Chemical Events in the Atmosphere and their Impact on Environment
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ROLE AND FATE OF OZONE IN THE ATMOSPHERE

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I. INTRODUCTION

A new dimension in global toxicology surfaced in the early 1970s with the introduction by Johnston [1] of the concept that rapid gas phase catalysis of ozone recombination to molecular oxygen by nitrogen oxides could alter stratospheric ozone concentrations. Not only did this provide a mechanism for reducing the atmosphere's ability to screen solar ultraviolet radiation, it also provided the means for disturbing natural patterns of heating and cooling in the upper atmosphere. In 1974, Rowland and Molina [2] presented their theory linking the surface release of fluorocarbons to the mid-stratospheric destruction of ozone by the catalytic reaction couplet:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

$$\overline{O_3 + O \rightarrow O_2 + O_2}$$

Photolytic decomposition of the fluorocarbon molecule augments the natural concentration of the Cl and ClO radicals, thereby accelerating the "odd oxygen" (ozone plus atomic oxygen) conversion to O_2.

That theory not only emphasized the importance of chlorine as a component of significant chemical importance to the unperturbed stratosphere, but also introduced the concept that the surface release of an inert and otherwise benign molecule, central to many aspects of our present society, could seriously deplete the concentration of a molecule in the upper atmosphere which is solely responsible for screening the surface of the Earth from potentially harmful near UV radiation. The work of these scientists profoundly altered our perspective of the global significance of such releases.

Important alterations to the global distribution of stratospheric ozone are currently predicted by the best available models which synthesize the chemistry, radiation and dynamics of the middle atmosphere. While these predictions have fluctuated significantly since the first crude estimates were offered in the mid-1970s [3], progress in many fields has brought a growing realization that the stratosphere may well be the first natural system to submit to the scientific method.

This tractability depends upon a rather unique and fortuitous combination of time constants which results in characteristic chemical response times being considerably shorter than dynamical time constants for many of the key mechanisms. Experimentally this means that "pure" chemical experiments can be executed *in situ*, to test photochemical hypotheses on the microscale within the atmosphere. On the other hand, dynamical experiments addressing the longer time scales can be conducted from Earth orbit via satellite to establish vertical and meridional transport maps.

While evidence that the prognosis is encouraging for defining the scientific bounds of the global problem, the last decade of research has yielded mixed results. Attempts to understand the photochemical structure of the stratosphere at the level of detail required to predict trends in global ozone have challenged, and often found inadequate, large areas of our understanding of gas phase photochemistry and kinetics. The stratospheric data base on trace reactive species which control the course of the chemical transformations in the atmosphere has yielded critical secrets but is in a rather primitive state.

It is not our purpose to comprehensively review the aeronomy of the stratosphere with the requisite discussion of such topics as dynamical meteorology, geochemistry, biochemical cycles, etc. Rather, we seek to summarize our current understanding of the photochemical structure of the stratosphere by focussing on the free radicals which control the rate of transformation between different classes of reactants within the atmosphere. Achieving this objective involves a discussion of recent advances in the kinetics and photochemistry of free radicals, developments in modelling and in the measurement of free radicals in the stratosphere, and finally a means of interpreting these atmospheric measurements in the context of our present understanding of the stratosphere.

In the course of the review, several unique characteristics of the stratosphere will become apparent. We will identify examples of how the mechanistic details of a single reaction can dramatically affect predictions of stratospheric change into the next century. This is a particularly fascinating aspect of these studies — namely that while a reasonably complete (chemical) description of the stratosphere requires approximately 200 reactions, details of the reaction mechanism of a single process can alter predictions of global ozone depletion by more than a factor of three.

This sensitivity of conclusion to a single reaction coupled with the needed to distill a vast number of reactions into tractable subsets, the effect of which can be interpreted and tested by observations, restricts the strategy used to test models with field observations. We seek, therefore, to distill the orchestra of reactions into a few rate limiting steps to highlight which measurements must be made to test the mechanisms central to theories of global ozone depletion.

In the third section, we review recent developments in the field of atmospheric free radical observations so we can explore how effectively these experiments have tested our understanding of atmospheric structure. The fourth section summarizes this progress and then presents the latest predictions of global ozone depletion resulting from fluorocarhon release. Recent and important changes have been reported in this aspect of the problem.

II. BREAKING DOWN THE REACTION SET

We first simplify the complete set of reactions needed to characterize the photochemical structure of the stratosphere, listed for reference in Appendix A, by classifying the reactants and products into three generic types: (a) "source" molecules which carry a given element to the stratosphere by upward diffusion from the lower atmosphere; (b) radicals which serve to scramble the chemical structure of the trace constituents while controlling the path and rate of transfer to (c) the "reservoir" molecules which are comprised of their terminal products of radical-radical recombination reactions. This last category is responsible for maintaining mass continuity for each element, by downward diffusion which matches the upward flux of the source molecule. Figure 1 summarizes this division superposed on a simple box model, indicating the spatial division between the surface, troposphere and stratosphere.

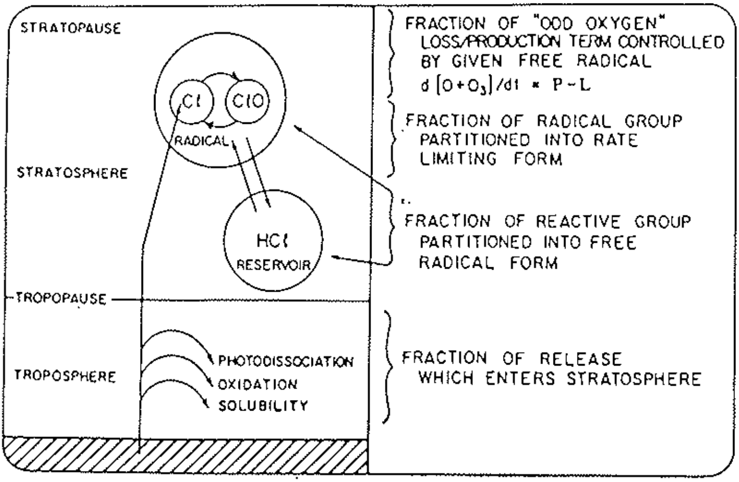


FIG. 1. Box model of the middle and lower atmosphere indicating the major removal processes for *source* molecules carried upward from the surface. The small complement of molecules which actually reach the lower stratosphere then become the precursors for free radical chain carrying reactions which are terminated by radical-radical recombination reactions to form *reservoir* molecules. Downward transport to the tropopause of these reservoir molecules maintains mass continuity.

Separation of reactants and products into the three categories, SOURCE — RADICAL — RESERVOIR is done both to abstract the pattern of change in the reaction network and to distinguish the different time constants associated with each category. The spatial division indicated in Figure 1 conveniently emphasizes the filtering between the stratosphere and the Earth's surface afforded by removal processes in the troposphere.

A vast proportion of the molecules released at the surface are rapidly removed by rain-out, oxidation, or photodissociation. In order to "qualify" as a source molecule, the release rate and tropospheric lifetime against removal by the three processes noted in Figure 1 must be such that a significant flux of molecules cross the tropopause. A significant amount of theoretical analysis and observational evidence (see WMO-82, NAS-84) has isolated those few molecules which are of quantitative significance to the photochemistry of the stratosphere. Those studies are summarized in Table 1 which classifies the major source molecules according to which free radical group each sustains. The mole fraction each comprises in the troposphere is also given. Rapid horizontal and vertical mixing in

TABLE 1 — *Major source molecules.*

Free Radical Group	Source Molecule(s)	Approximate Mole Fraction Trop
Oxides of Nitrogen "NO_x"	N_2O	300 ppb
Oxides of Hydrogen "HO_x"	CH_4	1700 ppb
	C_2H_6	1000 - 1500 ppb
	H_2	550 ppb
	H_2O*	5000 ppb
Oxides of Chlorine "ClO_x"	CH_3Cl	650 ppb
	CF_2Cl_2	300 ppb
	$CFCl_3$	190 ppb
	CCl_4	130 ppb
	CH_3CCl_3	170 ppb
Oxides of Bromine "BrO_x"	CH_3Br	15 ppb
Sulfur, HS, HS_2	OCS	510 ppb

the troposphere maintains, to first order, an invarient (or volume mixing ratio) mole fraction throughout that region of the atmosphere.

A brief glance at Appendix A reveals that each of the reactions involves a free radical either as a reactant or a product. Before dividing the complete reaction set into groups, we trace through the network of transformations:

$$\text{SOURCE} \rightarrow \text{RADICAL} \leftrightarrows \text{RESERVOIR}$$

for the oxides of nitrogen, which is a paradigm for each of the reaction families. This will clarify the reasons behind our subsequent classification strategy.

The primary fate of N_2O in the stratosphere is reaction with $O(^1D)$ (photolysis occurs but is quantitatively insignificant). The branching ratio into products

$$N_2O + O\,(^1D) \xrightarrow{a} NO + NO$$

$$\xrightarrow{b} N_2 + O_2$$

and the absolute rate constant has received considerable attention in the laboratory [5].

Nitric oxide is added to the stratosphere by the oxidation of N_2O in a rather wide altitude interval, as indicated by the observed decrease in N_2O shown in Figure 2.

Release of NO into the stratosphere initiates a rapid sequence of exchange reactions which couple NO and its companion radical NO_2 on time scales of minutes throughout the stratosphere by the reaction sequence

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

This sequence can be represented schematically by the diagram displayed in Figure 3.

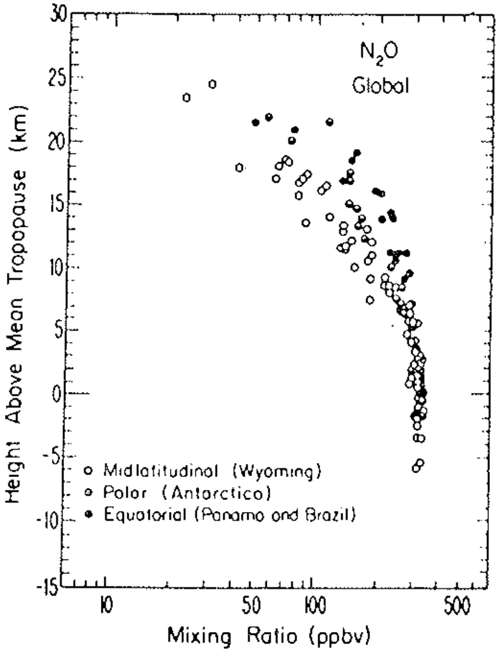


FIG. 2. Altitude dependence of N_2O in the stratosphere showing the oxidation of N_2O by $O(^1D)$ which yields NO.

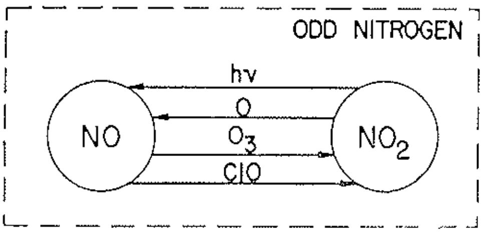


FIG. 3. Schematic of the NO-NO_2 reaction sequence showing the catalytic couplet which accelerates the recombination of ozone and atomic oxygen to molecular oxygen.

In the absence of a removal process, the sum of NO + NO_2 would of course build up indefinitely. What in fact occurs is a recombination step between NO_2 and the hydroxyl radical OH to form nitric acid:

$$OH + NO_2 \rightarrow HONO_2$$

The OH radical is formed in a parallel process to that of NO with CH_4 replacing N_2O as the source molecule shown in Figure 4.

Following the formation of $HONO_2$ by recombination (a mechanism which acting alone would reduce the concentration of NO and NO_2 by orders of magnitude below their observed values), an important pair of reactions

$$HONO_2 + h\nu \rightarrow OH + NO_2$$

$$HONO_2 + OH \rightarrow H_2O + NO_3$$

recycle the nitrogen oxides back into the free radical pool, as indicated in Figure 5.

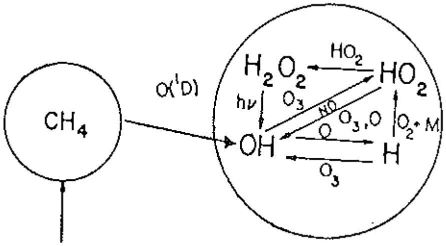


FIG. 4. Production of hydrogen radicals from methane oxidation by O (^{1}D).

