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Present State Of Knowledge Of The Upper Atmosphere

An Assessment Report

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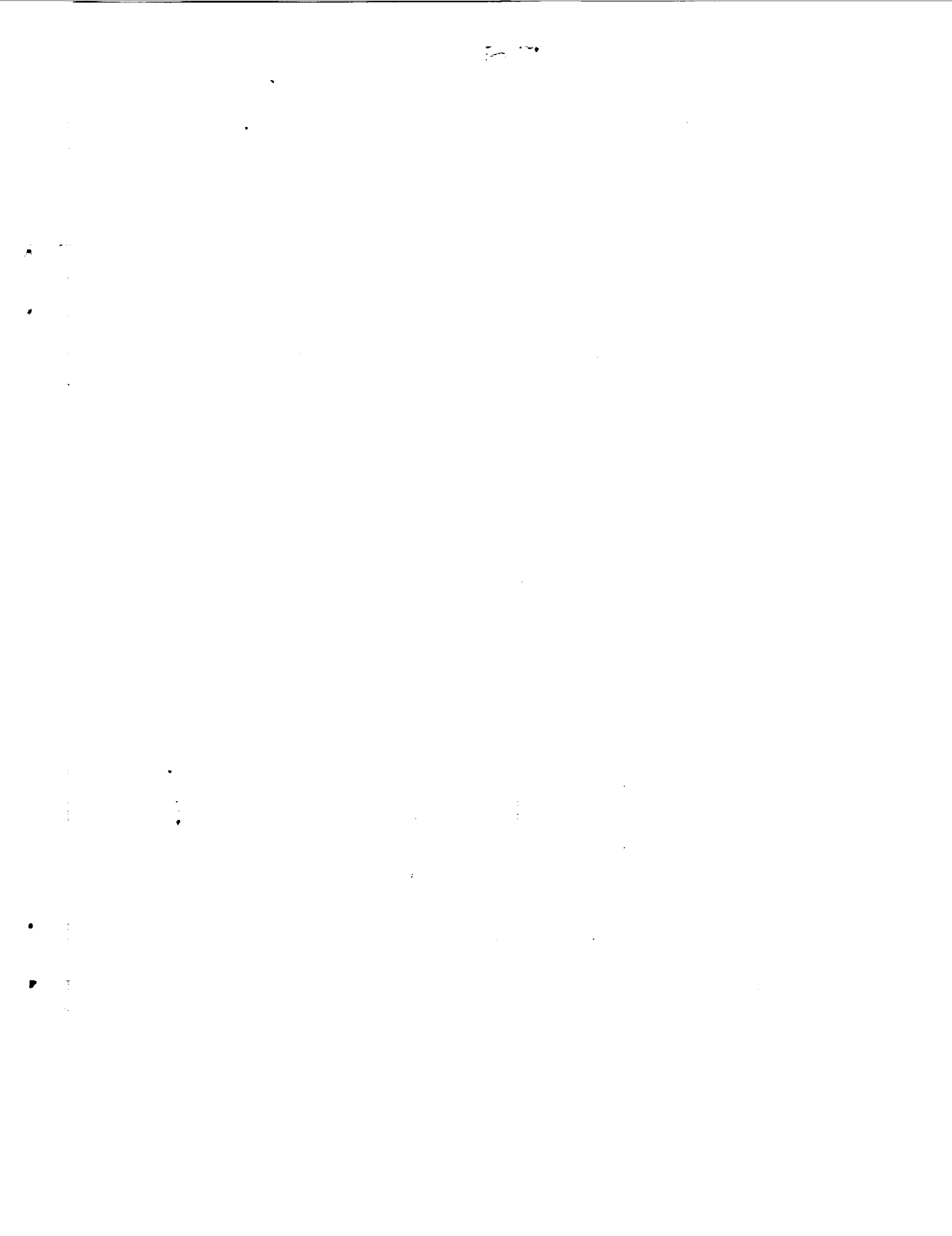
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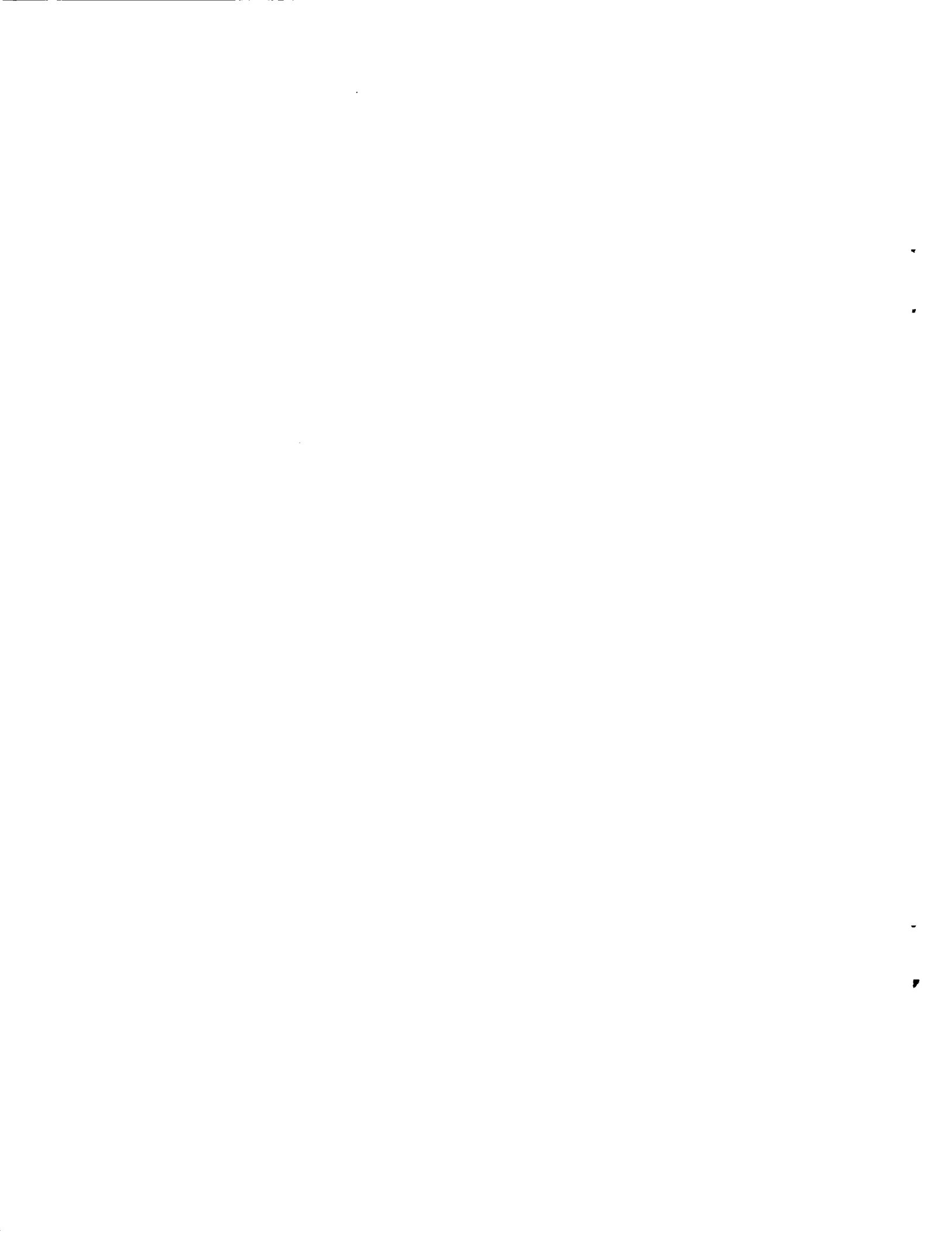
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I. Introduction

For several years, scientists have predicted that man-made pollutants could cause harmful effects by reducing stratospheric ozone amounts. In recognition of the importance of understanding such atmospheric perturbations, Congress directed NASA in June 1975 to "develop and carry out a comprehensive program of research, technology, and monitoring of the phenomena of the upper atmosphere so as to provide for an understanding of and to maintain the chemical and physical integrity of the Earth's upper atmosphere."

Responding to this Congressional mandate, NASA implemented a long-range upper atmospheric science program aimed at developing an organized, solid body of knowledge of upper atmospheric processes while providing, in the near term, assessments of potential effects of human activities on the atmosphere. As one of the specific assessment activities, NASA provided in September 1977 to Congress and the concerned regulatory agencies an evaluation of the effects of chlorofluorocarbon (CFC) releases on stratospheric ozone. This evaluation was based upon a report which resulted from a scientific workshop organized by NASA in January 1977.

Under the provisions of the Clean Air Act Amendments of 1977, the National Aeronautics and Space Administration is required to report both to the Environmental Protection Agency and to the Congress on the results of its programs relating to the stratosphere and mesosphere. The first report was due on January 1, 1980, with subsequent reports due on a 2-year interval. To provide the broadbase necessary for the first two reports, NASA organized workshops in June 1979 and May 1981. These workshop reports were entitled, "The Stratosphere: Present and Future," NASA Reference Publication 1049, and "The Stratosphere: Theory and Measurements," WMO Report #11. The latter workshop was co-sponsored by the World Meteorological Organization and by the

Federal Aviation Administration and the National Oceanic and Atmospheric Administration.

While previous NASA assessments have been based on the scientific findings of major workshops held at 2-year intervals it was felt that yet another major workshop within such a short timeframe was unjustified given that there have been no recent dramatic changes in our understanding of the key physical and chemical processes. Consequently, this current assessment was written by NASA scientists without organizing such a major workshop. The report was based on published articles, preprints, a series of small workshops, and the recent international United Nations Environment Program-Coordinating Committee on the Ozone Layer (UNEP CCOL) assessment. The scientific content and conclusions of this assessment were then reviewed by a small group of selected scientists.

II. Executive Summary

The Executive Summary has been subdivided into two sections. The first deals with issues relating to our current understanding of ozone predictions and trends. The second highlights recent and future anticipated developments that will improve our understanding of the system.

Ozone Predictions and Trends

- (1) As our knowledge of the physical and chemical processes controlling stratospheric ozone deepens, there continues to be concern that the total column and vertical distribution of atmospheric ozone will be affected by changing atmospheric concentrations of several trace substances, specifically chlorofluorocarbons, carbon dioxide, nitrous oxide, nitrogen oxides, and methane.

- (2) It is now well recognized that the effects of these trace substances on atmospheric ozone are strongly coupled and should not be considered in isolation.
- (3) There is strong evidence that the atmospheric concentrations of the chlorofluorocarbons, methylchloroform, carbon dioxide, nitrous oxide and methane are increasing. However, realistic scenarios for future atmospheric concentrations for some of these trace substances are difficult to deduce due to the current inadequate understanding of the sources and sinks for many of these substances. This is especially true for methane.
- (4) There have been no major changes in our concept of stratospheric photochemistry, i.e., it is viewed as a highly coupled oxygen/hydrogen/nitrogen/chlorine system. However, there have been minor but important changes in a few chemical rate coefficients. Perhaps the most significant recent changes have been in our improved understanding of the kinetic behavior of OH, HO₂, ClONO₂ and HO₂NO₂ which affect our description of the lower stratosphere. In addition, values employed for the absorption cross sections of O₂ in the Herzberg continuum have been reduced.
- (5) For the idealized case of continued release of fluorocarbons 11 and 12 at the 1977 release rates (340x10⁶ Kg/yr and 410x10⁶ Kg/yr respectively), a decrease in the ozone column of 3.3 to 5.5% is now predicted. These values were calculated with one-dimensional photochemical models, using reaction rate coefficients given in JPL Publication No. 82-57 with revised, smaller O₂ cross sections in the Herzberg continuum. Radiative feedback was not included in these calculations.

- (6) The range 3.3 to 5.5% is a measure of the precision amongst models which have some differences in assumptions, especially the vertical diffusion coefficient. The overall uncertainty in the prediction is larger than this range. Inclusion of radiative feedback increased the predicted decrease in ozone column to 3.6 - 6.3%.
- (7) Substantial ozone depletions continue to be predicted for the altitude region around 40 km in both the pure chlorofluorocarbon case and for the more realistic case where several trace gases are changing simultaneously (see #9). The predicted steady-state ozone depletion at 40 km for the idealized fluorocarbon 11 and 12 scenario is about 50%. Small percentage ozone increases are now predicted in the lower stratosphere where the ozone concentration is largest. Consequently, column ozone changes are due to differences in the magnitude of opposing effects in the upper and lower stratosphere.
- (8) A nonlinear response has been calculated in which the ozone column actually increases slightly for small added Cl_x and then decreases with further increases in Cl_x . Several models obtain this result while a number of others do not; however, all achieve similar ozone column decreases at steady state for continued 1977 release rates of fluorocarbons 11 and 12.
- (9) Calculations using realistic scenarios for projected increases in atmospheric concentrations of chlorofluorocarbons, NO_x , N_2O , CH_4 and CO_2 predict ozone column increases to dominate for the next few decades. For scenarios in which CH_4 is assumed to be constant at today's level, the ozone column is predicted to decrease after this initial period. A major uncertainty in the predicted evolution of the ozone column beyond the next few decades arises from the very

uncertain future course of atmospheric methane (CH_4) concentrations, i.e., if atmospheric CH_4 continues to increase at a substantial rate, the combined effect of CH_4 and fluorocarbons may never result in a decrease in column ozone.

