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ABSORPTION SPECTRA OF MOLECULAR IONS

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SVMMARIVM — Spectra absorpsionis molecularium ionum N_2^+,CO^+,CO_2^+, primum observata sunt in rapidis electricis ictibus in N_2, CO et CO_2. Iidem autem ictus in CH_4 ostendunt, sive in absorpsionis sive in emissionis spectro, novam simplicem quamdam striam, quod fieri potest ut causam habeat in ione C_2, quamquam id certo probari nondum potest.

A. INTRODUCTION

The investigations which I should like to describe here were stimulated by an astrophysical problem: the nature of the diffuse interstellar lines.

When the spectra of distant stars are studied one finds a few very sharp lines which do not belong to the star but have been definitely assigned to absorption by the interstellar medium: they are due to atoms and atomic ions (Na, K. Ca, Ca^+, Fe, Ti^+) and to diatomic molecules and molecular ions (CH, CH^+, CN, OH). There is no question about the identification of these sharp lines. In addition, however, a number of diffuse lines have been found of which the broad feature at 4430 Å

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is the best known example. According to the most recent work of HERBIG (1967) 27 diffuse lines are now known, ranging in width from 0.5 to 20 Å. None of these diffuse features has been identified.

While almost all astronomers believe that in some way these diffuse lines are due to the interstellar dust (without being able to give a specific identification), I have taken the view (HERZBERG, 1955, 1965, 1967) that they may be due to the interstellar gas since molecules, particularly polyatomic molecules, can exhibit diffuse absorption lines when there is a strong predissociation or pre-ionization. The question is only to find the right molecule.

In view of the large preponderance of hydrogen in the interstellar medium a molecule containing mostly H or only H seems to be the most likely candidate. On this basis, and considering a large number of conceivable identifications, I came to the conclusion that the molecular ions H_3^+ and CH_4^+ presented likely possibilities. I decided therefore to see whether absorption spectra of these and other ions could be obtained in the laboratory.

While emission spectra of diatomic molecular ions have been known for many years, no absorption spectra of any molecular ions had been observed in the laboratory when our work was started. The only known absorption spectrum of a molecular ion was that of CH^+, which is observed in the interstellar medium.

B. APPARATUS

It was clear from the beginning that molecular ions could only be observed in absorption in electric discharges. It was soon found that when the absorption spectra of DC discharges were studied no absorption of molecular ions was obtainable, even when the light of the source was sent through the discharge tube up to 60 times. The reason is that the concentration of molecular ions in DC discharges is not sufficient to record an absorption spectrum. We therefore turned to the study of the absorption spectra of flash discharges. In such flash discharges the instantaneous ion concentration is very much higher than in continuous discharges, and therefore one can hope to obtain a sufficient concentration to observe absorption. After a few initial difficulties we did obtain some of the well-known molecular ions in absorption. Fig. 1 shows absorption spectra obtained in discharges through nitrogen and mixtures of helium and carbon monoxide and carbon dioxide. The strongest absorption spectrum was obtained with nitrogen, namely, the very familiar N_2^+ bands at 3914 Å, which are also prominent in emission in the spectrum of the aurora. The observed intensities are in reasonable agreement with those predicted on the basis of the known f-values. Unfortunately, in spite of a good deal of searching we were unable to find any other spectra of N_2^+, CO^+, and CO_2^+ in other spectral regions.

C. Absorption spectra of flash discharges in CH_4

In line with my original suggestion we then started to investigate flash discharges in CH_4 with the aim of obtaining absorption spectra of CH_4^+, and also of CH_3^+, CH_2^+, and CH^+. Only in the case of CH^+ did we know definitely where to look because the emission spectrum of CH^+ is well-known in the laboratory and, as previously mentioned, CH^+ also appears in absorption in the interstellar medium. However, in spite of a good deal of experimentation with different pressures, different discharge energies and different gas mixtures, we were unable to observe the CH^+ spectrum in absorption. Similarly, the search for an absorption at the positions of the diffuse interstellar lines on the assumption that they are due