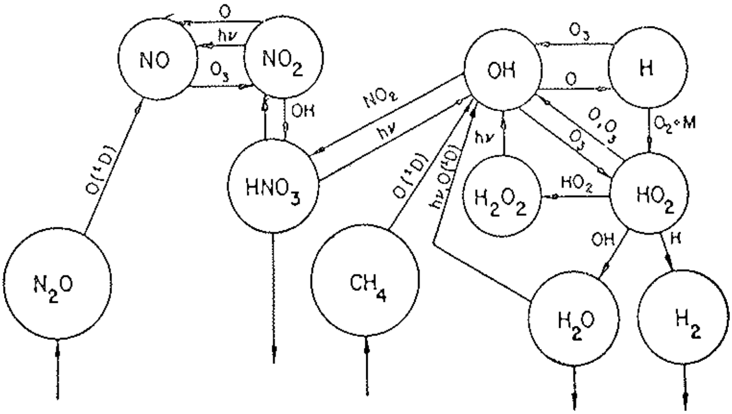


FIG. 5. Coupling of the NO_x radicals to the reservoir molecules $HONO_2$ and HONO.

This completes the first order description of transfer reactions within the NO_x system. From this particular example we abstract the following characteristics which hold for all of the radical groups noted in Table 1.

1. Irreversible destruction of the source molecules to initially form the free radicals, is a slow process compared with any other exchange reactions. Conversion from the source is matched at steady state by the downward mixing of the soluable reservoir term for "wash out" below the troposphere.

2. The cyclic nature of the exchange reactions within each radical system underlies the catalytic property of these transfer reactions. For example, the exchange between NO and NO_2 catalyzes the reformation of the O_2 bond at the expense of atomic oxygen and ozone

$$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2 \\ NO_2 + O \rightarrow NO + O_2 \\ \hline O + O_3 \rightarrow 2O_2 \end{array}$$

There are a significant number of other catalytic cycles which interconnect radicals and which interlink the various reaction families. For example, the conversion of NO to NO_2 is catalyzed by the presence of hydrogen radicals

$$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2 \\ HO_2 + NO \rightarrow OH + NO_2 \\ \hline NO + O_3 \rightarrow NO_2 + O \end{array}$$

and incidentally by the presence of free chlorine radicals

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \\ ClO + NO \rightarrow Cl + NO_2 \\ \hline NO + O_3 \rightarrow NO_2 + O_2 \end{array}$$

3. Consideration of the transfer rates corresponding to each of the major steps within and out of/into the NO_x cycle, tabulated below as a function of altitude (where the k's are bimolecular rate constants in units of $cm^3\ sec^{-1}$, bracketed quantities are concentrations in molecules cm^{-3}, and J is the photolytic rate in sec^{-1} such that each tabulated quantity is in units of molecules/cm^3-sec), underscores the fact that the conversion time within the radical group is dramatically shorter than the period for formation or removal and thus a steady state is established between NO and NO_2. Note also that from the point of view of ozone, there are two important reaction sets in the NO_x radical exchange which, when taken together, either constitute a null cycle or result in the reformation of 3 molecular oxygen honds at the expense of two molecules of ozone. This last point begins to reveal why for the purpose of testing hypotheses of chemical links hy observation of free radicals in the stratosphere, it is essential to break the full reaction complement into subsets which have a clearly defined objective of transforming compounds into or out of a given class of reactive compounds. For example, as used above, those reactions which transfer oxygen into and out of the "odd oxygen" pool, or those which transfer hydrogen into or out of the "odd hydrogen" class must first be isolated as a mechanism and then the rate determining step must be established.

We close this section by summarizing the chemistry of chlorine and ozone in the Earth's stratosphere. There are three essential elements in the Rowland-Molina mechanism linking the release of fluorocarbons to the gas phase catalytic destruction of ozone in the stratosphere:

1. Release of the halogen substituted methanes, principally CCl_3F

and CCl_2F_2 (FC-11 and FC-12) into the atmosphere is followed by rapid mixing of the compounds throughout the troposphere. To a first approximation, there are no physical or chemical removal processes at the surface or in the gas phase throughout the troposphere. This fact was established by comparing integrated release rates with global measurements by Lovelock, whose shipboard observations as a function of latitude formed a cornerstone in the early formulation of the hypothesis.

2. The uniform mixing of the compounds throughout the troposphere increased the mixing ratio of chlorine at the tropopause and thereby the flux of chlorine compounds into the stratosphere. Vertical mixing continues above the tropopause although at a slower rate dictated by the permanent "temperature inversion" characteristic of the stratosphere, until the molecules reach an altitude where the penetration of solar radiation in the wavelength interval between the major absorption continuum/band system of O_2 and O_3 occurs. Photons in this interval are weakly absorbed and have sufficient energy to photodissociate both CCl_3F and CCl_2F_2; $CCl_3F + h\nu \rightarrow CCl^2F + Cl$ and $CCl_2F_2 \rightarrow CClF_2 + Cl$ releasing atomic chlorine.

3. The principal fate of the chlorine atom released is reaction with ozone to form the chlorine monoxide free radical which in turn reacts with atomic oxygen to regenerate the chlorine atom thereby forming a homogeneous gas phase catalytic cycle amplifying the rate of odd oxygen destruction. Since (1) both reactions comprising the cycle are fast bimolecular processes and the couplet is completed on the time scale of tens of seconds, and (2) each chlorine atom resides in the stratosphere for a period of years, spending a significant fraction of that time in free radical form, it follows that an amount of chlorine orders of magnitude less than that of ozone can potentially alter the rate of ozone destruction in the stratosphere.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$\underline{ClO + O \rightarrow Cl + O_2}$$

$$O_3 + O \rightarrow O_2 + O_2$$

Figure 6 traces the major exchange reactions in the SOURCE → RADICAL ⇆ RESERVOIR system. The dominant natural source of chlorine in the stratosphere is CH_3Cl; the main synthetic contribution is from CCl_4, CF_2Cl_2 and $CFCl_3$. Atomic chlorine and chlorine monoxide are

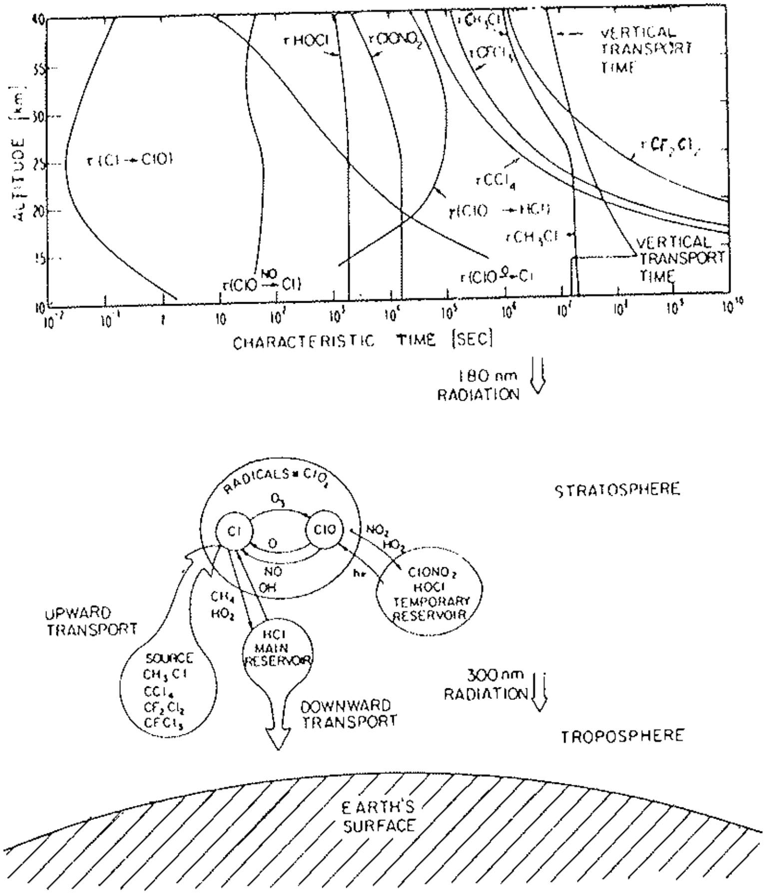


FIG. 6. Schematic of the chlorine reaction system in the stratosphere with an overview of the exchange times among the various subgroups of reactants.

the only important radicals. Exchange times between radicals and photolysis times converting the source molecules to free radicals are also summarized in Figure 6.

The dominant reservoir for chlorine in the stratosphere is HCl which diffuses downward to maintain Cl atom (bound and free) continuity. Two major temporary reservoirs (those molecules with a lifetime on the order of one diurnal period) are critical to the chlorine system. Chlorine nitrate, formed by the three body reaction

$$ClO + NO_2 + M \rightarrow ClONO_2 + M$$

and removed by photolysis

$$ClONO_2 + h\nu \rightarrow ClO + NO_2$$

constitutes (1) a major nighttime storage tank for chlorine radicals, and (2) a critically important coupling term between the chlorine and nitrogen systems. That single reaction is predominantly responsible for the diurnal behavior of ClO, summarized at four different altitudes in Figure 7, taken from the most recent work by Ko and Sze [6].

The other major reservoir for chlorine compounds is HOCl, formed in the bimolecular reaction

$$ClO + HO_2 \rightarrow HOCl + O_2$$

and removed by direct photolysis

$$HOCl + h\nu \rightarrow OH + Cl$$

As Figure 7 implies, current theories suggest that while the altitude interval at and below 36 km is dominated by a diurnal exchange between $ClONO_2$ and ClO, above 40 km the exchange is dominated by a nighttime transition between HOCl and ClO.

The critical question, then, revolves on how the validity of these major hypotheses linking fluorocarbon release at the Earth's surface to (global) changes in stratospheric ozone can be established. There are five elements in the case linking CFC release to changes in stratospheric ozone:

Part. 1: *The CFC release rate and the rate of build up in the troposphere; are there significant losses other than upward transport to the stratosphere?*

The source strength for CFC induced stratospheric ozone removal is, of course, the tropopause mixing ratio for each of the CFC compounds. This must be known to extremely high precision at selected positions across the globe in order to predict steady state concentrations corresponding to a given release rate. Intensive analysis of the time dependence of these mixing ratios over at least a decade is critical in order to establish a lower limit on the atmospheric lifetime.

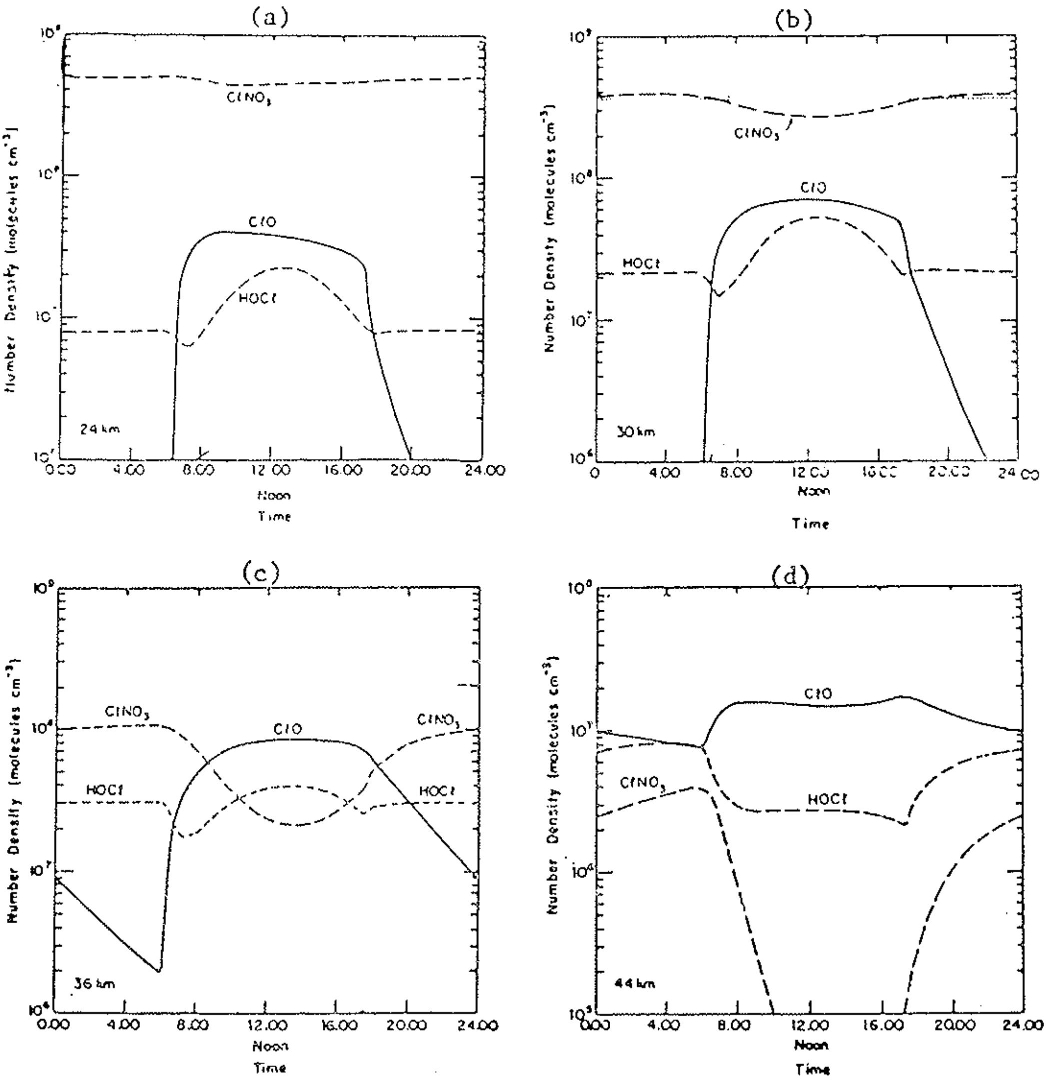


FIG. 7. Diurnal trace of the ClO, $ClONO_2$ and HOCl concentrations for 4 altitudes in the stratosphere; 24, 30, 36 and 44 km. Note the rapid but easily measured decay of ClO following sunset with considerably steeper decay rates at the lower altitudes reflecting the thermolecular behavior of the primary loss reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$. In the altitude interval above 40 km, the dominant diurnal behavior is the day-night exchange between ClO and HOCl. Results are from reference 6 by Ko and Sze.