- (10) One of the reasons for an ozone increase in the near-term scenarios is the predicted increase in tropospheric O_3 from the NO_x injected into the upper troposphere and lower stratosphere by subsonic aircraft. These predictions are more uncertain than those for the middle and upper stratosphere, because of the localized nature of the NO_x source coupled with the rather crude treatment of transport effects in the predictive models.
- (11) All the key radicals predicted to be important in controlling atmospheric ozone (HO , HO_2 , NO , NO_2 , Cl , ClO) have been observed in the stratosphere. However, while the observed abundances are consistent with current theory, the measurements are not yet adequate for substantially constraining the range of quantitative predictions of ozone depletion. However, the measurements of ClO , NO/HNO_3 , and C_2H_6 all support the current models which predict low OH and low ClO in the lower stratosphere, and give the predictions cited in this report (see #5).
- (12) The same photochemical models which yield reasonable agreement between predicted and observed concentration distribution for radical and reservoir species tend to underpredict the current day ozone concentration in the 35-60 km region where Cl_x is predicted to have its largest effect on stratospheric ozone.

- (13) Analysis of the Dobson network data for changes in the ozone column during the decade of the 1970's shows no evidence for statistically significant global trends. Results give a change of approximately $+0.4 \pm 1.4\%$ (2σ confidence level) during that time period consistent with the current predictions of ozone change from the multiple scenario calculations.
- (14) Trends in upper stratospheric ozone derived from Umkehr data corrected for the presence of atmospheric aerosols show a decrease of $0.3 \pm 0.16\%/year$ in layer 8 (38-43 km), consistent with the multiple scenario calculations. No statistically meaningful trend is apparent from the data for lower stratospheric ozone.
- (15) Results for fluorocarbon perturbations show significant sensitivity to the vertical diffusion parameterization used in one-dimensional photochemical models (-2.8% to -4.4% in one model). This sensitivity contributes to the uncertainty in quantitative predictions of ozone depletions using these models.
- (16) There is the potential for climate modification resulting from changes in the ozone distribution as well as from changes in other radiatively active trace species such as the chlorofluorocarbons, CO_2 , CH_4 , and N_2O . While there have been some calculations of these effects using rather simple models, much uncertainty remains concerning the computed climate effects both due to uncertainties in anticipated future constituent concentrations and due to the simplified physics in the models utilized to date.

Developments to Improve Our Understanding

- (a) Nimbus 7 data have been recently released to the scientific community providing for the first time global distributions of several species that are important in stratospheric NO_x and HO_x chemistry, i.e., N_2O , CH_4 , H_2O , NHO_3 , and NO_2 . Together with O_3 , temperature and solar flux data this constitutes the first data set for investigating the three-dimensional dynamical, chemical, and radiative processes that determine the evolution of stratospheric constituent fields. Future satellite missions (e.g. UARS) will give us a much more complete picture of the NO_x and HO_x chemistry in addition to giving us the first global measurements of ClO_x constituents. Also, UARS will include instrumentation for measuring stratospheric winds directly. These will be the first direct measurements of stratospheric dynamics.
- (b) Current and previous satellite observations have proven to be inadequate for determination of long term trends in ozone due to a lack of proper calibration. The first steps are now being taken toward implementing satellite instruments, calibration techniques, and data analysis efforts for the reliable determination of long-term trends in the total ozone column and the vertical distribution of ozone along with solar flux.
- (c) At the present time it is not always obvious whether differences between measurements of the same species, at different times, are due to measurement inaccuracy or to atmospheric variability. Consequently, several international intercomparison campaigns have been conducted for a large number of atmospheric constituents and the results are currently being evaluated.

- (d) Several in situ experimental techniques have recently been developed or improved for species for which there are inadequate atmospheric measurements, e.g. OH and HO₂. Measurements of OH throughout the stratosphere will substantially enhance our understanding of stratospheric photochemical processes. With the development of new instrumentation it may also be possible to make measurements of temporary reservoir species such as HO₂NO₂, ClONO₂, H₂O₂, and HOCl for which there are only upper limits or no measurements at all. The present lack of data on such species, which are thought to play an important role in the interfamily photochemistry of the lower stratosphere, is a serious concern. Also, new shuttle instruments promise to make more comprehensive measurements of stratospheric composition than have existed before.
- (e) Results from past intercomparison campaigns, and future well-coordinated field measurement campaigns in which photochemically coupled species will be measured simultaneously, should lead to critical tests of our description of atmospheric photochemistry, thus constraining the range of predicted ozone depletions.
- (f) One of the main efforts toward understanding constituent exchange processes between the troposphere and stratosphere has centered around understanding the distribution of stratospheric water vapor. Satellite measurements of stratospheric water vapor and aircraft exchange experiments promise to enhance our understanding of troposphere-stratosphere exchange. However, a number of difficulties remain in explaining the distribution of stratospheric water vapor given our present understanding of troposphere-stratosphere exchange and stratospheric chemistry.

- (g) Progress is being made in multidimensional representations of the stratosphere which should enable transport of ozone and catalytic species to be properly represented and eventually to include feedbacks due to temperature changes. Three-dimensional models are being used to provide insight into the appropriateness of simpler one and two-dimensional models for their various uses.

III. The Problem

Stratospheric composition is determined by an interesting and complex set of processes. The system is driven by solar ultraviolet radiation and depends critically on the nature of some of the molecules released at ground level which are transported slowly to the stratosphere by atmospheric motions. Central to the problem of stratospheric composition is the molecule ozone, O_3 . Ozone strongly absorbs ultraviolet radiation from the Sun at wavelengths between 200 and 320 nm. This radiation, if allowed to reach the ground in significant amounts, could have serious effects on human health, agricultural productivity and fisheries. The total amount of ozone in the vertical atmospheric column which is responsible for the nearly complete removal of this radiation would, if reduced to sea level pressure and temperature, be approximately three-tenths of a centimeter in thickness. It is never present at more than about 10 parts per million by volume in the stratosphere and remote regions of the troposphere.

The ozone layer has a continuous distribution with a peak concentration in the lower stratosphere between about 20 and 25 kilometers altitude. Figure 1 illustrates the standard definitions of the troposphere, stratosphere and mesosphere in terms of the profile of temperature with altitude and shows an average ozone distribution. The troposphere is heated from below by solar radiation absorbed at the surface and has the potential to be unstable and have rapid convective vertical motions such as in cumulus clouds. The stratosphere, on the other hand, is heated from above by the absorption by ozone of ultraviolet radiation between 200 and 320 nm and is in a permanent state of temperature inversion making it very stable towards vertical mixing. Because ozone provides the main heat source for the stratosphere its vertical distribution plays the primary role in determining the temperature structure

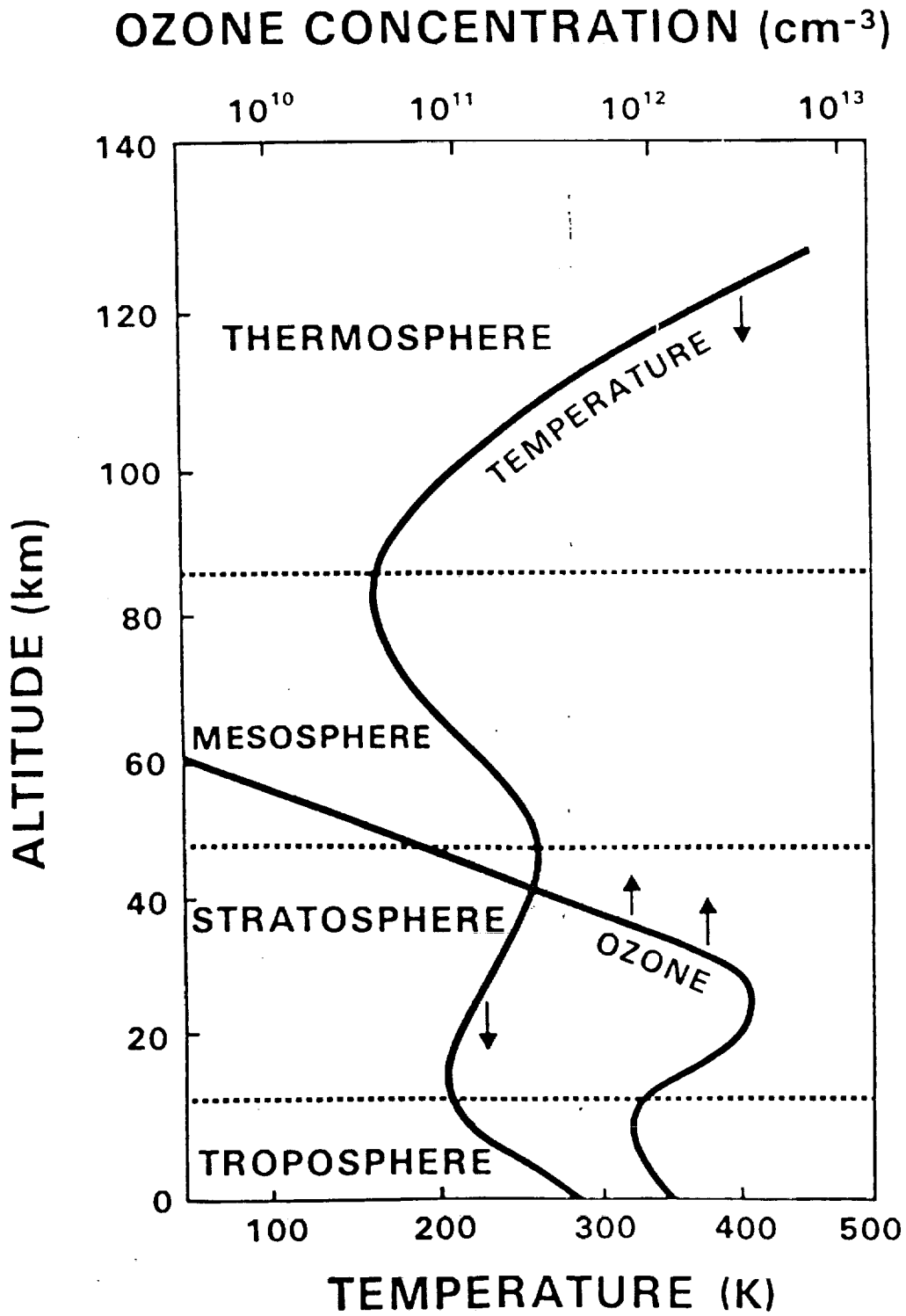


Figure 1 - Temperature profile and ozone distribution in the atmosphere

and the consequent motions of the stratosphere. It is thus critical in determining possible connections between the stratosphere and tropospheric weather and climate. These climatic interactions between the stratosphere and troposphere can take place by means of both radiative and dynamical coupling. A reduction in stratospheric O_3 modifies the surface temperature via two competing radiative processes. Less stratospheric O_3 implies less absorption of solar radiation in the stratosphere, allowing more solar radiation to reach the surface. This effect alone warms the surface. Less stratospheric absorption of solar radiation, however, reduces the downward emission of infrared radiation from the stratosphere to the troposphere. This effect alone cools the surface. For a uniform reduction of stratospheric O_3 , these two effects almost cancel each other usually leading to a small cooling of the troposphere. These radiative effects depend on the altitudes of ozone reduction as well as changes in column amounts of ozone, however. O_3 changes in the lower stratosphere and upper troposphere are found to be more effective than changes in other regions of the atmosphere in causing surface temperature change. Latitudinal variations are also important. If there are uniform fractional O_3 decreases everywhere, there will be greater changes in the radiative fluxes into the troposphere at high latitudes than in the tropics. Finally, the effects of changed O_3 on the solar radiation and infrared radiation into the troposphere will have different effects at different tropospheric altitudes. For instance, given a uniform O_3 decrease, the downward solar flux into the troposphere is increased leading to increased heating of the ground and the lowest layers of the troposphere. This uniform O_3 decrease also decreases the downward longwave radiative flux into the troposphere which decreases the heating in the high troposphere. These two effects superpose to decrease the tropospheric stability.

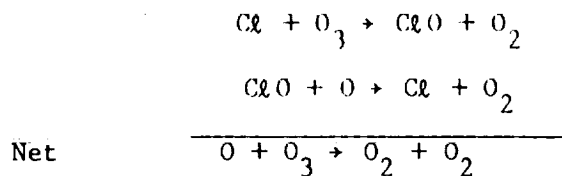
If the distribution of radiatively active trace constituents in the stratosphere (e.g. ozone) changes, then the distribution of heating and cooling rates will change, which will in turn change the stratospheric temperature distribution. The change in the temperature distribution can be accompanied by changes in not only the zonally averaged motions but also in the wave motions in the stratosphere which may even extend downward into the troposphere. Thus, one has a rather complicated situation in which the radiative, chemical, and dynamic effects are all interrelated.

Ultraviolet solar radiation produces ozone in the atmosphere. Wavelengths of less than 242 nm possess sufficient energy to dissociate molecular oxygen, O_2 , into its component O atoms. These O atoms in turn react rapidly with O_2 to form ozone, O_3 . The O_3 formed can subsequently absorb ultraviolet radiation in the 200-320 nm wavelength region, dissociating into an O atom and an O_2 molecule. Ozone is also dissociated, although to a much lesser extent, by visible and infrared radiation. These processes form a long chain in which the oxygen atom alternately attaches itself to an O_2 to form O_3 and then is detached, until finally, the O atom and an O_3 molecule react to reform two O_2 molecules.