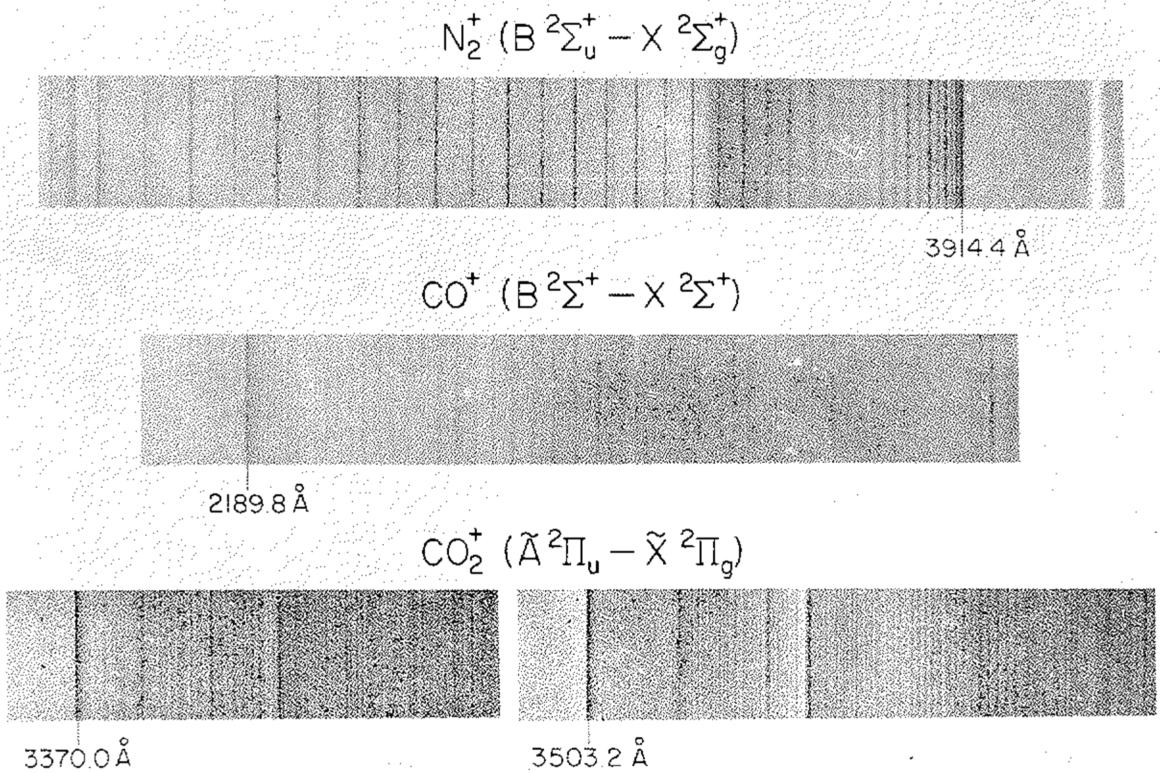

FIG. 1 — Absorption spectra of N_2^+, CO^+ and CO_2^+

These spectra were obtained with an absorption tube of 1 m length filled with (*a*) N_2, (*b*) a 20:1 He-CO mixture, (*c*) a 10:1 He-CO_2 mixture of 3 mm pressure through which a condensor of 1 μF charged to 10000 volts was discharged. The continuous background was supplied by a flash through a capillary tube filled with argon. The spectra were taken in the second order of a 3 m grating spectrograph.

to CH_4^+ has proved to be unsuccessful up to now. Nor have other spectra that could be assigned to the ions just mentioned or to CH_2^+ and CH_3^+ been observed in the visible, ultraviolet or vacuum ultraviolet regions.

However, under certain conditions a new and extremely simple band spectrum of the type $\Sigma - \Sigma$ was observed in absorption in discharges through CH_4 in the region 4800-5700 Å. (HERZBERG and LAGERQVIST, 1968). The 0 – 0 band of this system is at 5416 Å; it is shaded to the violet. There is no question that the new spectrum is due to a diatomic molecule; indeed, the absence of alternate lines in the branches, as well as the shifts obtained when $C^{12}H_4$ was replaced by $C^{13}H_4$, showed conclusively that the carrier of the new spectrum must contain two, and only two, carbon nuclei. It thus appeared at first that all we had done was obtain a new spectrum of the C_2 molecule for which already a considerable number of band systems are known.