Part. 2: *The fraction of halogen atoms transported across the tropopause which enter the "bank" of stratospheric halogen compounds in the middle and upper stratosphere.*

The residence time for retention of compounds within the stratosphere increases very rapidly from a low and highly variable quantity in the region just above the tropopause, to a period approaching a decade in the lower-middle stratosphere. Thus the altitude at which CFC photolysis occurs can have important consequences concerning the transfer of halogen compounds into the chemical inventory of the stratosphere, which is in turn a measure of the effectiveness of converting industrially produced halogen into active participants in the stratospheric chemistry.

Part 3: *Partitioning of the halogen compounds among the reservoir, temporary reservoir, and free radical forms. Partitioning of total chlorine into the rate limiting free radical in the dominant catalytic cycle.*

Given that the bottleneck establishing the rate of chlorine-induced ozone destruction is, to first order, the concentration of the rate limiting chlorine free radical in the dominant catalytic cycle destroying odd oxygen, it is essential to establish the propensity of the stratosphere for partitioning total chlorine into the rate limiting radical form. This ratio of ClO to total chlorine as a function of altitude is a quantity of first order importance.

Part. 4: *Quantitative significance of the dominant rate limiting catalytic steps to the total loss rate of odd oxygen as a function of altitude in the stratosphere.*

Odd oxygen destruction rates are, of course, controlled by different free radical groups at different altitudes. The altitude dependent partitioning of the loss side of the odd oxygen budget among the hydrogen, halogen, nitrogen and pure oxygen components provides the first order test of whether current estimates of global ozone production and destruction balance. In addition, such an analysis, when based on observed radical concentrations, defines the altitude interval within which a predicted ozone change would first be observable. Of equal importance, however, is that one must have a solid quantitative understanding of rate limiting processes in the *present day* atmosphere before one can confidently predict future trends. Since those trends point, in the case of CFCs, toward large changes in what is presently a rather small term in the odd oxygen balance in a limited altitude interval, establishing a detailed understanding of the dominant loss terms (i.e., the NO_2 rate limited steps) is essential.

Part 5: *Chemical link between radicals and temporary reservoirs in the halogen system and the major catalytic processes controlling the rate of odd oxygen removal throughout the stratosphere.*

Although the direct contribution of the chlorine rate limiting step to the odd oxygen loss rate is obviously a critical quantity, of equal importance is the coupling between the chlorine radicals and the other catalytic cycles, most notably the nitrogen system. Given the overwhelming contribution to the total ozone column from the altitude interval between 20 and 35 km where the NO_x system dominates, the large changes in chlorine mixing ratios predicted for the next century, second order coupling may prove to be the dominant consideration. This is why the temporary reservoirs hold the key to important elements in our understanding of the system and why a thorough understanding of HO_x-NO_x radical system in the middle and lower stratosphere is essential.

We turn next to the question of making those critical observations which will transform hypotheses, delineated in this section, to scientific fact. This step requires an approach of developing techniques used to make observations *of* and *within* the Earth's stratosphere.

III. Recent Advances in Atmospheric Measurements

Although it has been more than a decade since the scientific community was alerted to the critical need for the development of a new generation of instrumentation to address the question of global ozone depletion, it is only recently that truly novel and powerful combinations of techniques have begun to appear in the literature. The most notable of these include: (1) ground and balloon-borne mm-wave emission techniques originally developed for radioastronomy applications [7]; (2) far infrared interferometric techniques which achieve spectral resolution adequate to detect part per trillion concentrations in the stratosphere [8]; (2) satellite based high-resolution ($- 10^{-3}$ cm^{-1}) scanning interferometers with broad survey capabilities in the middle infrared and pressure modulated radiometry capable of mapping the global distribution of CH_4 and N_2O from Earth's orbit with vertical resolution corresponding to less than an atmospheric scale height [9]; (4) metal atmo lasers and eximer lasers capable of detecting radicals at the part per trillion level *in situ* or by lidar from balloon platforms [10]; and (5) balloon-borne tether systems which provide repetitive vertical soundings of the stratosphere over 15 km height increments from the tropopause to the stratopause [11].

We present here only a sampling of the most recent data obtained by those techniques to demonstrate the emerging ability of sophisticated field experiments to challenge the more fundamental hypotheses linking chemical releases at the surface with global ozone depletion.

1. *Ground based mm-wave emission spectroscopy*

One of the most dramatic examples of concrete progress in the field of stratospheric chemistry has come from the work of de Zafra, Solomon, Parrish and coworkers, who adopted radio astronomy techniques to the detection of stratospheric free radicals. Three key reactive constituents have been examined: ClO emissions at both 204 and 278 GHz from a number of sites in the northern hemispbere, with a rapidly growing seasonal coverage and sufficient time resolution to examine the exceedingly important diurnal behavior of the stratospheric column; HO_2 at 266 GHz from the Mauna Kea, Hawaii Observatory; and H_2O_2 at 270 GHz, again from the Mauna Kea site.

These observations have, first of all, provided the community with a truly independent way of observing the concentration of two critically important rate limiting radicals, ClO and HO_2. The importance of having completely independent methods for establishing the concentrations of radicals in the stratosphere cannot be overstated. As Section II demonstrates, the scientific case linking chemical release at the surface to ozone depletion in the stratosphere is directly testable only if the rate of catalytic conversion can be checked by observing the rate limiting step in the catalysis cycle. A vastly strongly scientific case can be established given independently acquired data sets using entirely different methods.

Table 2 summarizes the present state of knowledge obtained via the balloon-borne *in situ* optical techniques of Anderson *et al.* [12], and the ground-based mm-wave emission techniques of Solomon *et al.* [7].

In order to critique the differences between these techniques at the ± 30% level, it is necessary to consider both latitudinal, seasonal, and diurnal variation, all of which tend to improve the absolute correlation between the measurements of ClO. Thus, while significant differences

TABLE 2 — *Average* ClO *column densities.*

Site	Period	Observed Line Frequency (GHz)	Column Density ($\times 10^{14}$ cm^{-2}) (30 to 51 km)
Massachusetts	January - February 1980	204	0.7 ± 0.2 + 0.15
Massachusetts	February 1981	278	1.1 − 0.2
Arizona	May 1981 (day) (night)	278	0.7 ± 0.2 0.15 ± 0.04
Hawaii	Oct (12m - 4pm) 1982	278	0.70 ± 0.15
	Dec (12m - 4pm) 1982	278	0.80 ± 0.15
	June (12m - 4pm) 1983	278	0.96 ± 0.2
	Dec (12m - 4pm) 1983	278	0.70 ± 0.2
Texas	Anderson *et al.* (noon) 7-flight average, excluding 07/28/76 and 07/14/77	—	1.13

remain to be understood, the existence of ClO in the stratosphere at concentrations comparable to present predictions has been finally established. Such a critical step could not have been achieved with a single experimental approach.

Ground-based mm-wave emission techniques have recently provided definitive identification of HO_2 in the upper stratosphere, measurements which can be directly compared with previous *in situ* experiments [13]. Figure 8 presents those recent spectra. These observations can be used both to cross check *in situ* techniques, for which two have been reported, and to extend measurements of this key free radical above the maximum altitude attainable by balloons, specifically above 45 km. We thus find a critical combination of independent techniques with highly complementary temporal and spatial coverage evolving sucb that the vertical distribution of a key free radical will soon be established in the scientific literature.

Technology in mm-wave detection in the 200 to 400 GHz range has also advanced in the past three years to the point where temporal resolution from ground based observations has improved to such an extent that tbe diurnal behavior of several key radicals can be achieved. The most notable example is that by de Zafra ([14] who has reported vertical column ClO

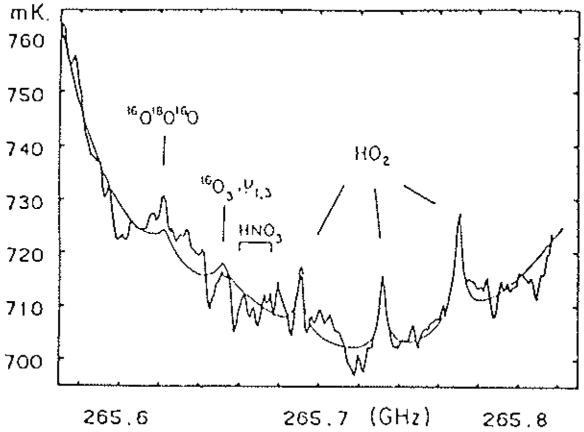


FIG. 8. Ground based mm-wave emission experiments of HO_2 obtained by de Zafre *et al.*

observations tracked throughout a series of 24-hour surveys. These results have been compared with the most recent calculations by Ko and Sze to test both the model's ability to predict the absolute concentration of ClO *and* its ability to predict the diurnal behavior of ClO. Providing the first step is achieved, the latter test is obviously far more stringent for it examines independently the rate of ClO production independently from the rate of destruction. The results of that comparison are summarized in Figure 9.

Two research groups have developed Fourier transform spectrometers for high resolution balloon-borne emission observations of stratospheric trace species. Traub and Chance [15] of the Harvard-Smithsonian Center for Astrophysics have reported results on H_2O_2, HCl, and OH obtained in the 80 to 240 cm^{-1} spectral region at an (apodized) resolution of 0.064 cm^{-1}. These results have contributed directly to reported literature values on HCl, and have placed an extremely restrictive upper limit on the stratospheric H_2O_2 concentrations. Traub and Chance [16] have also reported preliminary results on OH in the critical altitude region between 18 and 48 km. These results are particularly critical to advancement in the field because (a) the absolute calibration is direct and unambiguous and (b) observations can be obtained from a balloon platform at any time of the day or night, providing key diurnal data and, in addition, the flexibility to intercompare with other techniques.