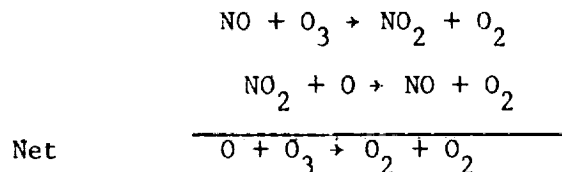
According to this very simple model, the ozone concentration is controlled by its production and loss rates. The ratio of the frequency of the ozone loss to production rate is directly dependent on the effective length of the chain. Since in its oscillation between O and O_3 the "odd" oxygen atom spends far more time as O_3 , the O_3 concentration depends directly on the chain length.

There exist chemical processes which can shorten this chain. Among these are the catalytic processes of the nitrogen, chlorine and hydrogen oxides (NO_x , ClO_x , HO_x). These processes have the same net effect as the reaction

of O and O₃. For example, the simplest catalytic cycle involving ClO_x is the two-reaction set:



and for NO_x



These sets (or cycles) are catalytic because, at the end, the Cl atom or NO molecule are again available to continue converting O and O₃ back to O₂.

The significance of the catalytic cycles is that small amounts of the catalytic species can affect ozone in a significant manner. We have already seen that parts per million of ozone are significant in determining the temperature structure of the stratosphere and its stability, and in determining the amount of uv radiation which reaches the ground. We now find that an even smaller amount of the catalytic oxides (in the part per billion range) are significant in controlling the amount of ozone.

The sources of these catalytic oxides are primarily at the surface of the Earth (an exception is the downward flux of NO_x from the thermosphere during the polar night). The oxides, HO_x, NO_x, and ClO_x, can be converted by interaction with one another into chemically inactive "reservoir" species. These reservoirs, such as nitric acid vapor, HNO₃, and hydrochloric acid vapor, HCl, are soluble in water and can be rapidly rained out in the troposphere. Thus direct release of catalytically active HO_x, NO_x, or ClO_x near the ground does not affect stratospheric ozone. The source molecules; methyl chloride, CH₃Cl; nitrous oxide, N₂O; fluorocarbons 11 and

12, CFCl_3 and CF_2Cl_2 ; methane, CH_4 ; and others, on the other hand, are insoluble and more or less unreactive. They have long residence times in the troposphere and are slowly transported to the stratosphere where they are broken down by ultraviolet solar radiation and other reactive species (e.g. the hydroxyl radical, HO) providing sources of HO_x , NO_x and ClO_x . It should be noted that the addition of HO_x , NO_x or ClO_x to the stratosphere will enhance ozone destruction due to these species alone but will, in addition, interfere with ozone destruction which would have been taking place through the other cycles. A critically important species in this context is the hydroxyl radical, HO, which in addition to being part of the HO_x catalytic cycle, plays a crucial role in both the NO_x and ClO_x cycles. By reaction with NO_2 , HO participates in the formation of the major NO_x reservoir, HNO_3 . It plays the opposite role with ClO_x , reacting with the major reservoir, HCl, to release Cl atoms. Thus, reactions which affect the HO concentration, tend to have opposite effects on the catalytic efficiency for ozone loss by NO_x and ClO_x .

Many mechanisms have been suggested by which human activities can alter the ozone concentrations in the atmosphere. Concern was first directed towards the effects of H_2O and NO_x generated in the stratosphere by the hot exhaust of supersonic transports. More recently the possible effects of the release of NO_x in the upper troposphere and lower stratosphere by subsonic aircraft have been calculated to lead to an increase in ozone. The increased production and utilization of nitrogen fertilizers has also become of concern. Any increase in the nitrogen fixation rate must eventually lead to an increase in the return rate of nitrogen to the atmosphere some of it in the form of N_2O , leading thus to an increase in stratospheric NO_x . Such a perturbation would have a very long time scale since the residence time of N_2O

in the atmosphere is more than a hundred years. Attention recently has been focussed on the fluorocarbons 11 and 12 and methyl chloroform CH_3CCl_3 . The fluorocarbons also have a long atmospheric residence time (50-100 years). The carbon cycle appears to be undergoing change as evidenced by increasing atmospheric concentrations of carbon dioxide, CO_2 , and methane, CH_4 . In contrast to the troposphere where the so-called greenhouse effect of CO_2 is expected to increase the temperature, the effect of CO_2 in the stratosphere will be a temperature decrease as CO_2 is the main infrared radiator which cools the stratosphere. The temperature decrease, through temperature dependent reaction rates, will lead to an increase in ozone in the middle and upper stratosphere. It has also been pointed out that the surface warming due to the direct radiative effect of such minor trace gases as N_2O , CH_4 , CFC's, CCl_4 , and CHCl_3 and the large stratospheric cooling (due to O_3 reduction) are very similar to the effects of a CO_2 increase.

IV. The Scientific Approach

The scientific method involves an interplay between theory and observation: theoretical predictions are made and observations are taken such that either confirmation or refutation of the theoretical concepts result. As theoretical understanding evolves, different observations are required to test changing theoretical concepts. It is by the continual interplay between theory and observation that science moves forward.

The application of the scientific method proceeds quite differently in the geophysical sciences than in the laboratory physical sciences, however. In the laboratory, one seeks to carry out controlled experiments such that theoretically predicted parameters may be measured thus verifying the theory. In the geophysical sciences, it is most difficult, and in some cases

Impossible, to carry out controlled experiments, so a different application of the scientific method is called for. This different application of the scientific method takes place by the construction of mathematical models of geophysical systems and the comparison between geophysical data and the modeled results.

Our application of these concepts to stratospheric predictions requires that our models of the present day stratosphere be verified by comparison against analysis of observations of the present day stratosphere. Inputs to these models include chemical reaction rates and absorption cross sections, which must be measured in the laboratory, and solar spectral irradiance, which must be measured at the top of the atmosphere. Certain parameterizations of processes not calculated in a self-consistent fashion must also be put into these models. For instance, vertical eddy diffusion profiles and tropospheric constituent loss rates must be put into a one-dimensional model. An eddy diffusion tensor field must be put into two-dimensional models. Three-dimensional models require inputs of subgrid processes such as those from gravity waves and turbulent diffusion. Once the models have been tested against observations, one has some confidence in our ability to predict future states of the stratosphere correctly using these models. Different types of data may be required to test different models. For instance, measurements of diurnal constituent variations are quite useful for checking the chemistry in the upper regions of one-dimensional models where transport effects may be neglected. Data should be averaged globally and temporally through the year to compare against profiles produced by one-dimensional models and averaged zonally as a function of time of year for comparison with two-dimensional models. Since three-dimensional models produce results at various geographical points at all model times, there are a variety of ways in which

the models can be compared to observations.

In some cases, models are checked against other models instead of observations. This seemingly odd situation results from the need to use varied levels of model complexity for various aspects of the problem. For instance, testing the predictions of a very complex photochemical scheme against that of a simple scheme can be accomplished for many purposes by a one-dimensional photochemical model, but three-dimensional general circulation models may be required to test the formulation of transport processes that are used in such a one-dimensional model.

As can be seen from the preceding discussion, the development of our understanding of the workings of the present day stratosphere and our ability to predict future stratospheric states will come from pursuing a balanced strategy of laboratory measurements, atmospheric measurements, and modeling of the atmosphere. It is also important that good communication exist among practitioners using these different approaches so that the knowledge generated in one of these areas can efficiently be used to further efforts in the other areas.

V. Atmospheric Chemistry

During the last few years considerable progress has been made in the laboratory measurement of rate coefficients, cross sections, primary quantum yields and product distributions for use in atmospheric modeling, both tropospheric and stratospheric. There is now a better data base for these reactions, including those exhibiting unexpected temperature and pressure dependence of rate coefficients, but our understanding of the chemical reaction mechanisms is still inadequate. A number of problems remain, ranging from small differences in results for a given parameter obtained by different

laboratories to the possibility that major processes have not been incorporated into the photochemical models. Since the previous assessment report of two years ago progress has been steady if less spectacular than during the preceding period, reflecting the improved quality of our data base. There have been no major changes in our concept of stratospheric chemistry, but rather a series of minor, yet still important, modifications to some rate coefficients. Perhaps the most significant changes have been in our improved understanding of the kinetic behavior of OH, HO₂, ClONO₂, and HO₂NO₂ species, and revision of the O₂ absorption cross sections which are needed to calculate the attenuation of solar UV flux in the wavelength region 175 to 220 nm.

The following discussion will emphasize the uncertainty in those processes which are not well defined, and for which the ozone perturbation calculations are sensitive, rather than discussing the large majority of processes for which the present data base is thought to be well established. Although there are still significant gaps in our knowledge of atmospheric chemistry, what we do know is far greater than what we do not, and has steadily improved over the past years. Increased emphasis is currently being placed on analysis of reaction products rather than relying solely on measuring the disappearance of reactants. This is particularly important for those reactions which may proceed via multiple reaction pathways. Investigations of reaction mechanisms over the full range of atmospheric temperatures and pressures are important, since extrapolation of results from outside the range where measurements were taken is sometimes unreliable. The partial pressures of other gases such as water vapor or oxygen may occasionally affect reaction rates, particularly for tropospheric reactions.

Tropospheric Chemistry

Processes which control the trace gas composition of the troposphere need to be understood for investigation of many problems in stratospheric chemistry. The troposphere serves as a source region for a large number of gases that play important roles in the photochemistry of the stratosphere. Since the concentrations of several of these gases are controlled by chemical sources and sinks in the troposphere, global changes in the chemical composition of the troposphere may alter the fluxes of these species to the stratosphere. The most important sink for many of these species, e.g. CH_3Cl , CH_3CCl_3 , etc., is reaction with OH. Any large-scale changes in tropospheric OH concentrations may, therefore, affect fluxes of some source gases to the stratosphere. Furthermore, tropospheric ozone contributes to the total ozone column and plays a significant role in the energy balance of the atmosphere. The chemistry of the global troposphere is complex with both homogeneous and heterogeneous (dry and wet scavenging) processes playing important roles. The homogeneous gas phase chemistry is governed by coupling between the carbon/nitrogen/hydrogen/oxygen systems and can be considered to be more complex than the chemistry of the stratosphere due to the presence of higher molecular weight hydrocarbons, longer photochemical lifetimes, higher total pressures, etc. Significant progress continues to be made in understanding the coupling between the different chemical families, as well as the details of the hydrocarbon oxidation mechanisms and the reactions of HO_2 which play a vital role in controlling tropospheric OH and ozone concentrations. These are important developments as there have been several recent reports of an increase in atmospheric methane concentrations, and even some evidence of an increase in atmospheric carbon monoxide concentrations. Reaction of OH with carbon monoxide is the dominant process for controlling OH

concentrations in the troposphere, yet this important reaction is still not fully understood. Our current understanding of heterogeneous processes is at best qualitative and represents an important void in our understanding of key tropospheric chemical processes.

Reactions involving sulfur compounds are generally considered to be unimportant in the homogeneous chemistry of the global clean troposphere but are quite significant in perturbed regions, i.e. urban areas, volcanic plumes, etc., leading to the formation of sulfate aerosols.

Stratospheric Chemistry

There are some distinct differences between the chemistry of the lower (<30 km) and upper (30-50 km) stratosphere. The chemistry of both regions is quite complex, with significant coupling between the HO_x, NO_x and ClO_x families. Extensive recent research has emphasized the importance of temporary reservoir species such as ClONO₂, N₂O₅ and HO₂NO₂ which act to lessen the efficiency of NO_x and ClO_x species in destroying ozone in the lower stratosphere. It is within this region of the stratosphere that both dynamics and photochemistry play key roles in controlling the trace gas distributions. In contrast, the key chemical processes above 30 km all involve atoms and small molecules due to the rapid photodissociation of the polyatomic molecules, with the height distribution of concentration determined predominantly by photochemistry, not transport.

The current state of understanding of chemical and photochemical processes for individual chemical "families" is discussed separately below, though it should be recognized that there is strong coupling between them. Indeed, it has been changes in our understanding of the interfamily coupling that has resulted in most of the major changes in calculated ozone depletions

over the past decade.

Odd-Oxygen Reactions (O_x)

The chemistry of the basic $O(^3P)$, $O(^1D)$, O_2 and O_3 system is well established, and with the exception of a small change in the rate parameters of the $O + O_3$ reaction, there have been no recent changes in recommended rate coefficients. There is some experimental interest in the roles of excited states of O_3 or O_2 , especially $O_2(^1\Delta)$, but at present there is no evidence that these states have any important effects on the overall chemistry of the stratosphere.

