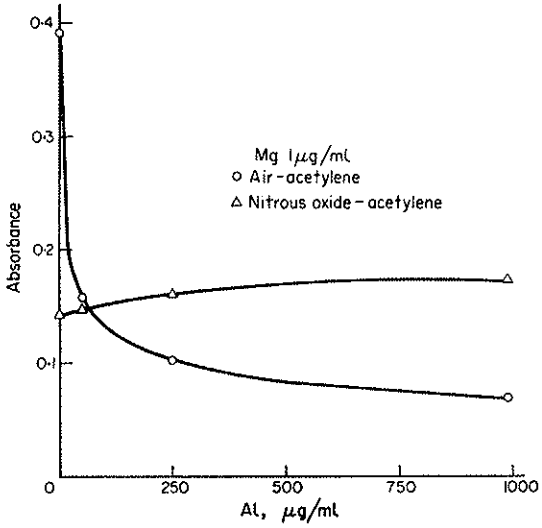

Fig. 6. Effect of aluminium on magnesium absorption in the air–acetylene and nitrous oxide–acetylene flames.

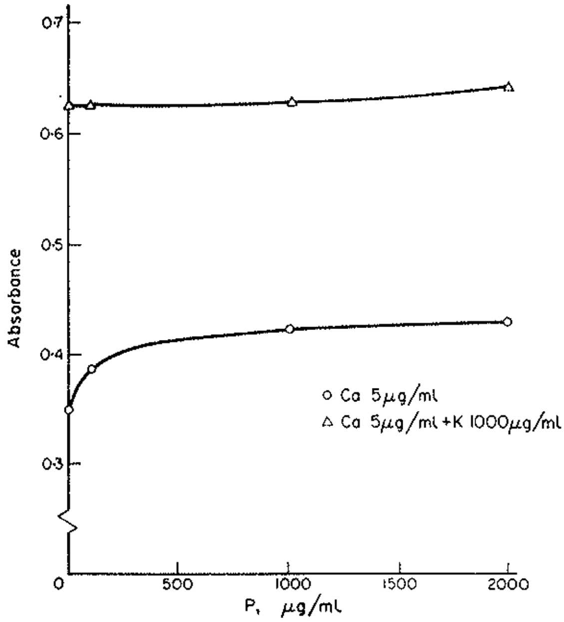

Fig. 7. Effect of phosphorus on calcium absorption in the nitrous oxide–acetylene flame.

Much of this enhancement is apparently due to a reduction in the extent of ionization of the calcium in the presence of phosphorus, as when ionization is completely suppressed by addition of excess potassium chloride the effect almost disappears. It is interesting to note that WENDT and FASSEL [26] have very recently observed a similar slight enhancement of calcium absorption by phosphorus and by aluminium when the solution is sprayed into an induction-coupled plasma.

While these enhancement effects are very slightly greater in a lean flame than in a rich one it can be said that with the nitrous oxide–acetylene flame, unlike the air–acetylene one, interference with the determination of the alkaline earth-metals is negligible, irrespective of what part of the flame is used.

7. CONCLUSIONS

With the new flames described here the total number of metals for which useful atomic absorption has been observed is brought to more than sixty, and the problems of chemical interference when determining the alkaline earth-metals have been largely overcome.

Ionization of a number of metals is observed in these flames, and methods of overcoming it have been developed. Loss of neutral atoms through ionization would probably limit the usefulness of flames or plasma jets of even higher temperature for analytical atomic absorption measurement.

Though the performance of both high-temperature flames is fairly similar, the authors recommend the use of the nitrous oxide–acetylene one for routine analytical work, as the need for supplies of special oxygen–nitrogen mixtures is avoided and this flame should be safe in the hands of relatively unskilled operators. The burner described here for use with the nitrous oxide–acetylene flame should be suitable for use with most commercial atomic absorption instruments, and it can, if necessary, be used as a "universal" burner, since it gives good sensitivity also with air–acetylene and air–coal gas mixtures.

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[26] R. H. WENDT and V. A. FASSEL, *Anal. Chem.* **38**, 337 (1966).