A second research group, headed by Dr. Bruno Carli of the Istituto

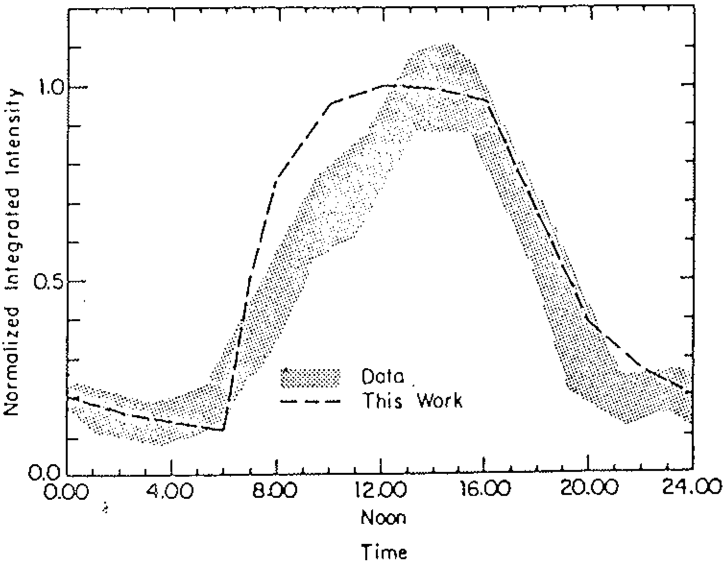


FIG. 9. Comparison between the normalized observed integrated intensity of the ClO emission from Solomon *et al.* and the synthetic intensity derived from calculated concentrations of ClO from Ko and Sze.

di Ricerca sulle Onde Elettromagnetiche IROE/CNR, Via Panciatichi, 56 - 50127 Firenze, Italy, have achieved a spectral resolution of 0.003 cm^{-1} in the 20 to 40 cm^{-1} spectral region using a balloon-borne Fourier transform interferometer. Preliminary results on both OH and ClO have been reported by this group [17]. The superb spectral resolution is a critical element in both the identification of lines and in the rejection of interfering spectral features to enhance the technique's detection threshold. In the next two years, results from the two groups will advance considerably the atmospheric chemistry community's grip on several key radicals.

2. *Satellite-based high-resolution interferometers and radiometers*

The first laboratory quality observations made from balloon platforms were middle infrared absorption experiments of trace atmospheric species using the sun as a source. This work has now been extended to shuttle and satellite-based observations using Fourier interferometers. The ATMOS instrument, developed under the leadership of C.B. Farmer and the NASA Jet Propulsion Laboratory, represents the flagship of this effort [8]. The proven spectral response of this instrument will provide global maps of HCl, HF, $HONO_2$, CH_4, N_2O, CF_2Cl_2, $CFCl_3$, and a number of other important reservoir molecules.

Development of satellite-based pressure-modulated radiometer (PMR) techniques by the Oxford University [9] research team has now dramatically demonstrated the power of global maps of CH_4 and H_2O for the interpretation and testing of two dimensional models. The first results of this work were reported by Jones and Pyle [9] in a comparison between satellite and *in situ* results using the Oxford two-dimensional model to interpret the results. A critically important extension of this work to include the relationships between methane and water vapor has been reported by Jones. The key concept in the work is that the sum $[CH_4] + [H_2O]$ is a conserved quantity in the stratosphere so that global maps of methane can be used to deduce the water vapor composition of the atmosphere. This has critical implications for deducing free radical concentrations from satellite measurements.

The Oxford results have recently been used by Solomon and Garcia to examine the distribution of long-lived tracers and chlorine species in the middle atmosphere. This important paper has crystallized many of the issues relating to the hydroxyl and chlorine species, particularly the relationship between the variability in methane concentration and the variability in ClO. Figure 10 summarizes the correlation between the two-dimensional model of Solomon and Garcia [18] and the Oxford CH_4 maps. These results are then used to define the expected variability in local ClO concentrations reported by *in situ* observations.

3. *Metal atom lasers and eximer lasers for* in situ *and LIDAR detection of radicals.*

The critical need to achieve high signal-to-noise ratios for spatially resolved measurement of several free radicals has spawned a number of research efforts aimed at improving our ability to observe such radicals as OH, HO_2, NO, NO_2, etc., with orders of magnitude better sensitivity than was previously available. A major impetus behind this research has been the realization that atmospheric variability on the spatial scale of a hundred meters in the vertical drives fluctuations in several of the key reactive species, which provide ample concentration variation to carry out covariance studies to establish cause and effect within subsets of free radical reaction sets.

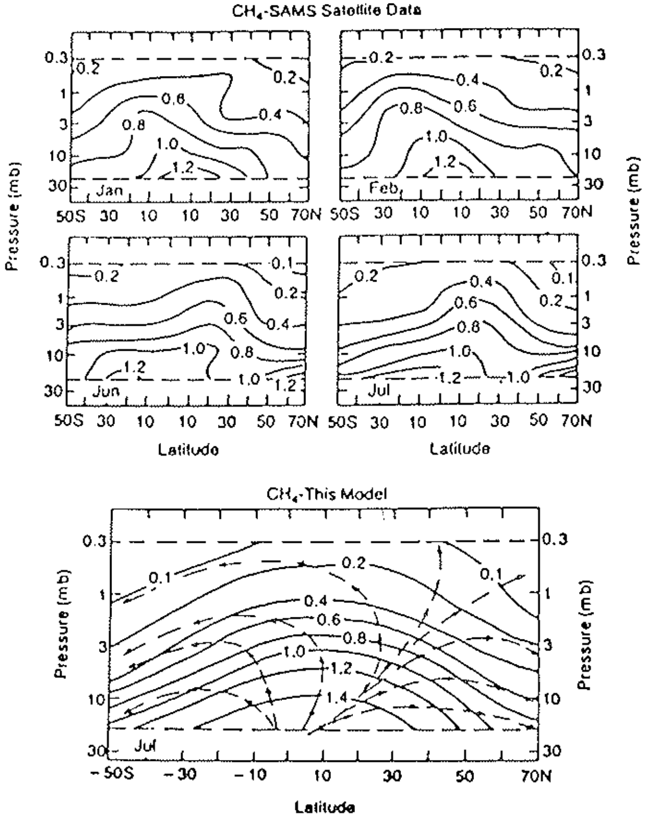


FIG. 10. Some monthly averaged observed distributions of atmospheric methane from the SAMS satellite, Jones and Pyle, near solstice conditions, compared to the model distribution for July by Solomon and Garcia. Light dashed arrows indicate the residual Eulerian stream function, showing the advection pattern.

Two groups within NASA, one at Goddard Space Flight Center, under the direction of Bill Heaps, and the other at the Jet Propulsion Lab under Laudenslager and McDermid, have respectively developed balloon-borne LIDAR methods for OH and developed eximer laser systems for extending the LIDAR method to lower detection thresholds. This research has important implications for both stratospheric and tropospheric research. Such laser ranging techniques also have important implications for intercomparison studies, particularly with mm-wave and far infrared emission ex periments.

Another approach to *in situ* free radical detection has been developed recently at the Harvard Center for Earth and Planetary Physics. That approach, summarized in Figure 11 employs a very high repetition rate copper vapor laser (20 kHz) to pump a dye laser which can be frequency doubled into the ultraviolet and tuned to one or more of the electronic absorption bands of OH, CH, NH, SH and NO_2. The objective of this approach is to provide high power levels with low peak power levels to achieve low detection thresholds by avoiding (a) saturation effects caused by laser induced depopulation of the quantum level pumped, and (b) photochemically induced OH formed by photochemical reactions initiated within the sample by the interrogating laser pulse. By confining the measurement volume to a detection chamber, two additional objectives are achieved. First, all contributions from Rayleigh scattering of solar radiation are eliminated by optical baffling techniques, and second, the contained nature of the flow allows for the option of combining chemical conversion with resonance fluorescence. For example, detection of the HO_2 radical, which does not possess allowed electronic transitions between bond states, can be accomplished with the same hardware used to detect OH by using the rapid bimolecular reaction

$$HO_2 + NO \rightarrow OH + NO_2$$

to convert one radical to another with ease in the time scale of the experiment.

Hardware for both the LIDAR and the *in situ* method is either under development or has been field tested on balloon platforms. Within the next 18 months, these results will surface in the scientific literature.

4. *Balloon-borne tether systems for repeated vertical scans obtained from a single balloon launch*

While previously obtained "snap shots" of the free radical concentration provided first order information on concentration regimes as a function of altitude, several drawbacks exist. Problems center primarily on adequate control over flow conditions, platform stability on a given flight, and, for the chemical conversion experiments (such as for ClO and HO_2 where nitric oxide was used to convert the radicals to Cl and OH, respectively), reactant gas mixing times.

Designated the "Reel Down" technique and depicted in Figure 12, a

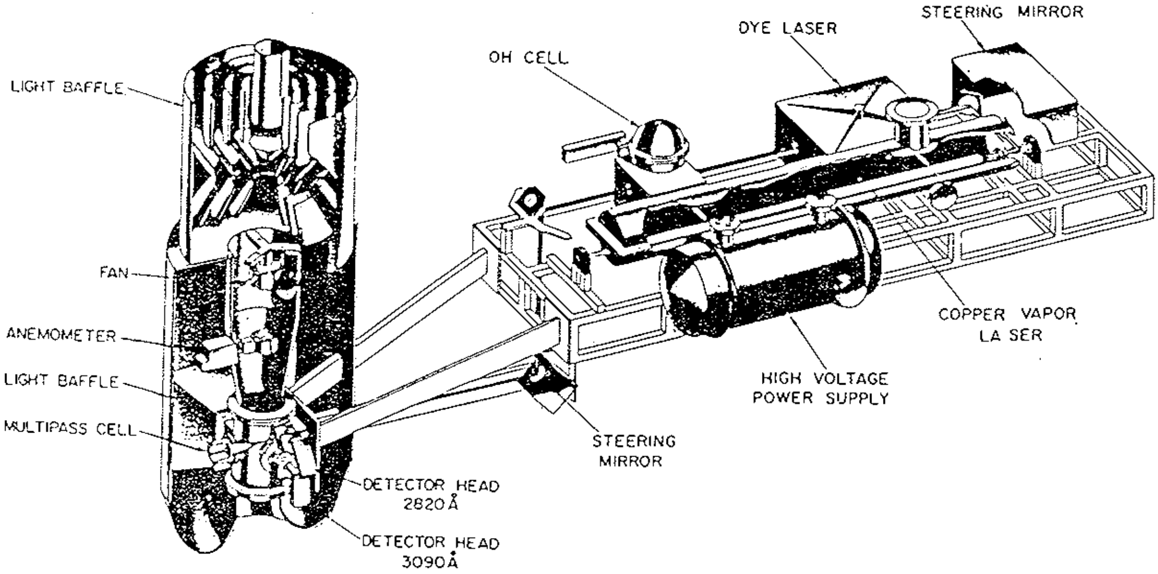


FIG. 11. Schematic view of the copper vapor laser pumped dye laser system developed at Harvard for the detection of OH and HO_2 radicals *in situ* from balloon-borne descent probes.

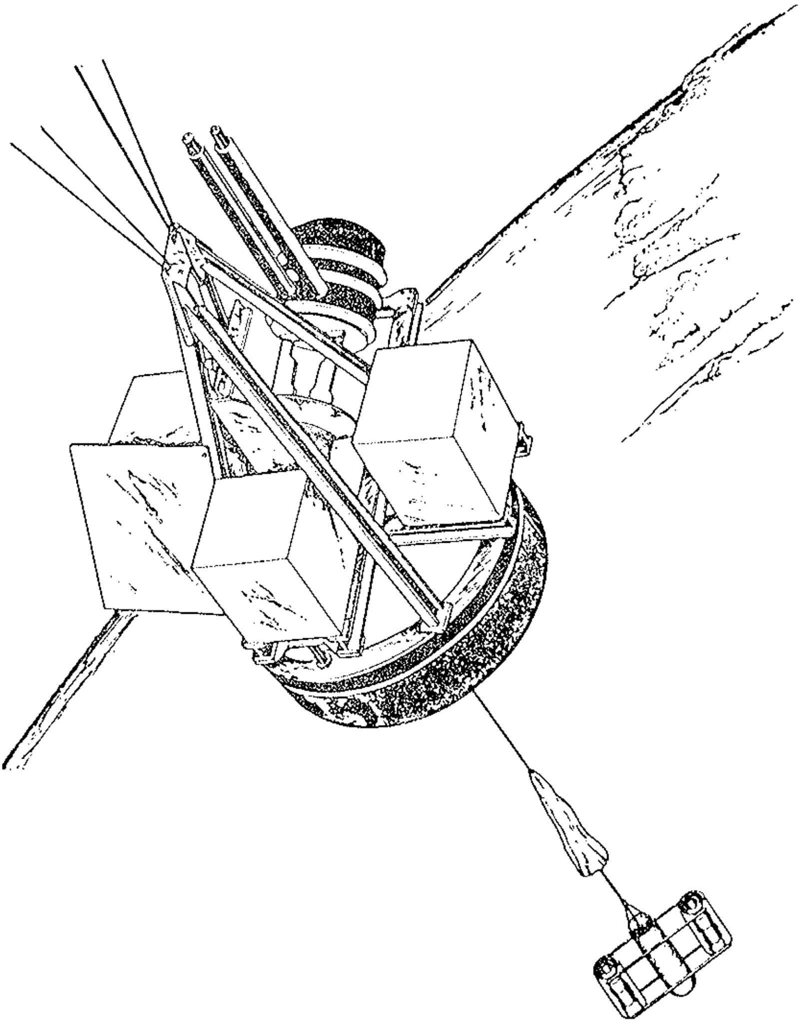


FIG. 12. Rendering of the Reel Down platform with associated suspended payload. This system is capable of vertical scans of greater than 10 km from a balloon floating at or below 40 km.

system was developed at the Harvard Center for Earth and Planetary Physics which consists of (a) a winching system borne by a helium research balloon to an altitude of ~ 40 km (where the atmospheric pressure is approximately 2 mm Hg) and (2) an instrument cluster which is lowered on a filament of Kevlar a distance of 10 km or more, and then retracted back to the winch station. Vertical soundings can be repeated several times for a given balloon launch.