UV radiation at wavelengths between 100 and 240 nm is absorbed by both molecular oxygen and ozone and by ozone alone between 240 and 320 nm. O_2 and O_3 control the penetration of solar uv radiation into the atmosphere and therefore determine atmospheric transmissivity in these spectral regions. In the O_2 Herzberg continuum ($\lambda > 200$ nm) the absorption cross section data used for atmospheric studies has until recently been based on laboratory measurements made at high pressures and extrapolated to low pressures for stratospheric applications. Using these values to calculate the penetration of solar radiation into the stratosphere results in an inconsistency with in situ observations. Recent laboratory data between 200 and 225 nm indicate lower O_2 cross sections which improve the agreement between in situ observations and calculations of the penetration of uv solar flux. This is important for the rate of odd oxygen production in the stratosphere and for other molecules such as N_2O , CCl_4 , CF_2Cl_2 and CFC_3 , which are photo-dissociated in the 200 ± 20 nm region.

Odd-Hydrogen Reactions (HO_x)

The rate coefficients for reactions which control the abundance of, and partitioning between, the odd-hydrogen radicals (OH and HO_2) are required with high accuracy because of the central role that they play in controlling the catalytic efficiencies of both the NO_x and ClO_x cycles. Changes in the recommended rate coefficients for the reactions of OH with HNO_3 and HO_2NO_2 were previously responsible for significant revisions of calculated ozone changes. Earlier work indicated unexpected pressure and temperature dependence of reactions involving the HO_x radicals. New results have been reported and adopted for the reactions of HO_2 with H , O , OH and HO_2 which lead to better characterization of the reactive channels and the pressure, temperature and water vapor dependences of the rate coefficients. Additional data on the pressure and temperature dependence of the $\text{OH} + \text{HO}_2$ reaction are still required.

Odd-Nitrogen Chemistry (NO_x)

The kinetics data base for this class of reactions has also been significantly improved with new data for the reactions $\text{OH} + \text{HNO}_3$, $\text{OH} + \text{HO}_2\text{NO}_2$ and $\text{HO}_2 + \text{NO}_2 + \text{M}$. While the negative temperature dependence for the $\text{OH} + \text{HNO}_3$ reaction is well established, the reaction mechanism is still unclear. Conflicting results have been reported for the temperature dependence of $\text{OH} + \text{HO}_2\text{NO}_2$, and the products of this reaction have not been identified. Utilizing the most recent data for $\text{OH} + \text{HO}_2\text{NO}_2$ results in lower predicted OH concentrations below 30 km and thus a reduction in the catalytic efficiency of ClO_x in this region. Moreover, the temperature dependence and products of the photodissociation of peroxyntic acid, HO_2NO_2 , are not established. These gaps in the data base lead to some uncertainty in the description of

HO₂NO₂ behavior in the lower stratosphere.

Studies of the processes involving NO₃ and N₂O₅ are now underway. Data have been reported for the temperature dependent absorption cross sections for N₂O₅, and data for NO₃ reactions are now just appearing. These species do not play a major direct role in controlling the ozone concentration, but do affect the odd nitrogen partitioning and are very important in the polar night.

Odd-Chlorine Reactions (ClO_x)

The overall kinetic data base for ClO_x reactions has improved significantly in recent years. There has been a significant revision in our understanding of HOCl, ClONO₂ and other ClO_x radical-radical reactions. The important rate coefficients for reactions such as Cl+O₃, NO+ClO, O+ClO, Cl+CH₄ and OH + HCl have not changed substantially since 1977, although there have recently been minor revisions in the rate parameters for OH+HCl (~12% increase at 240 K) and O+ClO (~12% decrease at 240 K) due to intensive reinvestigations of these key reactions. In the reaction of Cl with HO₂, HCl is the major product but the channel producing ClO+OH is now known to be more significant than previously thought, although still of little atmospheric importance. Recent kinetic studies of the HO+ClO and HO₂+ClO reactions suggest that formation of HCl is negligible, thus diminishing their potential importance in the stratosphere as chain terminators. The possible role of HOCl in the stratosphere is now thought to be minor in the light of recent improved knowledge of HO_x chemistry.

A major uncertainty at the time of the previous report was the question of whether or not other isomers of ClNO₃ are formed in the ClO+NO₂+M reaction, and, of lesser impact, the ClONO₂ photolysis products. It has now been shown that the only isomer of significance is ClONO₂, and that "fast" rather than

"slow" rate coefficients should be used for its formation. This reduces the catalytic efficiencies of both ClO_x and NO_x in the lower stratosphere. Discrepancies in the reported ClONO_2 photolysis products have also been resolved.

Hydrocarbon Chemistry

The observed increase in atmospheric methane concentrations underlines the need to understand its chemistry in the atmosphere. In the stratosphere, the reaction $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$ constitutes the main loss process for active chlorine. The dominant sink of methane is, however, its reaction with OH, leading to water vapor formation. The subsequent reactions in the methane oxidation cycle which, involve CH_3O_2 as the key intermediate, are becoming better known. However, information is needed about the reaction

$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$ and about reactions of CH_3O , especially with O_2 , at stratospheric temperatures. Uncertainties in reaction kinetics and mechanisms exist for other hydrocarbons such as C_2H_6 , C_3H_8 and C_2H_2 , which are useful as tracers to test the transport and chemistry used in models. Ethane and propane oxidation leads to the formation of peroxyacetylnitrate (PAN), which is a reservoir for active odd nitrogen in the troposphere and lower stratosphere.

Sulfur Chemistry

Reactions of sulfur compounds are relatively unimportant in stratospheric gas phase chemistry, except possibly in the case of massive injections of sulfur, such as the recent El Chichon eruption. Depending on the assumed mechanism for SO_2 oxidation, which is only now coming into focus, ambient OH concentrations could be either unperturbed or suppressed by nearly a factor of

10 in the lower stratosphere, A substantial reduction in OH concentrations would have significant consequences for NO_x and ClO_x chemistry. However, the most recent laboratory data suggest that SO_2 oxidation proceeds via an OH catalytic process, with only slight impact on OH concentration, consistent with recent observations of the rate of SO_2 oxidation following the El Chichon eruption. The conversion of SO_2 into sulfate aerosols can obviously impact the Earth's radiation budget.

VI. Models of Stratospheric Structure

The structure of the stratosphere is determined by a complex interplay among radiative, dynamical and chemical processes. Ideally we would like to model this system by including a relatively complete description of all of the relevant processes in a three-dimensional time dependent model. This is not yet possible, both because of limitations in computer resources and limitations in the complete understanding of all of the relevant processes. Thus, the problem of understanding the complete stratosphere is attacked with a hierarchy of models which vary in complexity and vary in completeness of description of each of the major aspects of the stratospheric system. Presently we have primarily dynamical models which have little or no chemistry and primarily chemical models which highly parameterize dynamics. We are working toward the goal of having completely integrated models of the entire system.

One convenient method of classifying stratospheric models is according to their dimensionality. A zero dimensional model considers chemistry in a box, i.e., at single points in the atmosphere decoupled from all other points. Such models (or sub-models) allow a detailed description of the chemical evolution of the system. They generally consider situations in which a

chemically dominated system is driven from equilibrium. One example is the diurnal variation of the solar input which can be isolated from the complexity of the overall system so that the problem of diurnal correlation of reacting species can be evaluated. This leads to accurate computation of the modification of the effective diurnal average rate of reaction as compared to that computed from average constituent concentrations. With zero-dimensional models, the impact of changes in rate coefficients or reaction mechanisms on the chemical system are readily evaluated. Of course, care must be taken to apply these models only to chemically dominated regions of the atmosphere. Another use is in the interpretation of atmospheric data in terms of chemical mechanisms. For instance, the problem of the absolute magnitude of the ozone concentration in the 1 mb region is best attacked by using measured temperature and water vapor together with a zero-dimensional photochemical model to determine whether or not ozone is consistent with the adopted photochemical mechanism.

The next level of complexity in atmospheric models is the one-dimensional model which considers variations in the vertical dimension. In this type of model, transport in the vertical dimension is parameterized as Fickian diffusion in which the same diffusion coefficient is used for each chemical species. In general, optimal values for the diffusion coefficient vs. altitude are obtained by fitting the distribution of one or more of the source gases. In one sense, one-dimensional models represent the globally and annually averaged stratosphere, in that the diffusion representation of transport attempts to account for globally averaged motions in which all horizontal motions average out. Yet in another sense, the models purport to represent a specific latitude (30°N) and a specific time of year (equinox) in that they use a diurnal march of zenith angles for the Sun appropriate to

those conditions. Thus, the photochemical driver is not globally averaged properly, and the models represent a hybrid situation. One-dimensional photochemical models are often coupled to one-dimensional radiative-convective models so that changes in ozone can feed back to affect the atmospheric temperature structure through heating by ozone absorption. These 1-D radiative-convective models can also be used to look at global climate effects that result from changes in radiatively active trace species. For instance, using this type of model it was estimated that a uniform column ozone decrease of 10% would give rise to a decrease in the globally averaged troposphere temperature of less than 0.1°K . Temperature dependent chemistry can then modify the ozone perturbations. A feedback which cannot be evaluated in one-dimensional models is that due to dynamical changes resulting when changes in the ozone distribution modify the net heating rate with resulting changes in transport. Despite the above shortcomings, one-dimensional models remain the principal tool with which evaluations are made of possible perturbations of the ozone layer.

The next level of complexity in the dimensionality of atmospheric models are two-dimensional models. These models attempt to simulate the latitudinal and seasonal variations in atmospheric structure. Some of these models use specified two-dimensional transport dynamics while others seek to model the evolution of the transport by zonally averaged meridional and vertical motions. A characteristic difficulty with such models is how to rationally specify the transport effects of asymmetric motions.

During the last two years, there have been several published studies of the stratosphere using two-dimensional models. Most of these have sought to model the present day stratospheric composition, although there have been studies of the effects of increased concentrations of CO_2 and fluorocarbons.

All of these models suffer from some defects in their dynamical formulation. For instance, one method used is to take a previously published mean meridional circulation that was calculated in the absence of asymmetric motions, and is meant to approximate the Lagrangian transport velocity field, together with a collection of diffusion coefficients taken from various sources. The magnitudes of the circulation and diffusion coefficients are often adjusted in a somewhat arbitrary manner to obtain better fits to some of the constituent data. Another method used is to compute the mean meridional motion self-consistently given the heating rates calculated from the modeled composition. Then meridional and vertical diffusion coefficients are specified independently in one of a variety of ways that is not necessarily consistent with the meridional circulation. Thus, present formulations of two-dimensional models, unlike those of one-dimensional models, are quite diverse and often contain physically questionable features. They do allow the seasonal and latitudinal effects to be modeled such that they may be tested against observations. They also allow predictions of the latitudinal and seasonal effects of constituent scenarios to be made. As will be indicated later, three-dimensional studies are being carried out so that we may better understand present formulations of two-dimensional models and hopefully construct future two-dimensional models that are more consistent with our physical understanding of the three-dimensional atmosphere than are the present ones.

Another type of two-dimensional model is aimed at looking at alterations in climate that might result from changed distributions of radiatively active trace constituents. Models of this type have been used to look at the changes in radiative fluxes into the troposphere as a result of ozone decreases. They indicate that if there was a uniform column decrease in O_3 , the high latitude

cooling would be about four times greater than that at low latitudes. It was also found that fractional decreases in tropospheric ozone would have the same cooling effect as the same fractional decrease in stratospheric ozone even though only about 10% of the total ozone is found in the troposphere.

Finally, there are the three-dimensional models. Some three-dimensional models are aimed at studying only certain features of the stratosphere and thus simplify, or in fact neglect, certain aspects of the physical drives of these motions. For example, instead of explicitly modeling the tropospheric motions, some three-dimensional models either use specified dynamical lower boundary conditions in the upper troposphere or lower stratosphere or use simplified formulations that force the tropospheric structure to look somewhat realistic. These simplified models are often referred to as mechanistic models to distinguish them from those three-dimensional general circulation models that seek to model the physics of the entire troposphere-stratosphere system. Troposphere-stratosphere general circulation models use a great deal of computer time and produce great amounts of output to analyze.

While there has been considerable activity in three-dimensional modeling of the stratosphere, no published works have appeared in the past two years that have integrated realistic chemistry into a three-dimensional general circulation model. Several groups intend to do such studies over the next several years, however.

In the past two years there have been publications of annual cycles by general circulation models that extend through the stratosphere. These have had some success in modeling features of the annual cycle in stratospheric temperatures and winds and have produced spontaneous stratospheric warming events that resemble those that are observed. Probably the most notable deficiency in these models are the excessively cold winter polar night

temperatures ($\approx 50^{\circ}\text{K}$ too cold at the winter polar stratopause) which are accompanied by excessive polar night westerlies that are about a factor of two too large. These deficiencies appear to be due to dynamical rather than radiative deficiencies. It is seen in these models that the planetary wave forcing of the winter stratosphere is less than what is observed. It is not yet clear what the cause for this might be. There is also the suggestion that gravity wave and turbulence effects might be playing an important role in determining stratospheric winds and temperatures. This deficiency in modeling winter polar winds and temperatures could translate into a serious error in modeling stratospheric transport and photochemistry in the regions where the modeled structure is in error given the effect of temperature-dependent reaction rates and the anticipated errors in transport.