There are, however, a number of difficulties with this assignment: neither the upper nor the lower state is a known state of C_2. Moreover, it seems impossible to find a reasonable interpretation of the new states among the expected but not yet observed states of C_2. The alternative would be that the new spectrum belongs to a C_2 ion, either positive or negative, and such ions were, of course, the aim of our investigation. A serious difficulty with this interpretation is that both the C_2^+ and the C_2^- ion would have to have doublet spectra, while the observed spectrum appears to be a singlet spectrum. It is, however, possible in such a simple spectrum that, since the expected splitting of the lines is the difference of the splittings of the upper and lower states, the doublet splitting is very small. Indeed we did observe that at high rotational quantum numbers the lines appear to broaden, suggesting an incipient doublet splitting. At any rate the arguments that seem to exclude the interpretation of the new spectrum as a spectrum of the neutral C_2 molecule are so strong that we are almost forced to assume that the spectrum is in fact a doublet spectrum.

The natural assumption then seemed to be that the spectrum was due to the C_2^+ molecule, but here again considerable difficulties arise regarding the possible electron configurations of the two states involved in the transition, and also the excitation conditions in the flash discharge: less discharge energy is required for the excitation of the new bands than for the excitation of the well-known Swan bands of the C_2 molecule. We therefore came reluctantly to the conclusion that the new spectrum may be due to the negative C_2 ion (C_2^-), and would indeed represent the first example of a clearly resolved spectrum of a negative molecular ion. If this assumption is made, since C_2^- has the same number of electrons as N_2^+ and since the new spectrum is in many respects extremely similar to that of N_2^+, there is no difficulty whatever with the electron configuration. It is the same one as for N_2^+.

The presence of a C_2^- ion in a flash discharge seems at first sight rather unlikely. However, experiments ten years ago by HONIG (1954) showed that C_2^- is an extremely prominent ion in the evaporation of graphite. He derived from the temperature dependence of the C_2^- ion an electron affinity of the order of 4 *e*V, a value that is ample to allow a stable excited state at an energy corresponding to 5400 Å.

Since it is difficult to get a conclusive spectroscopic proof for the identity of the absorber of the new spectrum we have proceeded to connect a mass spectrometer with our flash tube. Starting first with the detection of positive ions in a flash discharge we encountered many difficulties. When these had been overcome and a fairly reproducible operation of the mass spectrometer under flash conditions had been accomplished with positive ions we turned to the study of negative ions. In flash discharges in CH_4 we found a fairly high concentration of negative ions of mass 24, that is, of C_2^-. It does not, of course, follow immediately from the observation of C_2^- ions in the discharge and from the inability to account for the new band system as due to the neutral C_2 molecule that this spectrum is due to C_2^-, but we do feel that this interpretation is now a fairly reasonable one. We hope to confirm it further by ascertaining whether the intensity of the new band system varies as a function of the various discharge parameters in the same way as the number of C_2^- ions observed by the mass spectrometer.

D. Conclusion

We have also studied flash discharges in hydrogen in order to find a spectrum of H_3^+. A new spectrum was found in the vacuum ultraviolet which for some time was thought to be due to H_3^+, but it has turned out that this spectrum is a spectrum of H_2 under very special conditions. A spectrum of H_3^+ remains to be found, as does a spectrum of CH_4^+.

Although the output of molecular absorption spectra of ions is very modest, a beginning in the study of these spectra has been made. I believe that there is still a considerable possibility that the diffuse interstellar lines are due to CH_4^+. The question is only how to obtain a sufficiently high concentration of CH_4^+ in a laboratory absorption tube.

REFERENCES

HERBIG G.H., « I.A.U. Symposium » No. 31, p. 85 (1967).

HERZBERG G., « Mém Soc. Roy. Sci. », Liège (4), *15*, 291 (1955).

— « J. Opt. Soc. Amer. », *55*, 229 (1965).

— « I.A.U. Symposium », No. 31, p. 91 (1967).

HERZBERG G. and A. LAGERQVIST, to be published (1968).

HONIG R.E., « J. Chem. Phys. », *22*, 126 (1954).