Success of the Reel Down approach hinges on the stability of the system under stratospheric conditions (characterized by low pressures, but potentially large horizontal wind fields). Oscillatory motion developed in any axis of the suspended experiment cluster can compromise experimental control and thus the quality of the observations. A prototype system was constructed to test the feasibility of such a system in the stratosphere. Technical details are described in detail elsewhere [19].

The architecture of the individual instruments used to detect atoms and small free radicals by atomic and molecular resonance fluorescence or by laser-induced fluorescence is shown in Figure 13, but is discussed in detail elsewhere. Briefly, a nacelle, hollow through the core from nose to tail with an impeller in the anterior section, provides for the laminar flow of stratospheric air around and through the instrument. Detection of trace species is carried out at one (or more) optical axes within the nacelle. A major subset of the important stratospheric radicals can be detected using the configuration shown in Figure 13.

The first flight of the Reel Down system took place on 15 September 1982 from the National Scientific Balloon Facility in Palestine, Texas. When the balloon was properly positioned for the descent phase of the experiments, a pin locking the suspended instrument cluster to the winching system was pulled and the controlled descent phase was initiated by releasing a magnetically controlled brake. Descent velocity was selectable by command from the ground. A line velocity of 7 ± 1 m/sec was used for the experiment reported here. A full treatment of mechanical and electronic systems, as well as the data analysis regarding the dynamics of the system, appears elsewhere [19].

Briefly, dynamical behavior of both the suspended payload and the winching platform were documented in real time by a combination of accelerometers, gyros, load cells, solar sensors and a downward looking video monitor on the winch platform. As the descent phase unfoleded, several critical points became apparent:

1. Longitudinal oscillations of the system were observed at the expected periods ($\sim$ 15 seconds at 12 km extension) but the amplitudes were extremely small, typically $< 1\%$ of g. Transients introduced by commanded power level changes damped rapidly. No evidence was observed for the presence of acoustical energy in the line.

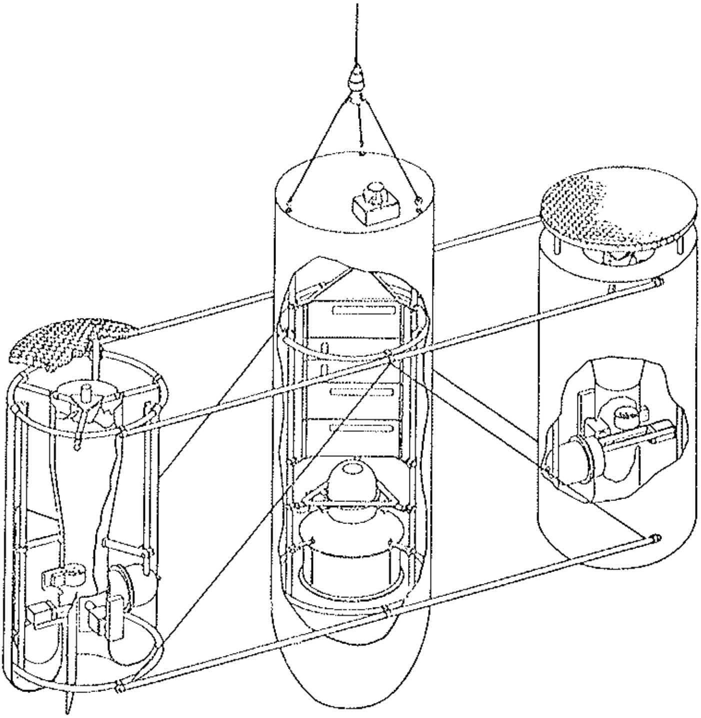


FIG. 13. Cross sectional perspective schematic of the suspended payload showing a cutaway of the detection nacelles with impeller driven flow through chambers, detection head and lamp modules used in the resonance fluorescence detection of radicals.

2. Around the azimuthal axis, the payload described one complete revolution for the remainder of the descent. Three revolutions were recorded in the opposite direction during the last half of the descent.

3. There was a virtual absence of pendulum motion and no measurable body centered perturbations developed. Data suggest a hang-off angle of 4° resulting from wind shear of ~ 7-9 m/sec between the balloon float altitude and the position of the suspended payload at full extension.

This new approach will be used to examine:

1. The covariance between related free radicals and ozone to establish cause and effect;

2. The diurnal behavior of the major free radicals to establish the rate of production and removal of the dominant radicals; and

3. The conversion rates for one radical to another within the same family to establish whether current coupling schemes successfully describe the quantitative conversion rates between radicals.

In summary, the past four years have witnessed a virtual revolution in the technology of stratospheric free radical and trace specie detection techniques. Sensitivities unparalleled even in the laboratory are now becoming available. Of equal importance, there is now a manifold of totally independent techniques extending from the far vacuum ultraviolet to the radio region of the electromagnetic spectrum. This research will lock down the vertical concentration of the major free radicals within the next five years — placing our understanding of the stratospheric ozone layer on a profoundly more satisfactory foundation.

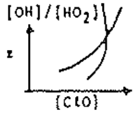
IV. PREDICTIONS OF FUTURE TRENDS IN STRATOSPHERIC OZONE: A REVIEW OF RECENT MODEL RESULTS

The history of nitrogen and halogen compound induced depletion of stratospheric ozone is repleant with unpredictable changes in predicted ozone reduction figures. Every two years the National Academy of Sciences of the United States publishes a report summarizing the latest research on stratospheric ozone depletion and attempts to bound the range of predicted ozone depletion levels for steady state conditions based on present levels of fluorocarbon production. Those estimates, summarized in Table 3 below, have ranged from three percent to nearly twenty percent. These predictions are punctuated by large and episodic changes caused by inclusion of a single reaction or a change in one or a very few kinetic rate parameters.

Such oscillatory behavior does not give those concerned with translating a scientific position into legislative action a consistent vantage point. While we are all concerned, to one degree or another, with the vitality of the Earth's ozone layer, a far clearer picture of the alternatives must emerge before economically difficult decisions are warranted on an international basis.

How can the validity of these predictions be placed in perspective? What were the causes of past vacillations and are we in a significantly different position today? First, we consider what constraints existed in the period from 1974 to 1984 which could have limited the range of predicted depletion levels. Inspection of Table 3 reveals that the major

TAB. 3

Year	Predicted ozone depletion from CFMs at steady state	Reason for Change	Comment
1973	0		
1974	10%	Chlorine catalyzed recombination of ozone included in odd oxgyen balance	Mechanism change
1975	7%	Refinement of Cl-ClO-HCl rate constants	"Tuning" of existent calculations
1975-1976	15%	Choice of rate constant for $OH + HO_2 \rightarrow$	Significant impact on $[OH] + [HO_2]$ throughout stratosphere
1976-1977	6%	Inclusion of $ClONO_2$ in calculations	Mechanism change
1977-1978	16%	Revision in $HO_2 + NO$ rate constant	Dramatic shift in $[OH]/[HO_2]$
1978-1979	16%	No major changes	
1979-1980 -1981	6%	Rate constant revision $OH + HONO_2 \rightarrow$ $OH + HO_2NO_2 \rightarrow$ $HO_2NO_2 + h\nu \rightarrow$ $OH + H_2O_2 \rightarrow$ $OH + HO_2 \rightarrow$	Dramatic change in $[OH] + [HO_2]$ in middle and lower stratosphere
1982-1983	4%	Rate constant revision $ClO + O \rightarrow Cl + O_2$ $OH + HCl \rightarrow H_2O + Cl$ $HO_2 + O \rightarrow OH + O_2$	Tuning of model
1984	4% until [ClO] $[NO_2]$ sharp drop at higher ClO	Titration of NO_2 from system by ClO titration	No change in mechanism, no change in rate constant

shifts in predicted ozone levels into the next century are directly reflected in shifts in model calculated OH profiles of the present day atmosphere. Figure 14 sketches this coupling between the calculated OH concentration throughout the stratosphere and predicted ozone depletion levels at steady state.

This provides us with the first major test of the validity of predicted ozone depletion figures — how well do the observed and predicted middle and lower stratospheric OH concentrations in the present atmosphere correlate? The conclusion is clear. There are no dependable middle and lower stratospheric OH observations. Thus, the exceedingly

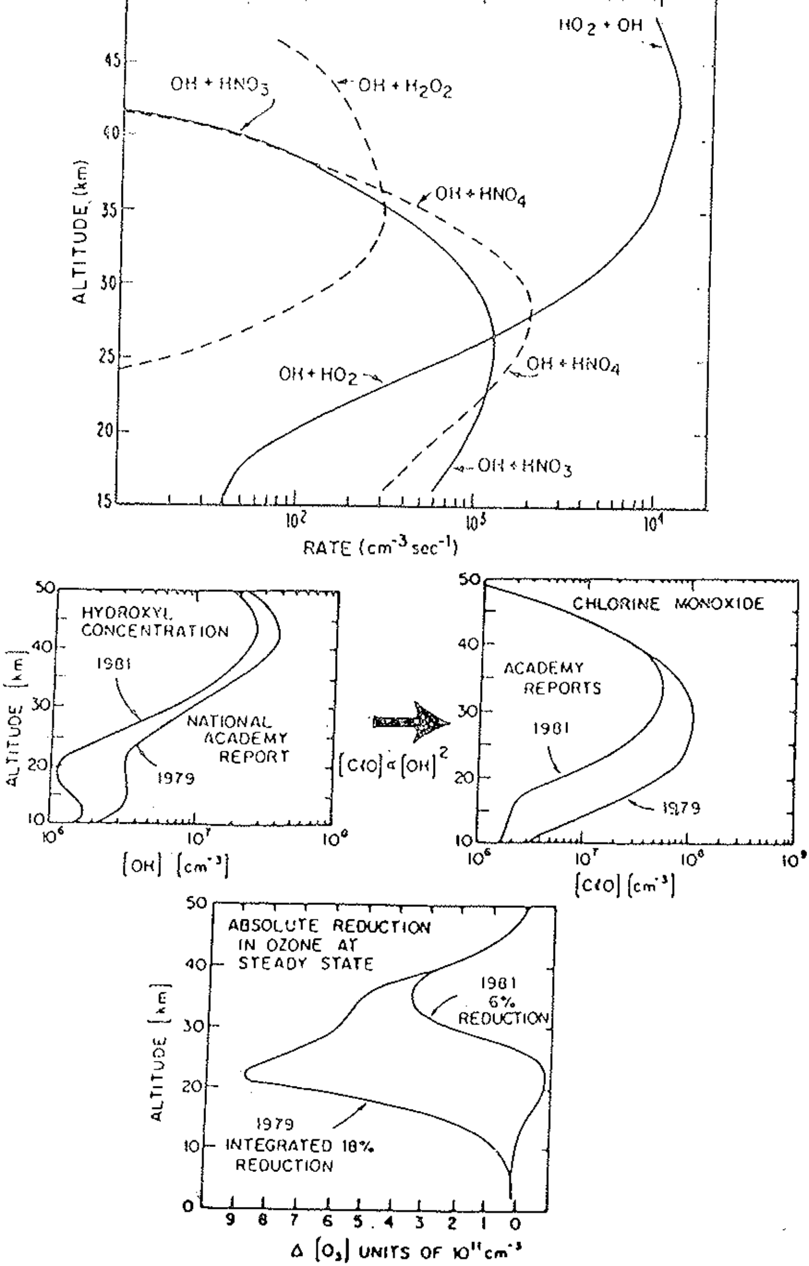


FIG. 14. Coupling between the HO_x, ClO_x and ozone reaction systems shown as a sequence linking the assumed removal process for OH radicals in panel (a), dominated by the reaction set

$$OH + HO_2 \rightarrow H_2O + O_2$$

$$OH + HONO_2 \rightarrow H_2O + NO_3$$

$$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$$

to the resulting concentration of OH in panel (b). OH profiles are shown with and without the nitric and pernitric acid removal mechanism for OH. The impact on the stratospheric distribution of ClO of changing the calculated OH concentration is shown in panel (c), and important constraint remains untested. Within the next two years, however, the new observational techniques described in Section III will dramatically change this situation. Balloon-borne far-infrared emissions measurements from both the Traub *et al.* [16] and Carli *et al.* [17] research efforts will be available, as will balloon-borne LIDAR data from Heaps *et al.* *In situ* measurements of OH, HO_2 and H_2O within the same volume element will be available from the Harvard group. These data, when taken together, will permanently eliminate OH as a free variable in stratospheric modelling, thus eliminating a major dimension of uncertainty.