One area of recent success of stratospheric three-dimensional models has been their success in forecasting observed changes in the stratospheric circulation. In the past two years there have been several studies which indicate that troposphere-stratosphere general circulation models can successfully forecast the stratospheric circulation for periods of about 7-10 days. These studies together with simpler mechanistic models should give us a clearer understanding of the mechanisms of stratospheric warmings and their associated mass transport. Already, studies with mechanistic three-dimensional models have been used to look at the respective contributions to ozone transport by the mean meridional circulation that is forced by the net heating distribution versus the ozone transport by planetary waves. Studies of this type should be very useful in looking into the appropriateness of various two-dimensional model formulations and in paving the way towards formulating two-dimensional models with a firmer physical basis. It is perhaps in this area of looking into, and improving, the formulation of

simpler lower dimensional photochemical models where three-dimensional models can make their most important contributions to predicting future states of the stratosphere.

Three-dimensional models have been used to look at climatic effects of ozone changes. One of the most important results from such studies is the relatively large sensitivity in tropical tropopause temperatures that is predicted to accompany a change in column ozone. Such changes in the tropical tropopause temperature should give rise to changed stratospheric H_2O since we believe that stratospheric water vapor amounts are regulated by freezing out in the cold tropical tropopause entry region. Stratospheric water vapor have important radiative and chemical consequences since H_2O is radiatively active and is an important factor in HO_x chemistry.

Modern general circulation models of the troposphere-stratosphere system use full formulations of solar and infrared radiative transfer. As was previously stated, the problem of the too-cold winter pole near the stratosphere in general circulation models appears to be due to deficiencies in the dynamical heating rather than deficiencies in the radiative heating. There has been a suggestion, however, that improvements in radiative transfer can give a marked improvement in the modeled winter polar lower stratosphere. In order to meaningfully compare stratospheric general circulation models, the distributions of net radiative heating, and thus the drive for dynamics should be compared.

VII. Atmospheric Observations

Atmospheric observations are required to check the validity of models at all accessible points. The comparison of theory and observation is essential if we are to test our ability to describe the present atmosphere. Various in

situ and remote sensing techniques are now being used to determine the atmospheric concentrations of a large number of chemical species from the ground, aircraft, balloon and rocket platforms. This type of data is required to test the radiative-chemical aspects of the models. To date there have been some measurements of most of the key atmospheric constituents, with the exception of the temporary reservoirs, e.g. ClONO_2 , HO_2NO_2 , etc., which have at best only been tentatively identified. While many of these observations have been isolated measurements of a single species they have not only demonstrated the presence of these species in the atmosphere but also provided a vital yet limited test of our knowledge of atmospheric photochemistry. Obtaining measurements of these key species with the accuracy and precision, and temporal and spatial resolution required to critically test the validity of the photochemical models is a difficult task due to their low atmospheric concentrations, i.e., parts per million to sub-parts per trillion. It is now well recognized that the simultaneous measurement of several photochemically coupled species in the same air mass is necessary for the required critical test of photochemical theory; such tests are not possible from isolated measurements of single species. To date, however, there have been only a limited number of such simultaneous measurements with which to test theory. Before comparing theoretical descriptions of the present atmosphere with observations, it is vital to have an understanding of the accuracy and precision of the observations. At present it is not always obvious whether differences between measurements of the same species, at different times, are due to measurement inaccuracy or to atmospheric variability. Once the quality of the data is understood from the various intercomparison campaigns that have recently been conducted, and the newly developed instrumentation discussed later is demonstrated, it should be possible to make the type of measurements

required to critically test the photochemical models. The data collected from the recent remote sensor campaign described later will provide the most comprehensive set of known quality data with which to test photochemical models. It should also be noted that a capability to measure several species globally from satellites has now been demonstrated, and that a data base is now available to test certain features of the chemical, radiative and dynamical aspects of multidimensional models. In the longer term, these field and satellite programs will overcome our greatest problem, i.e., the shortage of data.

As indicated earlier, one of our greatest shortcomings is a lack of understanding of the accuracy and precision of atmospheric measurements. Consequently, a major effort was recently initiated to conduct a series of international intercomparison balloon measurement campaigns aimed at determining the accuracy with which the vertical distributions of key atmospheric constituents can be obtained. Numerous different instruments using similar and dissimilar experimental techniques were used to simultaneously measure a wide range of key atmospheric constituents in the same air mass. The data from these campaigns is currently being evaluated and should be available within the next six months. These include

- (a) Several campaigns employing both in situ and remote sensing balloon-borne and rocket-borne ozone instruments.
- (b) Two campaigns utilizing remote sensing balloon-borne instruments (13 on the first, and 18 on the second), using 8 different techniques including grating spectrometers, radiometers and Fourier transform interferometers, to measure several key atmospheric constituents including HNO_3 , NO_2 , NO , HCl , HF , O_3 , N_2O , CH_4 , H_2O , HO , etc. These sensors utilized the visible, infrared, far-infrared and microwave

regions of the electromagnetic spectrum in both the absorption and emission mode. These balloon measurements were supported by ground-based and aircraft-borne instruments which measured the total column content for a number of chemical species, and by meteorological and atmospheric aerosol data.

- (c) Three campaigns employing in situ and remote sensing balloon-borne water vapor instruments.

Several additional intercomparisons of balloon-borne instruments are planned, including:

- (a) In situ grab sampling techniques for source gases;
- (b) In situ and remote sensing techniques for CO;
- (c) In situ and remote sensing techniques for O₃;

Within the last two years, several newly developed in situ and remote sensing techniques have been demonstrated for species for which there had been inadequate measurements, e.g. OH. In addition, some existing techniques have been, or are being, improved which will result in greater sensitivity for a number of species, e.g. CO and O₃ by balloon-borne microwave emission. This newly developed and improved instrumentation will augment existing instrumentation in order to measure nearly all key atmospheric species over a significant altitude range with the accuracy and precision required to critically test our description of atmospheric photochemistry. An exception to this may be in the important area of the temporary reservoirs, where there are no reliable measurements to date, and where the prospects for future measurements are difficult to assess. In principle there may be hope of utilizing a high resolution infrared interferometer. Techniques that have been demonstrated within the last two years include:

- (a) Two balloon-borne far-infrared emission interferometers for remote

- sensing detection of OH;
- (b) Balloon-borne laser induced fluorescence systems for in situ and ranging detection of OH;
 - (c) A ground-based microwave emission system for remote detection of CO and HO_2 ;
 - (d) A balloon-borne laser diode absorption system for in situ detection of NO and NO_2 .

A platform, called reel-up/reel-down, has also been demonstrated whereby an instrumented package can be lowered and then subsequently raised ~ 10 km on a cable relative to a balloon-borne platform floating in the mid-upper stratosphere. This allows the atmosphere to be probed with highly sensitive in situ fluorescence instruments with high vertical resolution (~ 30 m) many times per balloon flight resulting in a substantial enhancement in the scientific return, e.g. the diurnal variability of several species can be studied in this manner, as can the fine structure in the vertical distribution of the chemical composition.

The only two parameters for which there are long-term extensive satellite and ground-based global data sets are ozone and temperature. However, a significant step forward has occurred with the validation and release of data obtained by instruments flown on the Nimbus 7, Atmospheric Explorer II, and Solar Mesospheric Explorer Satellites. This includes seven months of Limb Infrared Monitor of the Stratosphere (LIMS) data (HNO_3 , NO_2 , O_3 , H_2O , temperature), the first year of Stratospheric and Mesospheric Sounder (SAMS) data (N_2O , CH_4 , temperature), the first two years of Solar Backscatter Ultraviolet/Total Ozone Monitoring System (SBUV/TOMS) data [O_3 (column and vertical distribution) and solar flux] and the first two years of Stratospheric Aerosol and Gas Experiment (SAGE) data (O_3 , NO_2 , aerosols). In

addition, five years of polar stratospheric aerosol data are available from the SAM II experiment. These data have now been processed and archived at the National Space Science Data Center in Washington, D.C. In addition, the data from the SME satellite (O_3 , NO_2 , aerosols and solar flux) are now becoming available.

Our current knowledge of both source gases and reactive trace species will now be briefly reviewed, with emphasis on those species which can directly influence the concentration of ozone in the stratosphere.

Source Gases

Over the past few years we have become aware of a growing number of atmospheric trace gas species whose concentrations have been increasing, at least in part as a result of man's activities, and many of which are expected to affect ozone by virtue of their involvement in tropospheric and stratospheric chemistry. The list of such species includes CFC's, other halocarbons, nitrous oxide, other nitrogen oxides, carbon monoxide, carbon dioxide and, as reported most recently, methane. All of these gases are infrared active and may contribute to an increase in the temperature of the troposphere. In contrast to these other radiatively active trace species, only CO_2 will significantly change (decrease) the temperature of the stratosphere. Of these, most information is available concerning the sources of CFC's 11 and 12 and CO_2 . The key issues are the tropospheric concentrations of the source gases, the rates of change of the source gas concentrations in the troposphere, identification of the key sources and sinks for these source gases, and how the source gases are transformed into active species in the stratosphere. Prior to discussing the individual source gases by family a few general comments about their behavior in the stratosphere should be made.

Individual vertical profiles at several latitudes have been obtained for H_2 , CH_4 , N_2O , CF_2Cl_2 and CFC_3 , while in addition zonally averaged vertical profiles have also been obtained for N_2O and CH_4 from satellite. While their individual rates of decrease in the vertical direction are different, they all exhibit the same general zonal and vertical distribution. In the tropics, the profiles show less vertical changes in the 10-35 km region than in the higher latitudes. There is significantly more scatter in individual data sets in the altitude range where transport and chemical lifetimes become comparable. Theoretical models seem to be able to represent the qualitative features of each source gas distribution, but not all aspects of the available quantitative details. The most notable discrepancy is the underestimation of vertical fall-off. The new lower O_2 cross sections reduce the magnitude of this discrepancy but do not eliminate the problem. These differences have little impact on the overall budgets of the trace species families NO_x , ClO_x and HO_x in the region of greatest interest. There are only a few mid-latitude CH_3Cl and CO vertical profiles available, and they are in general agreement with theoretical estimates. The present lack of an extensive data base for these species prevents more refined analysis.

Chlorine

The dominant sources of stratospheric ClO_x are the photolysis of CF_2Cl_2 , CFC_3 , CCl_4 , and the reactions of CH_3Cl and CH_3CCl_3 with HO radicals. Atmospheric measurements of CFC's 11 and 12 have revealed a steady increase throughout the troposphere over the past decade. Such measurements are important in determining the accuracy of global release estimates, and can also be used to derive atmospheric lifetimes for CFC's 11 and 12. A network of five observing stations has been set up in locations remote from significant CFC sources, to acquire long-term data for CFC 11 and 12 (together

with carbon tetrachloride, methyl chloroform and nitrous oxide), with the specific objective of establishing atmospheric lifetimes. Analysis of the first three years data from these stations by the trend technique has shown the atmospheric lifetime of CFC 11 to lie between 60 and 160 years (one standard deviation limits), with a central value of ~80 years. For CFC 12 the lifetime obtained from these data was in excess of 80 years. Further atmospheric measurements, particularly with more accurate estimates of production and release, would help to refine these estimates. These results indicated that for both CFC's 11 and 12 tropospheric sinks are relatively unimportant. There will be a continuing need to maintain a global measurement network of high quality for CFC's 11 and 12 together with other chlorocarbons, for a much longer period, to provide an independent check on release data.

Extensive atmospheric measurement data are now available for CH_3CCl_3 and CCl_4 , but there are a number of other halocarbons for which the data base is inadequate, e.g. CH_3Cl . Atmospheric concentrations of CH_3CCl_3 continue to increase and the best estimates of its atmospheric lifetime still range from 5-10 years.

Nitrogen

The dominant source of stratospheric NO_x is the reaction of $\text{O}(^1\text{D})$ atoms with N_2O to form NO . Other less quantified sources of stratospheric NO_x are the downward transport of NO_x in the polar night due to the thermospheric production of NO from particle precipitation, and the upward transport of NO_x formed by lightning activity in the troposphere. There has also been some speculation that N_2O may be chemically produced within the stratosphere. Another source of NO_x important in atmospheric modeling is the emission of NO_x from aircraft. Recent studies indicate that the present atmospheric N_2O concentration (~300 ppb) is about 3 to 5 percent above its pre-industrial

value, and is increasing at a rate of about 0.2 percent per year. It could increase by a further 5 to 7 percent by the year 2000, depending on the level of agricultural production, increased use of chemical fertilizer and fossil fuel combustion.

The satellite data for N_2O are currently being interpreted and will provide an improved understanding of stratospheric circulation and the global rate of production of NO_x through the $O(^1D) + N_2O$ reaction. $O(^1D)$ concentrations can be calculated from the solar flux and O_3 data determined by other instruments on Nimbus 7.

Carbon

Since 1958 there have been continuous ground-based measurements of CO_2 at two sites which have shown that the atmospheric concentration is increasing as a result of combustion and deforestation at a rate of ~ 1.5 ppm per year ($\sim 0.5\%$ per year), and is expected to reach double the pre-industrial level (~ 280 ppm) by about the year 2030. This is important as CO_2 plays a key role in the radiation budget of the atmosphere. Increased levels of CO_2 would cause a decrease in the temperature of the stratosphere, and thus lead to an increase in the concentration of stratospheric ozone by affecting the rates of the key chemical reactions which control its concentration.