The second major test of model validity is the predicted distribution of ClO in the stratosphere. On this particular point, the data base is considerably stronger. *In situ* optical techniques, ground-based and balloon-borne laser heterodyne observations have reached the literature. There is substantial agreement between the first two data sets and a major controversy surrounding the latter two. Major technical advancements already achieved will bring to the scientific literature a consensus on this key point in the next two years. *In situ* methods have and will employ the Reel Down approach to vastly strengthen the quality of those observations; new detector technology has improved dramatically the signal-to-noise ratio of both the ground-based and balloon-borne mm-wave emission experiments; and laboratory calibration procedures will be incorporated into the laser heterodyne radiometer field preparation. Taken together, these experiments will solidify the data base on the mid latitude vertical distribution of the key rate limiting chlorine radical between the tropopause and the stratopause. The strictness of this constraint can be grasped first by recalling from Section II the fact that ultimately the bottleneck establishing the rate of chlorine catalyzed destruction of ozone is the reaction $ClO + O \rightarrow Cl + O_2$ so the establishment of the concentration of O and ClO quantitatively defines the ozone destruction rate by chlorine. The same point can be made in a somewhat different way by examining the last two panels of Figure 14, which shows the relationship between the percentage change in ozone as a function of altitude and the ClO concentration as a function of altitude. Firmly establishing the vertical distribution of ClO eliminates any proposed mechanism for ozone destruction which involves any change in the ClO distribution.

A third critical test for current ozone depletion calculations is the diurnal behavior of ClO as a function of altitude. Figure 15, taken from a recent treatment by Ko and Sze [6], summarizes the distinctive signature of ClO concentration as a function of time and of altitude following sunset. This altitude-dependent decay of ClO following sunset defines with great precision the primary mechanism coupling the chlorine and nitrogen systems in the stratosphere because the removal of ClO at night occurs, it is believed, as a result of the thermolecular reaction

$$\mathrm{ClO} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{ClONO_2} + \mathrm{M}$$

If this mechanism functions as it is currently believed to, both the observed rate of disappearance of ClO as a function of altitude (i.e., pressure) and the observed reappearance of ClO via the direct photolysis of $\mathrm{ClONO_2}$

$$\mathrm{ClONO_2} + h\nu \rightarrow \mathrm{ClO} + \mathrm{NO_2}$$

must correlate with the calculations. Initial ground-based observations of the total column [ClO] confirms the general diurnal behavior. With both high time resolution and high spatial resolution afforded by the *in situ* techniques coupled with the Reel Down technique, the current picture can be tested with great precision.

While many other fundamentally important measurements can be described, we move on to review the most recent appraisals of ozone depletion levels because recent advances in the area have significantly changed our outlook on this subject.

With little doubt, the most significant change in our understanding of fluorocarbon induced ozone destruction, both qualitatively and quantitatively, since the Rowland-Molina proposition of radical catalyzed recombination of ozone by Cl and ClO in 1974, is described in a recent paper in *Nature* by Prather *et al.* [20]. What that paper defines is the dramatically non-linear dependence of ozone depletion on added chlorine at high levels of total $\mathrm{Cl_x} = \mathrm{Cl} + \mathrm{ClO} + \mathrm{HCl} + \mathrm{ClONO_2} + \mathrm{HOCl}$. The critical point is that at levels of $\mathrm{Cl_x}$ approaching 15 ppbv, ClO "titrates" $\mathrm{NO_2}$ out of the system via the previously described thermolecular reaction

$$\mathrm{ClO} + \mathrm{NO_2} + \mathrm{M} \rightarrow \mathrm{ClONO_2} + \mathrm{M}\,.$$

Under conditions in which $[\mathrm{ClO}] \geq [\mathrm{NO_2}]$, the photochemical structure of the middle and lower stratosphere undergoes a profound change. First the titration of $\mathrm{NO_2}$ from the system takes all forms of $\mathrm{NO_x}$ with it, specifically, NO and $\mathrm{HONO_2}$ (see pages 345-349 of this report). This

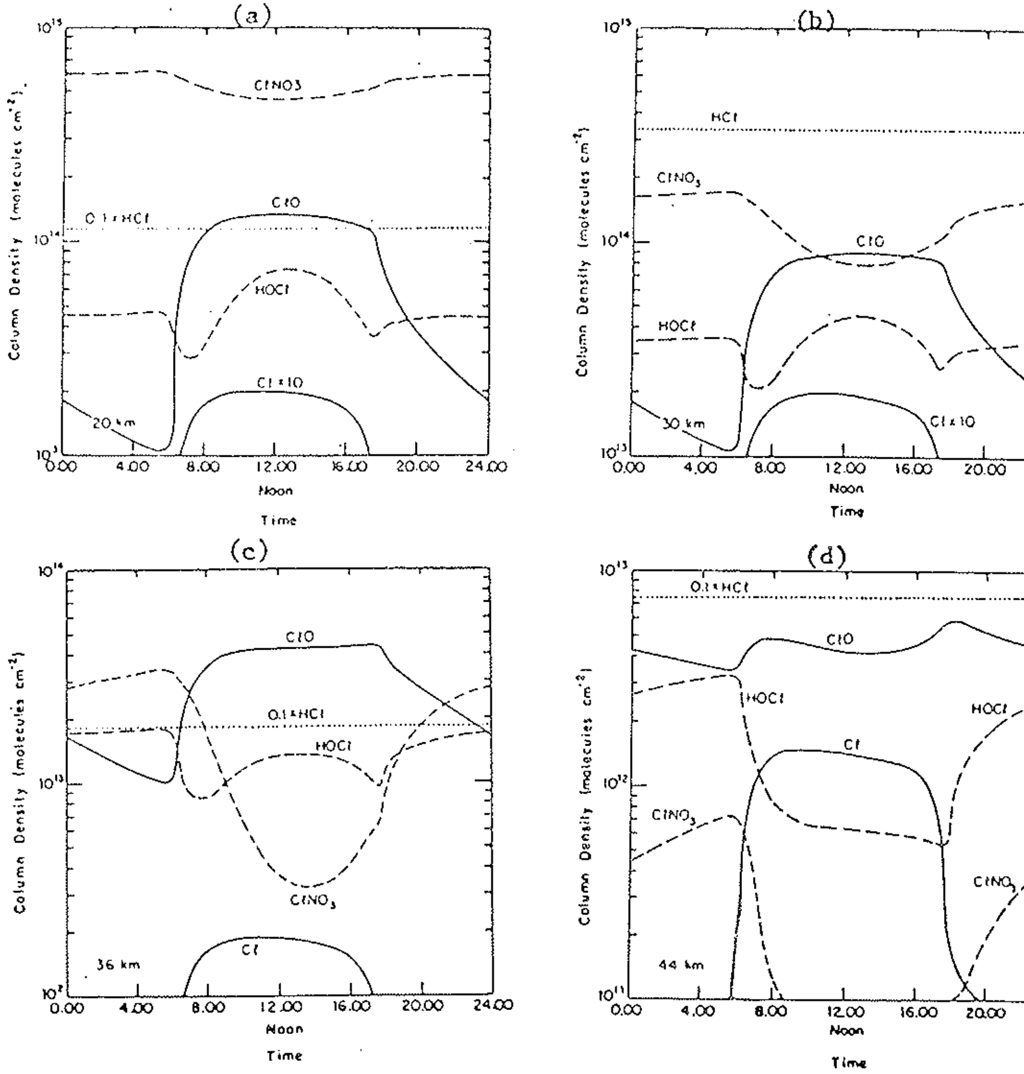


FIG. 15. The diurnal variation of the column densities of HCl, ClO, Cl, $ClONO_2$ and HOCl from Ko and Sze. *Calculated* values are for column abundances above 20 km, 30 km, 36 km and 44 km in panels (a), (b), (c) and (d), respectively. Calculations correspond to 19°N latitude for December conditions.

eliminates the major loss mechanism for OH below 30 km, specifically the reaction

$$OH + HONO_2 \rightarrow H_2O + NO_3\,.$$

Significantly increased levels of OH act to shift the balance of inorganic chlorine, from the non reactive form, HCl, to the reactive radicals, Cl and ClO, via the reaction

$$HCl + OH \rightarrow Cl + H_2O\,.$$

Suppressed levels of NO act to block the conversion of ClO to Cl by the reaction

$$ClO + NO \rightarrow Cl + NO_2$$

which both increases the ClO concentration directly and slows the removal of Cl radicals via the reaction

$$Cl + CH_4 \rightarrow HCl + CH_4$$

which is the dominant mechanism converting radicals back to the relatively non reactive form, HCl. Finally, enhanced levels of OH accelerate the oxidation of methane in the stratosphere and thereby suppress further the conversion of Cl and ClO to HCl by the above reaction.

Taken together, the effects are profound. Figure 16 from the Prather *et al.* [20] paper summarizes the dependence of column integrated ozone on total Cl_x for three different mixing ratios of NO_x: 13, 16.2, and 19.5 ppb by volume. The asterisk denotes the point at which the ozone column has dropped by 10%.

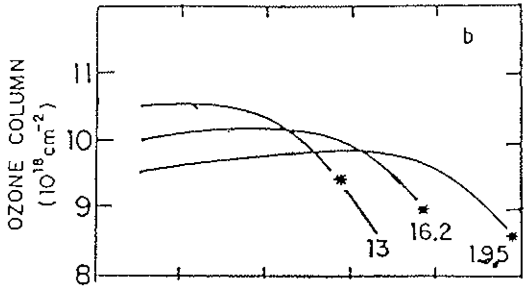


FIG. 16. The column abundance of ozone as a function of stratospheric chlorine for three assumed mixing ratios (by volume) of $NO_x = NO + NO_2 + HONO_2$ taken from Prather *et al.*

Note that very little change in total O_3 column occurs over a broad range of Cl_x mixing ratios, but that once $[ClO] \approx [NO_2]$, a very rapid decrease is predicted. The delay between now and the time at which we approach this titration condition is summarized in Figure 17. At a rate of increase of 3% per year, the 16 ppbv level is reached in the middle of the next century. Quite clearly, the issue is not academic since the world is moving in a direction such that a 3% per year increase may well be conservative. We quote directly from the conclusion of Prather *et al.*:

> In summary, our models suggest that growth in release of chlorinated and brominated halocarbons can pose future problems for stratospheric O_3. There are reasons to believe that the chemistry of the lower stratosphere might undergo a significant change if the concentration of chlorine were to rise above that of NO_x. The concentration of OH could increase markedly and ozone could drop, with reductions potentially larger than 15% in the column density of O_3. Ozone is expected to remain relatively constant prior to the onset of the NO_x to chlorine transition below 30 km. It is important to monitor not only the total column density of O_3, but to search also for evidence of change in the chemical composition of the lower stratosphere.
>
> The large effects predicted here occur primarily below 30 km and involve major changes in the chemistry of radicals such as OH and ClO. Observational data for these species are totally inadequate at lower altitudes and are urgently required to test the validity of current models in a region containing the bulk of atmospheric O_3.

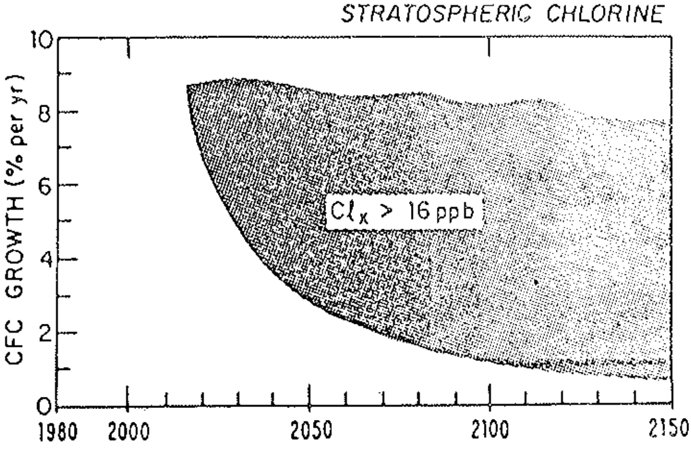


FIG. 17. Relationship between the rate of increase in fluorocarbon production and the year at which the stratosphere will *exceed* 16 ppb of Cl_x.

The present results are based on a one-dimensional model. They should be extended to consider variations of stratospheric chemistry with latitude and season. Extension of the model to more than one dimension may be particularly important in studying the impact of high concentrations of chlorine since results should depend sensitively on details of the calculated latitudinal distributions of chlorine and NO_x.

Investigations of the radical chemistry of the stratosphere have focused in past on the region above 30 km. It is clear that the emphasis must shift now to lower altitudes.

Perhaps the most profound turn of events introduced by the Prather *et al.* paper is the fact that these conclusions are simple, robust and testable. They depend only on the amount of OH and ClO present in the middle and lower stratosphere and on the coupling between ClO and NO_2, all directly testable using the techniques discussed in Section III.

We conclude by noting that while the subject of chemically induced changes to the ozone layer have been surrounded by uncertainty and by controversy, we stand on the edge of a series of major advances which will establish a far more profound scientific underpinning for this subject. It is now believed by students of this subject that the stratosphere may well be the first natural system of global extent which will submit to the scientific method.

APPENDIX A

1. $O(^1D) + N_2 \rightarrow O(^3P) + N_2$
2. $O(^1D) + O_2 \rightarrow O(^3P) + O_2$
3. $O(^1D) + N_2O \rightarrow NO + NO \rightarrow N_2 + O_2$
4. $O\ ^1D) + CH_4 \rightarrow OH + CH_3$
5. $OH + CH_4 \rightarrow CH_3 + H_2O$
6. $OH + CO \rightarrow CO_2 + H$
7. $CO + O + M \rightarrow CO_2 + M$
8. $O(^1D) + H_2O \rightarrow OH + OH$
9. $O(^1D) + H_2 \rightarrow OH + H$
10. $O + OH \rightarrow O_2 + H$
11. $H + O_3 \rightarrow OH + O_2$
12. $OH + O_3 \rightarrow HO_2 + O_2$
13. $HO_2 + O_3 \rightarrow OH + 2O_2$
14. $O + H_2O_2 \rightarrow O_2 + H_2O \rightarrow OH + HO_2$
15. $H + H_2O_2 \rightarrow H_2 + HO_2 \rightarrow OH + H_2O$
16. $H + HO_2 \rightarrow H_2 + O_2 \rightarrow OH + OH$
17. $H + O_2 + M \rightarrow HO_2 + M$
18. $OH + OH \rightarrow H_2O + O$
19. $O + HO_2 \rightarrow OH + O_2$
20. $OH + H_2 \rightarrow H_2O + H$
21. $O + H_2 \rightarrow OH + H$
22. $OH + H_2O_2 \rightarrow HO_2 + H_2O$
23. $OH + HO_2 \rightarrow H_2O_2 + O_2$
24. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
25. $N + O_2 \rightarrow NO + O$
26. $OH + HCl \rightarrow H_2O + Cl$
27. $Cl + H_2 \rightarrow HCl + H$
28. $H + HCl \rightarrow Cl + H_2$
29. $O + HCl \rightarrow OH + Cl$
30. $Cl + O_3 \rightarrow ClO + O_2$
31. $Cl + Cl + M \rightarrow Cl_2 + M$
32. $ClO + NO \rightarrow Cl + NO_2$
33. $ClO + O \rightarrow Cl + O_2$
34. $ClO + NO_2 + M \rightarrow ClNO_3 + M$
35. $O + ClNO_3 \rightarrow$ products
36. $OH + ClNO_3 \rightarrow$ products
37. $H + Cl_2 \rightarrow HCl + Cl$
38. $O + Cl_2 \rightarrow ClO + Cl$
39. $H + ClO \rightarrow OH + Cl$
40. $Cl + H_2O_2 \rightarrow HCl + HO_2$
41. $Cl + HO_2 \rightarrow HCl + O_2$
42. $ClO + HO_2 \rightarrow HOCl + O_2$
43. $OH + HOCl \rightarrow H_2O + ClO$
44. $Cl + CH_4 \rightarrow CH_3 + HCl$
45. $OH + CH_3Cl \rightarrow$ products
46. $OH + CH_3CCl_3 \rightarrow$ products
47. $OH + CH_2O \rightarrow HCO + H_2O$
48. $N + NO \rightarrow N_2 + O$
49. $O + NO_2 \rightarrow NO + O_2$
50. $O_3 + NO \rightarrow NO_2 + O_2$
51. $H + NO_2 \rightarrow OH + NO$
52. $O_3 + NO_2 \rightarrow O_2 + NO_3$
53. $O + NO + M \rightarrow NO_2 + M$
54. $O + NO_2 + M \rightarrow NO_3 + M$
55. $NO + NO_3 \rightarrow NO_2 + NO_2$
56. $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$
57. $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$
58. $N + NO_2 \rightarrow N_2O + O$
59. $OH + HNO_3 \rightarrow H_2O + NO_3$
60. $HO_2 + NO \rightarrow OH + NO_3$
61. $N + O_3 \rightarrow NO + O_2$
62. $OH + NO + M \rightarrow HNO_2 + M$
63. $O + HNO_3 \rightarrow OH + NO_3$
64. $H + HNO_3 \rightarrow H_2 + NO_3$
65. $O + O_2 + M \rightarrow O_3 + M$
66. $O + O_3 \rightarrow O_2 + O_2$
67. $O + O + M \rightarrow O_2 + M$
68. $NO + NO + O_2 \rightarrow NO_2 + NO_2$
69. $NO_2 + NO_3 + M \rightarrow N_2O_3 + M$
70. $N_2O_6 + M \rightarrow NO_2 + NO_3$
71. $N + OH \rightarrow NO + H$
72. $N + O \rightarrow NO + h\nu$
73. $H + H + M \rightarrow H_2 + M$
74. $NO + O \rightarrow NO_2 + M$
75. $OH + HNO_3 \rightarrow H_2O + NO_2$
76. $HO_2 + NO_2 \rightarrow HNO_2 + O_2$

77. $HO_2 + NO_2 \underset{\to}{M} HO_2NO_2$
78. $HO_2NO_2 \underset{\to}{M} HO_2 + NO_2$
79. $OH + HO_2NO_2 \to H_2O + O_2 + NO_2$
80. $OH + CH_3OOH \to CH_3O_2 + H_2O$
81. $CH_3OO + NO \to CH_3O + NO_2$
82. $CH_3OO + HO_2 \to CH_3OOH + O_2$
83. $CH_3OO + CH_3OO \to 2CH_3O + O_2$
84. $OH + NO_2 + M \to HNO_3 + M$
85. soluble gas → precipitation scavenging (CH_3OOH)
86. $NO + h\nu \to N + O$
87. $N_2O_5 + h\nu \to NO_2 + NO_3$
88. $NO_2 + h\nu \to NO + O$
89. $HNO_2 + h\nu \to OH + NO$
90. $HNO_3 + h\nu \to OH + NO_2$
91. $N_2O + h\nu \to N_2 + O(^1D)$
92. $NO_3 + h\nu \underset{\to}{1} NO + O_2 \underset{\to}{2} NO_2 + O$
93. $O_3 + h\nu \to O_2 + O$
94. $O_2 + h\nu \to O + O$
95. $H_2O + h\nu \to H + OH$
96. $CH_4 + h\nu \to CH_2 + H_2$
97. $CO_2 + h\nu \to CO + O$
98. $H_2O_2 + h\nu \to OH + OH$
99. $CH_3OOH + h\nu \to CH_3O + OH$
100. $HO_2 + h\nu \to OH + H$
101. $H_2CO + h\nu \to HCO + H \to H_2 + CO$
102. $Cl_2 + h\nu \to Cl + Cl$
103. $HCl + h\nu \to H + Cl$
104. $ClO + h\nu \to Cl + O$
105. $ClNO_3 + h\nu \to ClO + NO_2$
106. $CCl_2F_2 + h\nu \to CCl_2F + Cl$
107. $CCl_3F + h\nu \to CCl_2F + Cl$
108. $CCl_4 + h\nu \to CCl_3 + Cl$
109. $CH_3Cl + h\nu \to CH_3 + Cl$
110. $CH_3CCl_3 + h\nu \to CH_3CCl_2 + Cl$
111. $HOCl + h\nu \to OH + Cl$
112. $HO_2NO_2 + h\nu \to OH + NO_3$
113. $BrONO_2 + h\nu \to Br + NO_3$
114. $BrO + h\nu \to Br + O$
115. $HOBr + h\nu \to OH + Br$
116. $Br_2 + h\nu \to Br + Br$
117. $CH_3Br + h\nu \to CH_3 + Br$
118. $Br + O_3 \to BrO + O_2$
119. $Br + HO_2 \to HBr + O_2$
120. $Br + H_2O_2 \to HBr + HO_2$
121. $OH + HBr \to H_2O + Br$
122. $O + HBr \to OH + Br$
123. $BrO + NO \to Br + NO_2$
124. $BrO + O \to Br + O_2$
125. $BrO + BrO \to 2Br + O_2$
126. $BrO + ClO \to Br + Cl + O_2$.

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DISCUSSION

KNABE

I have two questions: the story or the depletion of the ozone has been of great concern in the last years, and I missed in your paper the present judgment on this. You showed differences in ozone reduction from 16 or 18 to 6% or 8%. Does it have any meaning? That would be the first question. The other question: I have had many discussions with industrialists, politicians etc. and they use the example of ozone and of fluorocarbons as proof that warnings of scientists to do something or to stop the use of certain chemicals are meaningless, and not really justified. In your opinion, the warning of the National Academy of Science has it been justified?

ANDERSON

I would comment that arriving at one number and holding to that number in an area of this complexity is not a reasonable expectation and it is not the way the subject unfolds. The uncertainties associated with this fluorocarbon-ozone question remained in the region from 4 to 20% for a number of years and as you could gather from the discussion, the scientific issues are to this day unfolding. Now to address the first aspect of your problem briefly, if you detect a rate-limiting free radical in the catalytic cycle that is destroying ozone by virtue of the increasing concentration of the parent molecule that drives that rate of the free radical, then you in fact are at a point where the complexities of the dynamics of the atmosphere are eliminated from the problem. But if you take the next step back and ask: well, why has the projected number oscillated from 5% to 18% back to 10%, you find the reason for that in the concentration of the free radicals which are producing ClO rate-limiting free radical from the chlorine bank that exists in the middle stratosphere. If the observations of the ClO were believed in 1979 and the ozone depletion from that rate-limiting distribution was calculated it would in fact have been 6%, just as it is now in the model calculations when superposed on the rate-limiting free radical. So the changes in the projected percentage decrease in ozone, — in large measure the data on which any reasonable man would base those projections — have in fact not changed. Now, after saying that, I am the last person to say that the subject is finished, because there are significant issues to be resolved here and we cannot expect a topic of this complexity to center in on a conclusion and then not have it deviate. For example, I am extremely interested in getting to the bottom of this discrepancy between the laser heterodyne absorption measurements of ClO and the in situ emission experiments because if there is no ClO in the atmosphere there is no fluorocarbon.

HARE

The speed at which things go in this business means that those of us who are on the fringes of it are always out of date, because by the time you have mastered the chemistry of 1979, you have replaced it with the chemistry of 1983. So let me ask this question. There has been a great deal of emphasis here on ClO and on the role of chlorine in the ozone depletion but years ago from Paul Crutzen I learned the lesson that it was the nitrous oxide of the stratosphere and not Sherry Rowland's halocarbons that really held the control of the thing. Joking aside, the upfluxing molecules that do the damage — or do the necessary control, — what are they? They are water vapor, they are methane, clearly they are synthetic halocarbons, but what is left of the statement that I had learned a few years ago that perhaps the major control is that due to N_2O on its way up?