Observations of atmospheric methane concentrations over the past four to five years have shown that it is increasing at a rate of one to two percent per year. In addition there is also evidence, albeit somewhat less certain, from air trapped in ice-core samples that the pre-industrial atmospheric concentration of CH_4 may have been only approximately one third to one-half of today's concentrations (i.e., ~ 0.6 ppm). The lifetime of CH_4 in the atmosphere probably lies between six and twelve years and the magnitude of the global source is also rather uncertain. At this time there is only speculation as to

the factors contributing to this rise: are the source strengths increasing or is the atmospheric lifetime increasing? Methane plays a central role in both tropospheric and stratospheric photochemistry. In the stratosphere it contributes to the water budget through its oxidation and is involved in limiting the ClO_x catalytic efficiency for O_3 destruction by converting active atomic chlorine into hydrogen chloride. A quantitative understanding of its role in the stratosphere should be elucidated by utilizing the global CH_4 distribution obtained from the SAMS instrument.

There is also some provisional evidence that the atmospheric concentrations of carbon monoxide may be increasing. This would be quite significant for tropospheric photochemistry as CO controls the OH concentration which in turn limits the tropospheric lifetime for many source gases, e.g. CH_4 , CH_3Cl , CH_3CCl_3 , etc.

Hydrogen

The dominant source of stratospheric HO_x radicals is the reaction of $\text{O}(^1\text{D})$ atoms with water vapor to form OH radicals. The distribution of H_2O in the stratosphere remains difficult to understand. Current theory fails to account for many of the aspects of the fluctuations and distributions of stratospheric water vapor, e.g. why does the vertical profile for H_2O show a minimum 2-3 km above the tropopause? The source of the difficulty appears to lie both in the data quality and in a lack of theoretical understanding. It is expected that current efforts in (a) H_2O instrument intercomparisons, (b) understanding the exchange mechanisms for H_2O across the tropopause, and (c) interpretation of the LIMS H_2O data and SAMS CH_4 data, will produce an improved data base, which may lead to better understanding of this important gas in the stratosphere. As stated above, the stratospheric concentration of water vapor may increase due to increased levels of CH_4 . In addition, changes

in tropical tropopause temperatures resulting from modified atmospheric composition could also change the water content of the stratosphere.

LIMS has provided the first detailed view of the global water distribution. There is a persistently low mixing ratio of about ~2-3 ppmv in the tropical lower stratosphere, a poleward gradient at all times during the 7-month mission, and evidence of increasing mixing ratio with altitude at tropical and mid-latitudes. Perhaps even more interesting is the picture of the general two-dimensional (altitude versus latitude) stratospheric circulation revealed by the data. The strongest circulation appears to be toward the winter pole at high altitudes as theory would predict and there is evidence of lower stratospheric transport toward the summer pole. This picture is reinforced in CH_4 and N_2O data from the SAMS experiment which shows mixing ratio enhancements or depressions that tend to coincide with areas where the LIMS H_2O would suggest strong or weak circulation.

Stratospheric Distribution of Reactive Trace Species

In this section the observations of stratospheric trace species will be compared to the predictions of current photochemical models.

Odd-Oxygen Family

The oxygen species of interest in the stratosphere are ground state atomic oxygen $\text{O}(^3\text{P})$, excited-state atomic oxygen $\text{O}(^1\text{D})$, singlet molecular oxygen $\text{O}_2(^1\Delta)$ and ozone O_3 . There exist only six profiles of $\text{O}(^3\text{P})$ and one of $\text{O}_2(^1\Delta)$ in the stratosphere. $\text{O}(^1\text{D})$ has not been measured in the stratosphere because of its low concentrations. The relevant comparison for $\text{O}(^3\text{P})$ measurements is the ratio $\text{O}(^3\text{P})/\text{O}_3$. Comparisons of the measured ratios with those predicted by models show good agreement; however, the data base is limited and, therefore, not adequate to critically test these models.

Satellite observations have now provided a picture of the global mean distribution of ozone and its variations with a coverage not previously possible. Both the geographical distribution of the total ozone in a vertical column, and its concentration as a function of altitude have been measured as a function of time. These data have been analyzed into monthly mean global maps, zonal mean values as a function of time, the annual mean values over the globe (which vary with longitude) and temporal variations of the global total ozone. This latter quantity is not constant, but varies from season to season, and from one year to the next, making a search for trends very difficult. The entire 7-year BUV data set has been used to determine variations in the zonal means and in the longitudinal waves in total ozone. The satellite maps of total ozone confirm the major features found previously by ground-based measurements, and add a great deal of detail not available otherwise, particularly in the Southern Hemisphere.

Since total ozone is dominated by its concentration at levels where it is a nearly conservative tracer, total ozone distributions are dominated by circulation processes. This is shown clearly by a comparison between TOMS maps and conventional meteorological analyses which shows a coincidence between the location of the jet stream and the location of high horizontal gradients in total ozone.

Satellite observations of ozone profiles have provided a much more detailed picture of the vertical and latitudinal distribution of ozone than existed previously. High values occur somewhat above 10 mbar in the tropics, with a tongue of high values extending toward high latitudes near 5 mbar, especially in the winter hemisphere, where they can reach 2 mbar at 60°. These extensions, which may depend on the temperature dependence of the chemistry or on transport processes, were first discovered in the satellite

observations.

Data exhibiting general agreement with our theoretical picture of ozone transport have been presented. These data showed that there was an underlying region in which motions dominate the ozone distribution, and an overlying photochemically controlled region in which the temperature dependence of ozone reaction rates significantly affects the ozone distribution. The latitudinal distribution of these regions shows dynamic control extending up to only 30 km at low latitudes, but at least up to 60 km in high winter latitudes with a chemically controlled region above. The region between is characterized by the largest eddy transports. This type of information on the latitudinal variations of these regions provides useful tests for numerical models.

The ability to measure ozone both day and night with the limb IR technique allows a study of the diurnal variation of ozone. Initial results have been presented. These show detectable diurnal variations above 50 km, with magnitudes which support present theoretical expectations. However, there appears to be some disagreement between these observations and theory on the detailed temporal variation.

Simultaneous observation of temperature and ozone has allowed the study of the relation between the temperature and ozone perturbations associated with planetary waves and other dynamical phenomena in the stratosphere. With winds inferred from the temperature field, the transport of ozone by resolved phenomena has been computed.

In other studies, using SME data, results show that the ozone density in the mesosphere changes from day to day and with the seasons. The main cause appears to be temperature variations. Ozone density and temperature are inversely related, i.e., when temperatures are high ozone levels are low and vice versa. This dependence is also seen in seasonal patterns and orbit-to-

orbit variations. Maximum mesospheric ozone occurs in the winter hemisphere and the variations are greater in winter than in summer. Comparison of ozone levels with the latest model calculations at 1 mb and 0.1 mb show observations by SME to be higher by 10 percent to 30 percent. Similar problems are also noted in attempting to reconcile model calculations with LIMS and rocket measurements of O_3 in the upper stratosphere and mesosphere.

One test of the response of the atmosphere to an external perturbation is solar polar events. Results have been derived from SME and UV data for the measurement of ozone such proton events. Ozone levels were observed to decrease by up to 60 percent in the high latitude upper stratosphere and mesosphere. 1-D model calculations have been carried out giving good agreement with the observed O_3 depletions. The primary cause for this effect is production of odd hydrogen ($H+OH+HO_2$) which catalytically destroys ozone.

Odd-Hydrogen Family

Although the HO_x species play a central role in stratospheric photochemistry, knowledge of atmospheric concentrations of OH, HO_2 and H_2O_2 is inadequate. The available observations for both OH and HO_2 can do little more than demonstrate the existence of these radicals in the stratosphere and provide a crude picture of the altitude dependence of absolute concentration above 30 km. For lower altitudes, there are no published data at present, and this is a serious gap in our knowledge. This limited data base is understandable considering the difficulty of the measurements. However, several new techniques have recently been developed to measure the vertical distributions of OH and HO_2 radicals. These techniques have already been deployed and the data is currently being evaluated. This type of data will enable a critical testing of our understanding of HO_x photochemistry when obtained in

conjunction with other relevant data, e.g. H_2O and O_3 concentrations. Ground-based measurements of the total column of OH, and of the distribution of HO_2 above ~25 km, do reflect some constraint on these key species, and are indeed consistent with model predictions. OH distribution with altitude and latitude have been calculated using LIMS NO_2 and HNO_3 data by assuming photochemical equilibrium. The derived OH concentrations appear to compare well with theory. The situation for hydrogen peroxide is less satisfactory, since there are no positive observations of this species in the stratosphere and prospects for its detection in the near future are marginal. In the absence of detailed knowledge of OH, HO_2 and H_2O_2 there is no adequate test for the validity of HO_x chemistry in the models, which is urgently needed due to its control of NO_x and ClO_x photochemistry. The partitioning of NO_x and ClO_x species between active radicals and inactive reservoir species is controlled by the atmospheric concentration of OH, i.e., the ratios $ClO:HCl$ and $NO_2:HNO_3$ are both controlled by OH.

Odd-Nitrogen Family

The odd-nitrogen species considered important in the chemistry of the stratosphere are N, NO, NO_2 , NO_3 , N_2O_5 , HNO_3 , HO_2NO_2 and $ClONO_2$. Measurements have been made of stratospheric NO, NO_2 , HNO_3 and NO_3 . HCN has also been detected, but this species is not thought to be important in the photochemistry of the stratosphere. Tentative identification has been made of N_2O_5 and $ClONO_2$, and an upper limit of the abundance of HO_2NO_2 has been reported. The absence of good data for the temporary reservoir distributions is serious, e.g. HO_2NO_2 plays a key role below 30 km in both HO_x and NO_x photochemistry, and O_3 depletion calculations are sensitive to the treatment of its chemistry. Several measurement techniques have been used for NO, NO_2 ,

and HNO_3 . The balloon data exhibit considerable scatter, and it is difficult to determine changes in the vertical distribution of NO , NO_2 and HNO_3 with either season or latitude. It is not clear at present whether the scatter is instrumental or due to atmospheric variability. However, this issue may be partially resolved by the recent remote sensor intercomparison. Diurnal variations of NO and NO_2 are well established, and column density measurements show seasonal and latitudinal variations for NO , NO_2 and HNO_3 .

Model-predicted profiles of NO and NO_2 in the middle latitudes lie within the range of measurements. However, the variations in reported atmospheric concentrations are sufficiently large that comparison between observation and theory is not a critical test of model performance. In middle latitudes, the model predictions and observed concentrations of HNO_3 are now in better, although not entirely adequate, agreement above 30 km by using the revised O_2 cross sections. The upper limit reported for HO_2NO_2 at approximately 30 km is significantly lower than model predictions. Generally, it appears that available measurements of NO_x species have yet to provide a critical test of model performance.

The LIMS data for NO_2 and HNO_3 now allow the NO_x photochemistry and transport to be analyzed on a global scale. The data have been used to examine those processes which may contribute to the formation and maintenance of the so-called "Noxon cliff." From some ground-based measurements made in 1975 dramatic decreases in the column sum of NO_2 near sunrise and sunset were observed at various times during the winter. These were usually seen between the latitudes 40° to 50°N . The phenomenon was of interest because of the sharp gradients observed, its recurring nature, and the fact that no stratospheric models in existence at that time could predict gradients which approached the severity of those observed. An analysis of LIMS data which

shows a very similar phenomenon has indicated that the gradients are associated with the presence of a strong wave number one feature in the temperature and geopotential height field. Calculations suggest that the sharp gradients are formed and sustained by the conversion of NO_2 to N_2O_5 as the air parcels move along trajectories defined by the geopotential height field.

It is clear from LIMS and SME data that NO_2 exhibits rapid latitudinal variations in winter and shows hemispheric asymmetry with generally higher vertical column amount in the summer hemisphere. It also appears that southern summer values are greater than abundances in the northern summer presumably because of differences in the circulation patterns. LIMS HNO_3 data show that this gas is highly variable with both latitude and season. The mixing ratio is smallest in the tropics and largest in the winter hemisphere at high latitudes. The data also show that O_3 , NO_2 , and HNO_3 levels are strongly affected during a major stratospheric warming event. The results demonstrate for example, that O_3 tends to propagate downward in altitude during a high latitude warming situation, NO_2 latitudinal gradients are greatly reduced, and the HNO_3 high altitude longitudinal gradients are diminished.

The distribution of odd nitrogen in the upper stratosphere (above 35 km) in regions that do not include the polar night has been studied and a much sharper decline of odd nitrogen with increasing altitude was observed than is predicted by models (both one and two-dimensional) which suggests transport of odd nitrogen from the middle and upper stratosphere to the lower mesosphere where it may be photochemically destroyed. In the polar night region there is apparently a transport of odd nitrogen from the lower mesosphere into the stratosphere at high latitudes. LIMS data show nighttime NO_2 (NO_x) mixing

ratios at 70 km which are as high as 175 ppbv and there is a very steep altitude gradient with mixing ratio falling to near 10 ppbv at 50 km. There is also a clear trend of increasing mixing ratio with time from early December to mid January at all levels from the upper stratosphere to the 70 km level. The polar stereographic distribution exhibits significant longitudinal variability and high mixing ratios are strongly correlated with the position of geopotential lows suggesting localized downward transport. The net global effect appears to be a transport of odd nitrogen from the stratosphere to the mesosphere but further, detailed studies must be conducted to confirm this.

Odd-Chlorine Family

The ClO_x species consist of Cl and ClO (radical species), HOCl and ClONO_2 (temporary reservoirs) and HCl (sink species). The key species is the ClO radical, which participate directly in the destruction of ozone. Since the last assessment the ClO data base has been enlarged by measurements utilizing the ground-based microwave emission technique. These new measurements largely confirm previous balloon-based vertical profile measurements which utilized the in situ resonance fluorescence and remote-sensing microwave emission techniques. The ground-based microwave measurements utilized two spectral transitions in order to enhance the confidence that the species being observed was ClO . The emission lines were observed at exactly the correct wavelengths and the intensity ratio of the two lines was that predicted from theoretical considerations. The line positions and intensity ratio checks make it difficult to believe that the species being observed was not ClO . The balloon-based microwave measurements utilized one of the same spectral transitions. The in situ balloon measurements rely on converting ClO into Cl through chemical conversion by NO followed by resonance

fluorescence detection of Cl utilizing a spectrally pure atomic lamp. Again it is difficult to understand how the species being observed is not ClO. As stated earlier, the microwave and resonance fluorescence data sets largely agree with each other. It should be noted, however, that the resonance fluorescence data exhibits rather large day-to-day variability which is not easily explained. The ground-based microwave data exhibits day-to-day variability but of much smaller magnitude.

The infrared absorption laser heterodyne radiometric technique has also been utilized to measure ClO. The reinterpreted data reported from a single balloon-borne measurement are consistent with the data previously discussed above 35 km, but not at lower altitudes where the concentrations observed are significantly lower. It should be noted the quality of these data was less than desirable. The experiments argues that the rapid falloff with altitude can be explained by ClO being rapidly converted to ClONO₂ at sunset, when the observations were made. However, while qualitatively correct the argument appears to be quantitatively incorrect based on theoretical considerations and microwave observations of the diurnal behavior of ClO (discussed later). The same technique has also been used to measure the total column content of ClO from the ground. No positive identification of ClO has been made to date by this method and an upper limit for the ClO concentration of a factor of 6 less than the average of the resonance fluorescence observations has been reported. This is obviously an important and significant discrepancy in our understanding of ClO. The line positions of ClO in the 850 cm⁻¹ region are known accurately, but there is considerable uncertainty as to the correct line strength. However, the discrepancy will probably not be resolved simply by the redetermination of new ClO line strengths.

The weight of evidence favors the resonance fluorescence and microwave

measurements as being correct, but this does not mean that the infrared results can yet be rejected. Intensive efforts are currently underway to resolve the discrepancy through a series of laboratory and field experiments. If the microwave and resonance fluorescence data are accepted then the agreement with current theory is quite good over the complete altitude range. The earlier discrepancy at 40 km has been apparently resolved through changes in the $O+HO_2$ rate coefficient. In addition, there is good agreement between the predicted diurnal behavior of ClO and that observed from the ground-based and, to a lesser extent, the balloon-borne microwave technique. This implies that $ClONO_2$ plays a key role in atmospheric photochemistry.

The measured C_2H_6 concentrations are reasonably consistent with these low ClO measurements and current theoretical predictions for atomic chlorine in the lower stratosphere. Measurements of the concentrations of atomic chlorine in the upper stratosphere (~40 km) are limited yet consistent with the observations of ClO and the photochemical partitioning between Cl and ClO .

Measurements of HCl consist of vertical profiles from 14 to 40 km supported by ground and airborne total column measurements. Observations show a variability within approximately a factor of three and the altitude of the maximum HCl abundance and any seasonal variations cannot be clearly established. Calculated HCl profiles fall towards the middle to high end of the observations up to about 30 km, but the data at 35 to 40 km possibly indicate an HCl mixing ratio (~2 ppbv) somewhat higher than calculated values. Recent observed latitudinal variations in the HCl column are modeled fairly successfully. Calculated concentrations of the important temporary reservoir species, chlorine nitrate ($ClONO_2$) and hypochlorous

acid (HOC₂), remain below the detection limits for the observational techniques so far employed.

Aerosols

SAM II measurements are providing, for the first time, a polar aerosol climatology (in the 64° to 84° range of each hemisphere) which is showing the spatial and temporal variability of this stratospheric species. The period 1978-1979 appeared to be a period of normal background aerosol with values of stratospheric optical depths of about 0.0015 at 1 μm. The longitudinal and seasonal structure is correlated well with temperature and synoptic meteorology. SAM II data have revealed that during both polar winters, Polar Stratospheric Clouds (PSC's) are formed in regions of cold temperatures, with a 50 percent probability of occurrence for temperatures of 194K. The PSC's increase the weekly-averaged stratospheric optical depths by an order of magnitude. A cleansing of the Antarctic stratospheric aerosol is obvious after each wintertime PSC season.

The 4-year aerosol climatology being developed by the SAM II experiment clearly shows that the major perturbation to stratospheric aerosols (excluding PSC's) is of volcanic origin. Since 1979, a series of volcanic eruptions have perturbed the stratospheric aerosol in an additive manner. The time of arrival of the volcanic material in high latitudes has depended upon the location of the particular volcano and the season in which it erupted.

SAGE measurements are providing a near-global distribution (72°N-72°S) of aerosols with approximately 1 km vertical resolution allowing investigations of spatial and temporal variability, sources, sinks and transport. The measured aerosol extinction ratio supports the idea of an equatorial source with maximum values near 5°S at about 30 km altitude. Also seen in the SAGE

measurements is the increased cirrus cloud activity over the equatorial latitudes with possible penetrations into the stratosphere. Cirrus clouds appear to form most often in mid-latitudes and over the Equator. Regions where the probability of occurrence approaches 50 percent are also observed near the 20° to 30° latitude bands in the Northern and Southern Hemisphere.

Dynamics

As stratospheric satellite data have become increasingly available during the past few years, there have been several published observational analyses of stratospheric dynamics. Some of these are analyses of individual events, and others are climatological analyses of multiyear data sets. Satellite stratospheric temperature data have been used to derive diagnostics on the major wavenumber two stratospheric warming of February 1979, and this analysis has been compared with a modeled wavenumber two warming to focus on similarities and differences between modeled and observed results. Similar data were used to compare the evolution of the wavenumber two warming of February 1979 with the wavenumber one warming of February 1980. TIROS N data for January and February 1979 has also been used to derive Ertel potential vorticity in the lower stratosphere which led to evidence for "breaking" Rossby waves and the existence of a "surf-zone" in the stratosphere. The results have important implications in demonstrating irreversible mixing of a conserved tracer. LIMS data have also been used to illustrate the same phenomena for ozone which is approximately conserved in the lower stratosphere. Conventional data along with satellite data have been used to indicate that the wavenumber one amplification in January 1979, together with the minimum in wavenumber two during this period, preconditioned the stratosphere for the major wavenumber two warming of February 1979. Analysis

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of LIMS temperature data has also been used to argue for the importance of wave-wave interactions during active wintertime periods. There are also numerous recent examples of satellite data being used to identify new phenomena or to confirm the existence of phenomena predicted by theory. Data from the Nimbus 5 SCR and Nimbus 6 PMR have been used to identify a 2-day wave in the middle atmosphere which had previously been seen in rocketsonde data. This wave has tentatively been identified as a mixed Rossby-gravity wave mode, confirming theoretical model studies. SCR data from Nimbus 4 and 5 have been analyzed to show evidence for an eastward moving 4-day wave. Several mechanisms have been advanced to explain this phenomenon including barotropic instability, but at present the true origin of such a mode is unclear. Nimbus 7 LIMS data analysis has identified equatorial Kelvin waves which are theorized to play an important role in the observed quasi-biennial and semiannual oscillations of stratospheric equatorial winds, a phenomenon that has been known for many years, but not fully understood because of lack of a sufficient data base.

In the area of climatological studies of the stratosphere, there have been several different published studies of multiyear data sets. Monthly mean zonal winds, planetary wave distributions, and quasi-geostrophic refractive index squared fields have been derived from SCR data for the period January 1973 through 1977. Average Northern Hemisphere winter monthly general circulation statistics from 1000-0.4 mb have been computed using daily NOAA/NMC data for the winters of 1978-79, 1979-80, 1980-81 and 1981-82. Some of these data have been used to examine the zonal momentum budget and to infer the size of the required gravity wave induced drag on the upper stratosphere circulation. These studies have shown that there is a great deal of interannual variability in the stratospheric circulation. This has important

Implications both for testing model results against observations and for using information on stratospheric transport that has been derived from a limited number of years data or from a single model year's results for multiyear transport-photochemistry calculations.

Intercomparisons of satellite temperature data and derived dynamical quantities have been conducted with LIMS and SAMS data from Nimbus 7 and SSU data from TIROS N. Comparisons of the satellite data with conventionally analyzed meteorological radiosonde and rocketsonde data were also conducted. The general agreement among the various data provides confidence in the validity of the satellite data. These intercomparisons promise to provide insight into the uncertainties associated with derived quantities and their usefulness in quantitative diagnostic studies of the budgets of heat, momentum, potential vorticity, and constituents.

Ground-Based Measurements of Gravity Waves and Turbulence

It has become increasingly apparent in recent years that scales of motion too small to be resolved in three-dimensional models are very important in determining the heat, momentum, and constituent budgets of the mesosphere. It has been suggested that these small-scale motions (gravity waves and turbulence) may also be quite important in determining stratospheric structure. Sensitive radars have demonstrated the capability to observe gravity wave velocities and turbulence in the stratosphere, and lidars have shown their capability of observing gravity wave temperature variations in the stratosphere. Effort is being made toward developing the theoretical framework and obtaining observed data on gravity waves and turbulence so that we may understand the influence of these small-scale motions on the global structure of the stratosphere and mesosphere sufficiently to include their

effects properly in three-dimensional models.

Troposphere-Stratosphere Exchange

In order to understand how man's activities affect the stratosphere, it is necessary that we understand how tropospheric and stratospheric air are exchanged. One particular aspect of this problem is to understand the stratospheric water budget. One idea put forward to explain the observed small values of water vapor mixing ratios in the stratosphere is that practically all stratospheric air must enter from the troposphere through the tropical tropopause in locations where the temperature is less than -80°C . Analysis of tropopause temperatures indicates that these very low temperatures exist mainly over Indonesia in the winter and India in the summer. This implies that virtually all stratospheric air must pass through these entry regions. Tests of this physical picture require aircraft measurements of the dynamics and composition at these proposed entry regions.

VIII. Model Predictions

As discussed in Section II above, one of the primary reasons for the scientific study of the upper atmosphere concerns possible long-term changes in the total column content and the vertical distribution of ozone. In much the same way that measurements of the composition of the present-day atmosphere allow us to test the ability of our theoretical models to describe the mechanisms that control the distribution of the chemical constituents, long-term measurement of the change (or lack thereof) in key parameters, e.g. ozone, provides a partial test of the model's ability to predict the response of the atmosphere to changing conditions.

Our goal is to understand how the atmosphere will respond to the variety

of changing conditions which have been occurring and will continue to occur. The first step in attempting to understand the atmospheric response to changing conditions is to consider the idealized case of an individual perturbation. These individual perturbations determined from model computations assume that one particular input to the model (e.g. chlorofluorocarbon release) is changed while all others are held constant. The model is then usually integrated until a steady state is reached and the ozone concentration is compared to a similar calculation without chlorofluorocarbon release.

Predicted changes in the total column ozone at steady-state due to the continued release of fluorocarbons 11 and 12 at 1977 release rates have again declined since the previous assessment (January 1982 based on the 1981 WMO/U.S. Agencies Report). Agreement on the exact number is surprisingly consistent considering that less effort was made to constrain modelers to a single set of rate coefficients for this report than was the case for previous reports. However, it should be noted that most modelers used the same chemistry. The results received from the modelers thus vary somewhat due to differences in input parameters (e.g. the vertical diffusion coefficient).

Table 1 contains the results reported by various modeling groups plus a few results inferred from their reported values. Care must be taken to read the notes accompanying the table because they spell out which are the actual results from the model, which are extrapolated, and what logic was used in the extrapolation. The table shows steady-state calculations of the changes in ozone column amount for the idealized release of fluorocarbons 11 and 12 in an otherwise unchanged atmosphere. An attempt has been made to normalize all results to the 1977 fluorocarbon release rates of 0.94×10^7 molecules F-11/cm²/sec (340×10^6 Kg/yr) and 1.30×10^7 molecules F-12/cm²/sec (414×10^6

TABLE 1

Depletions in the ozone column obtained by various modeling groups for the idealized addition of fluorocarbons 11 and 12 at the 1977 release rates to an otherwise unchanged atmosphere. Results are for the steady-state, and the release rates are $0.94 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ ($340 \times 10^6 \text{ Kg/yr}$) F-11 and $1.30 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ ($414 \times 10^6 \text{ Kg/yr}$) F-12. Results in parenthesis are for the older, higher O_2 dissociation cross sections in the Herzberg continuum as discussed in the text. Chemistry is, in general, from the JPL 82-57 review.