ANDERSON

The question is very well placed and I did not address the issue of nitrogen because of the time limitations and also we do not have a good method of detecting the rate-limiting radical in the nitrogen, but as soon as we do of course at least a third of the talk will be on this fellow here. The importance of the nitrogen system globally is established by remote measurements of NO_2. 75% of the global destruction of ozone is a result of the nitrogen catalytic cycle that Dr. Rowland showed yesterday. And the reason it is so crucial to the nitrogen system, to the chlorine system is that when we begin to talk about ozone depletion levels resulting from the release of chlorine, we have to be very, very careful about the coupling of chlorine into the step that forms NO_2 as the non-linearities in the system at low ozone depletion levels from one family reaction can couple into another family and have a reverse effect. That is fairly important and you can see the hint of that in the distribution I showed of chlorine oxide-ozone destruction as a function of altitude, where the curve showed actually more ozone at certain levels resulting from the intrusion of chlorine compounds, and that comes from the coupling between the chlorine and the nitrogen system. So, as we begin to approach smaller and smaller numbers in the chlorine system, we have to understand the chemistry of stratosphere ozone in the main to a much higher level in order to extract a good projection of ozone depletion into the next century.

CRUTZEN

I wanted to clarify here maybe a little more about what Jim said. The different catalytic species have their different domains in the atmsopbere wbere they are active and the oxides of nitrogen are the most active between 25 and 45 kilometers, where they mainly control the levels of ozone. Below 25 kilometers the oxides of hydrogen start to come back into a major role, and at about 45 kilometers the oxides of hydrogen, like OH and HO_2 do the job. And in between chlorine is doing a little bit here and there, and it is of course increasingly doing its work. The main source of the oxides of nitrogen in the stratosphere is oxidation of N_2O leading to NO. Very important to consider in this whole issue is not only the total ozone changes which are taking place. I think what has not changed very much in the past regarding predictions of ozone depletion is what is happening around 35, 40 kilometers. Chlorine oxides are breaking down ozone — I think we have not changed our opinion there. What has changed is our feeling or understanding of what is happening below 35-30 kilometers, where most of the ozone is, and tbat will be a major problem in the future. It is my understanding from a recent study we did in the last years, that there are still major problems bringing the production of ozone and the destruction of ozone below 35 kilometers into agreement is, in my opinion, a large surplus of ozone production if one uses currenr for the chemical processes. Now coming back to total ozone, total ozone is not the entire issue. We may well see in the future a redistribution of ozone showing higher levels in the atmosphere, about 35 kilometers or 30 km., to lower levels, and then one gets into the questions regarding climatic changes. When the total ozone issue gets better, normally it is compensated by more worries about the climatic issue.

ROWLAND

The comparison that Jim showed between 1979 and 1981, the depletion of ozone at the altitude of around 40 kilometers was almost unchanged, that down around 20 kilometers one has the change from a substantial loss to an appreciable gain of ozone. One then has to ask why one is worried about a change in the ozone concentration in the atmosphere, and if your only concern is the penetration of ultraviolet radiation to the surface of the earth, where it could have a biological effect, then it does not make any difference whether the ozone is at 35 kilometers or at 20 kilometers. So that then you are interested only in the total column of ozone. If you are concerned about what was just said, that to the extent that you may be altering the stratospheric temperature structure, then the increase of ozone at a lower altitude tends to make much worse the fact that you have decreased it at a higher altitude. These two effects are making the possibility of temperature structure change and possible climatic change more important, and so as we move back and forth between having a lot of depletion at 25 km. and making ozone at 25 km., this shifts it toward climatic change. I think we ought also to look at what has been observed in the atmosphere as well because there are two papers going around now — one I think is just published and one is in press in the Journal of Geophysical Research — which are measurements of the ozone at an altitude around 40 km. Both of these papers are concerned about the measurements with the Dobson instrument from ground level. And each of these papers says that there has been a decrease in the concentration of ozone at the layers which correspond to the 40 km level. The significance of tbe 40 km. level is that is the altitude at which the models have now for nearly ten years predicted that the effect of chlorine would be the greatest; and so the observation that there is a decrease at the altitude for which the chlorine effect is predicted to be greatest comes close to being a confirmation of ozone loss in the stratosphere at the predicted level, confirming the over-all hypotheses not in the microscopic level, that Anderson is talking about here, but in the total loss of process in the atmosphere itself.

One of the complications that is occurring in this is that the measurements of tropospheric ozone, at least in some locations, are showing substantial increases. Since most of the ozone is not in the troposphere, a substantial increase in the troposphere represents a small increase in the total amount of ozone, and it is quite possible that the summation of a tropospheric increase and a stratospheric decrease end up giving you a negligible change overall at least at the location where that measurement is being made. This again takes you back to asking the question of what your concern is and if it is ultraviolet penetration, then again it does not make any difference where the ozone is. It is my feeling that the rearrangement of the temperature structure of the atmosphere is probably the more important effect.

Fiocco

In a document which is being circulated in draft the question of the ozone was written down in the sense that the total effect would be one that we would not have to worry about, and this question of the adjustment in climatic changes of course is very important. So I think that those that have a chance of seeing this document should be very well aware of the way in which it has been written. It seems to me that if we compensate the effect in the stratosphere with the effect in the lower stratosphere, then we have emptied the question completely.

Hare

In wishing to pose that awkward question, I forgot to say what must I think be in all of our minds, that is to express appreciation for not only the extraordinary development of experimental technique that has made possible these soundings — I mean the transformation that is being wrought is quite extraordinary to anyone who is not in daily touch with it. And secondly, to thank not only the last speaker, but two or three speakers that have preceded him, for the clarity with which it is being done. It really has been a revelation.

Liberti

I have many data about the ground ozone concentration as chemists are working in the ground concentration. My question is the following: usually we have a very low ozone concentration, which is around 40 ppb, which goes up in summer to 100, 150. Now we are considering the first figure as due to the diffusion from the ozone layer, and the other one to the photochemical smog, which brings to the action of ozone. Is this a correct attitude or not?

Anderson

Well, the ozone concentration in the absence of the local smog contribution, it is my strong feeling that at that level the ozone is not produced in the stratosphere but is of chemical origin, driven primarily by the natural hydrocarbon oxidation cycles, as Chameides talked about yesterday. The large increase on that of course is the photochemical contribution, and there are a lot of mechanisms involved in that production term. So I do not know how far you want to dive into this question at this time. The ozone that you find in the upper troposphere may in isolated cases come directly from the stratosphere, and certainly globally integrated ozone in the troposphere has a component from the stratosphere, but when you get down to the ground that you are discussing, that is not a major contributor.

PHILIPS

It seems very clear from what is being said that climatic changes may be more important than total UV reaching the earth's surface. Is anyone prepared to speculate just how much redistribution has to take place to see specified climatic changes? I mean can anyone quantify what we would eexpect to see from a redistribution?

ANDERSON

That is a very difficult question. I would not comment on that. It is an extremely delicate question.

ROWLAND

When I spoke in Munich in 1981, the German industrial people sent a man down to ask a number of questions. And one of the statements which he made at that time was that the carbon dioxide problem is going to disrupt the atmosphere so badly that it does not make any difference what else we put into it. This I think probably goes along with the attitude expressed by Dr Knabe, or rather by people that had spoken to him: that the only way that you can judge whether something is a problem, in the American vernacular the term is "Wait until we see the bodies in the street, and then we will admit that we have a problem". I think the fact that we are putting something into the atmosphere, which is accumulating over a very steady period of time and will be there for the next hundred years, is by itself already a serious problem, that you put in something which is so long-lasting that looking into its long-term effects is something that we have to be very much concerned about. And the other is the fact that the models are now predicting that there will be only about a 6% loss. I am not sure that I believe the models of the middle atmosphere that well that I am ready to say that there is not going to be a change in total ozone. And I guess the reason that I think about it in this way is that the place which I think is one of the best or maybe the best ozone measurement station in the world is at Arosa in Switzerland. They have the longest record; they have been measuring total ozone for more than 50 years, and they keep a 50-year average, and it varies quite a bit, but their yearly average has not been up to their 50-year average since about 1971. Now, the fact that the ozone over Arosa has been low for about 10 or 12 years relative to where it has been for 50 years may be just an accident of the location in Arosa, but it may also be that the measurements at many other stations which are not of equivalent competence to the ones at Arosa that are being averaged in with them are giving the misleading interpretation. It is not clear to me that we are not seeing a total ozone change as well.

CRUTZEN

I did not want to leave one of the questions totally unanswered, about the climatic impact of ozone changes in the stratosphere. I cannot from the top of my head give you numbers, but they are sizable and they are being considered in different reports by say, the Academy of Sciences in the U.S. or in the Meteorological Organization report which came out two years ago. Other problems related to climate exist regarding tropospheric ozone and the direct impact of fluorocarbons especially on climate. Even in the troposphere the accumulation of fluorocarbons at steady state will lead to a temperature increase by, if I remember correctly, some 3/10ths of a degree Celsius, but maybe Professor Revelle will present these numbers today later.

ROWLAND

There is one other comment that I think I would like to add here. It has to do with the climate and the temperature structure of the stratosphere, and this again is the report of Dr. Angel, that the measurements of the temperature in the stratosphere at the altitude of the stratopause have shown a drop over the decade starting at about 1970 or 1971, of about 5°C, It is a measurement made as the average of about 1000 measurements every year. And the temperature *has* dropped at the stratopause over that period of time. For unexplained reasons, and with I am sure the total consequence of that not evaluated, I have not seen a satisfactory explanation of the drop nor an evaluation of what the consequences of it would be.

KNABE

I would like to ask another question. We are measuring at some German stations high ozone concentrations all day and night in areas about 100 or

200 kilometers apart from the industrial areas. All measurements many years ago show a peak in the day and a sink at night, this was attributed to the elimination of ozone by reaction with NO. In the remote areas, we do not have this NO during the night-time. My question is: shouldn't we have some OH radicals or some other mechanisms to reduce this high ozone concentration?

ANDERSON

First, the chemical environment under the conditions described is a result of the isoprenes and hydrocarbons released in the forest and is dependent more on the hydrocarbon chemical cycles than on the NO_x cycles.

CHAMEIDES

The classical picture of course is that ozone in continental regions disappears at night because the boundary layer is capped and the ozone gets removed at the ground. In the absence of NO remissions, it is rather difficult to remove ozone chemically as well, though actually it is rather surprising that the ozone does not vary at night and perhaps you are not getting a good capping on the boundary layer.

FIOCCO

I would like to say something about the importance of the measurements in this ozone issue. If we compare the amount of money spent on space and satellite instrumentation — numbers that I do not know — I guess that we will come out with a rather unbalanced ratio, considering in the end that what we rely upon is always the Dobson measurements to a large extent. This network was designed about 40 years ago, and since then very little measurements of cross-sections have been made, so I would say that (a) it would be very important to complement each Dobson measurement with stratospheric measurement, because otherwise it is not possible to make a correction properly. You have always to guess what tbe stratospheric ozone does to your measurements — so tbe two instruments should really go together. One should have a laser Dobson situated in the same place where the Umker measurements are to be made. There is no question that perhaps the Umker technique itself could be somewhat improved by, first, better knowledge of the cross sections as I said, and do perbaps a little more sophisticated spectroscopic analysis, using several lines instead of only two or four.

ANDERSON

There is a great deal of truth in what you say. I would insert one warning, and that is the extreme localization of the chlorine-induced ozone destruction in 40 km region speaks strongly for the global monitoring of ozone in this region because the early warning will show up there in a very dramatic way, and that is the region which is most difficult to diagnose from the ground. However, the contribution of ground-based observations globally to this issue is extremely great and the movement to the satellite-based system should not de-focus from search on the ground-based measurements, both laboratory measurements and the field observations.

HOWARD

This is a technical question: I noticed you had a chemi-luminescent detector in the kit on your flight instruments for detection of NO. At one time you were using resonance fluorescence; I was curious what happened in the evolution of that system.

ANDERSON

The NO resonance fluorescence metbod as applied to the use of plasma discharge devices is an extremely poor approach, and the reason for that is the fragmentation step within the plasma aligned with the apparent temperature of NO produced in the fragmentation process following electron impact is so large that the lines broaden to the point where it is a very poor source. I strongly believe, because of the work done at NOAA, on NO chemiluminescence, that is the finest approach to the in situ detection of NO in the stratosphere. Now that in the next two to three years the use of Rahman shifted laser will be possible for NO analysis the much greater level of sensitivity will be applied to the troposphere problem, but I believe that for the light-weight airborne stratospberic experiments the chemiluminescence metbod will be the hasis by which progress is made.