	Without Temperature Feedback		With Temperature Feedback	
Size and Ko	-3.3%	(-4.6%)	-3.6%	(-5.1%) ¹
Owens	-3.3%	(-4.4%)	-4.3%	(-5.7%)
Wuebbles*	-3.3% ²		-4.2% ³	
Cicerone*	-4.2% ⁴		-	
Prather	-4%		-	
Herman	-5% ⁵		-	
Turco	-4.3%		-	
Pyle	-		-	(-7.2%) ⁶
Liu*	-	(-5.4%) ⁷	-	
Isaksen	-5% ⁸		-	
Callis	-5.5%		-6.3%	

*Obtain significant nonlinearity as a function of Cl_x release rate.

Notes for Table 1

1. Estimated by multiplying fixed temperature calculations by 1.1 (Sze, personal communication).
2. Estimated by multiplying model with fast $\text{OH}+\text{HNO}_4$ by 1.27 according to sensitivity test (Wuebbles, personal communication).
3. Estimated from temperature feedback effect from slightly different case.
4. Small O_2 cross section slightly higher than Herman and Mentall -might contribute a few tenths of O_3 depletion. Depletion calculated above 10 km only. Number in Table assumes no change below 10 km.
5. Scaled from result with very low diffusion coefficient which led to $\text{Cl}_x = 9.6$ ppbv and give -6.1%.
6. Two-dimensional model
7. Scaled from results with larger fluxes (may be somewhat smaller due to nonlinearity).
8. Two-dimensional model result.
Not certain about O_2 cross section used.

Kg/yr). Results are shown with and without radiation/temperature feedback and with and without the newly reported smaller absorption cross sections for the O_2 Herzberg continuum, which are discussed in Section IV above. The chemistry is that given in the JPL-82-57 kinetics evaluation. Section IV discusses the reasoning which led to the assumption that recent revisions in the $O+ClO$ and $OH+HCl$ rate coefficients are approximately cancelling. The current, most-probable result for steady-state release at 1977 rates appears to be in the range of a 3.3-5.5% decrease in the ozone column. This includes smaller O_2 photolysis cross sections, as recently proposed, but no temperature feedback. Inclusion of temperature feedback increases these numbers to 3.6 to 6.3%. The uncertainty in the amount of change due to radiative feedback is probably related to the fact that the radiative models used for such feedback calculations have not been intercompared. Some of the results probably diverge from one another because of differences in inputs and assumptions which have not been fully spelled out.

The models continue to predict ozone depletions, centered about 40 km, comparable in magnitude to those in previous reports (~45-65%). In the lower stratosphere increases are now predicted, which are the source of a great deal of the uncertainty in the column ozone calculation. The radiative feedback decreases the predicted ozone depletion in the upper stratosphere and lessens the increase in the lower stratosphere which more than offsets the upper stratosphere, leading to a larger predicted decrease in the column of ozone. Although this can be considered a known feedback which is clearly to be included in these calculations, its primary effect on the column is in the lower stratosphere, a region where one-dimensional models are the most uncertain. Thus, radiative feedback calculations should be viewed with some caution.

A further interesting development is a reported nonlinear ozone depletion due to increasing Cl_x . This question seems to sharply divide the modelers into two groups: those who obtain a highly nonlinear effect such that the ozone column actually increases for small added Cl_x , and those who obtain only a weak nonlinear effect with no ozone increase evident. Both groups obtain about the same answer for large perturbations (e.g. steady-state release at 1977 rates). Necessary conditions for this nonlinearity have been explained to include a combination of low OH concentrations in the lower stratosphere and fast chlorine nitrate formation. Under these conditions addition of chlorine would interfere with NO_x catalysis in a NO_x -dominated lower stratosphere. Eventually this effect would saturate, and chlorine catalysis would dominate the perturbation. Sufficient conditions for the highly nonlinear effect are not obvious since a number of modelers reported an inability to obtain such a result, despite their significant efforts to do so. A full understanding of the coupling of HO_x - NO_x - Cl_x in the lower stratosphere, and its implications, remains an active and important area of research.

As stated earlier, there is evidence that the tropospheric burden of N_2O is increasing at a rate of 0.2 percent per year. A doubling of the N_2O flux from the troposphere to the stratosphere in the models is now predicted to result in about a 10-15% depletion in the ozone column. Current photochemical models predict that injections of NO_x at either 17 or 20 km (from a hypothetical fleet of supersonic aircraft) would result in a decrease in the stratospheric column of ozone. This contrasts to earlier estimates which reported ozone increases. However, injections of NO_x in the upper troposphere (from subsonic aircraft) and the lowest regions of the stratosphere are still predicted to result in the production of ozone in the troposphere and lower

stratosphere.

Figure 2 summarizes how ozone depletion predictions have evolved since 1974 for both ClO_x and NO_x injections. An important point to note in this figure is the tendency for the evaluations of NO_x and ClO_x perturbations to be inversely related. Many of the changes in rate coefficients have led to changes in the calculated lower stratospheric HO concentration. Since no measurements of OH have yet been reported in this region it remains as an unconstrained parameter which affects the NO_x and ClO_x catalytic cycles in the opposite direction. HO reacts with NO_2 to form HNO_3 , an important reservoir for NO_x while it also reacts with HCl returning chlorine to catalytically active ClO_x . One exception to this general tendency is the discovery of the importance of chlorine nitrate formation where both NO_x and ClO_x are tied up in the reservoir. The low concentrations of ClO observed below 30 km are consistent with the calculations that predict 3-5% depletion in column ozone, but not the earlier calculations that predicted 15-18% depletion in column ozone.

Recently more emphasis has been placed on understanding the coupling between the effects of all the atmospheric constituents whose concentrations are changing (such as N_2O , CO_2 , CH_4 and NO_x) and the chlorofluorocarbons. Only through such attempts to model the combined effects of all potential perturbations can we obtain a prediction from theory as to how ozone should change such that we can test this prediction with atmospheric data. The combination of all of these effects into a prediction for the future changes in ozone is, of course, critically dependent on the assumptions of future scenarios for the fluxes of various components. This makes ozone depletion scenarios quite uncertain. For instance, the doubling of CO_2 levels (estimated to occur by the year 2050) is predicted to decrease the potential

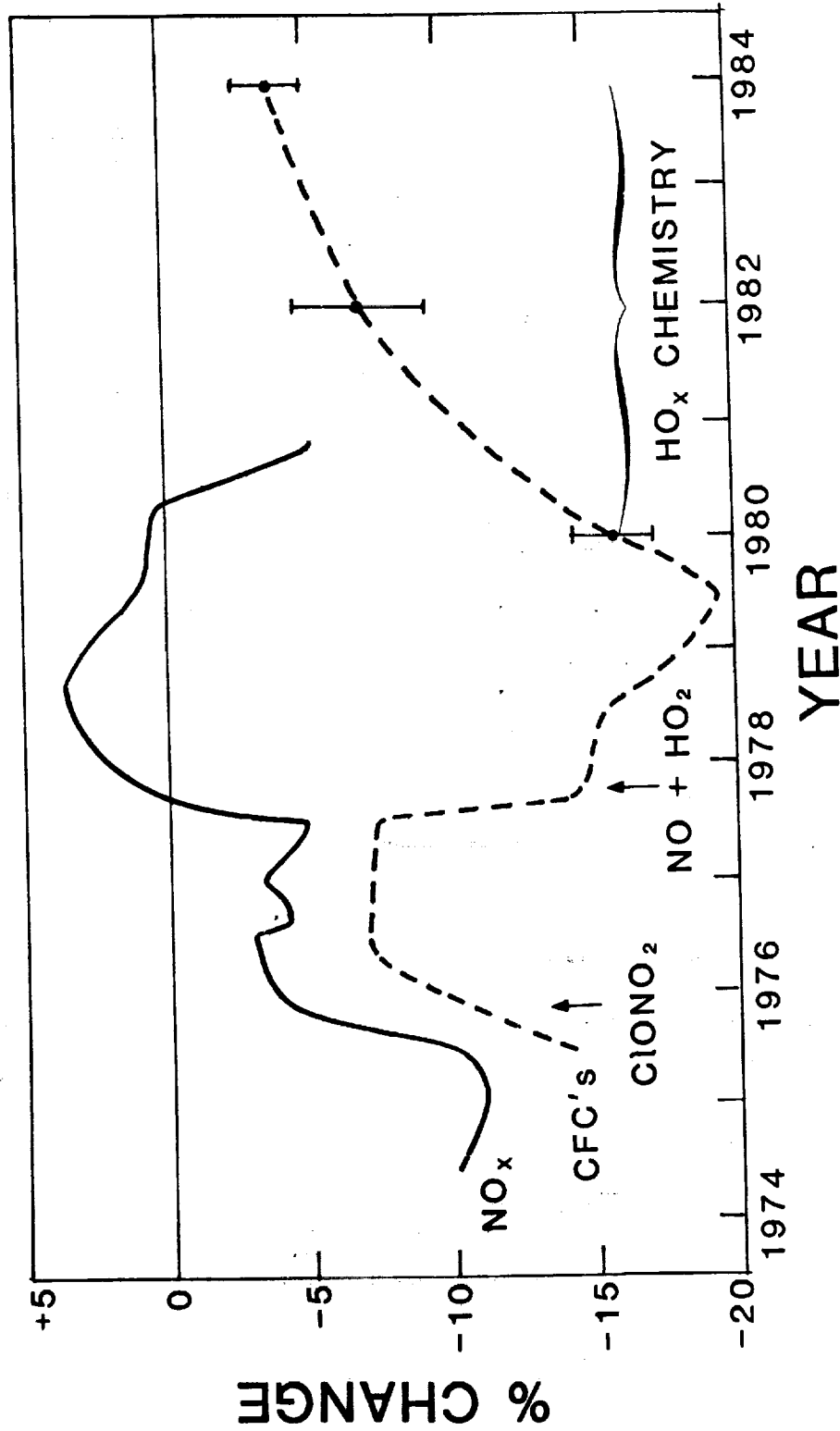


Figure 2. Column ozone depletion predictions from 1974 to 1984

fluorocarbon impact on ozone column by modifying the temperature of the stratosphere and thus affecting the rates of the temperature dependent chemical reactions.

As stated earlier, evidence has now been found that methane is increasing at ~1.5%/year, but significant doubt exists as to how far forward in time this increase can be projected. An increase in methane should increase water and HO_x in the middle and upper stratosphere giving rise to ozone decreases, however, a more important impact of increasing methane is its impact on chlorine and nitrogen chemistry. Methane is the principal reactant to convert catalytically active ClO_x to the HCl reservoir. The most significant variable in the scenario calculations is whether or not methane is assumed to continue its rate of increase. Assumption of a continued increase at 1.5% per year implies that total ozone column decreases do not occur in the overall scenario. Assuming constant methane, decreases in the ozone column are predicted to occur after a few decades. This implies great uncertainty in scenario predictions because the cause of the methane increase is not known and it is not possible to predict its future course with much certainty.

A principal feature of these scenario calculations in our last report 2 years ago, was that column ozone change up to the present time should have been very small or even positive due to cancelling effects and that depletions greater than 1% would not take place until fluorocarbons began to dominate. Methane increase further enhances the positive tendencies. It must be remembered that even when no significant changes in the ozone column are predicted, significant changes are being predicted in the altitude distribution of ozone, with decreases above 30 km and increases below. These can have consequences on the radiative balance of the stratosphere and perhaps the atmosphere as a whole.

Ozone Trend Detection

Attempts to infer trends in the globally averaged total ozone abundance have utilized both the ground-based network of Dobson stations and measurements from the Nimbus 4 BUV instrument. With the availability of a data base covering 4 years, studies in the near future will also include data from the Nimbus 7 SBUV experiment.

Statistical regression models devoted to total ozone trend studies must take account of the annual, semiannual and quasi-biennial cycles as well as a long term linear change. In addition, to obtain a globally averaged value from the Dobson network it is necessary to consider the representativeness of the geographic coverage obtained. Analysis of data for the periods 1970-1979 show no evidence of statistically significant global trends, with estimates of $+0.3 \pm 1.3\%$ (1970-78) and $+0.5 \pm 1.4\%$ (1970-79). The error bars represent 95% confidence limits with 36 Dobson stations entering the means. Note that these results indicate increases in ozone, although not at a significant level.

In principle, the global coverage obtained by satellites is preferred to the more limited geographic coverage provided by the Dobson network. However, the total ozone data provided by the Nimbus 4 BUV experiment indicates an instrument drift of approximately 0.5% per year relative to the ground-based measurements. Unless such long term drifts can be eliminated or corrected in future satellite experiments, the Dobson network will remain the only viable data source for the detection of trends in total ozone.

The accumulation of a long term data base for stratospheric ozone as a function of altitude is now beginning to allow meaningful searches for long term trends arising from the mechanisms discussed above. Because the data base for ozone profiles is of shorter duration than that for total ozone it is

important to acknowledge the existence of other agents capable of driving variability over extended times, for example, the variability of the ultra-violet solar spectrum over the 11-year cycle. Whereas the response of upper stratospheric ozone to the chlorine released from CFC's is predicted to be a long term decrease, approaching a steady state in the next century, the solar cycle variation has a cyclical character that would alternately interfere constructively and destructively with the longer term changes. The need for an ozone data base covering very long time periods here becomes apparent if one is to isolate changes arising from one or the other source.

The confirmation of a long term trend in stratospheric ozone would be an event of considerable scientific importance. However, efforts toward this end require data bases whose temporal continuity and precision exceed those achieved in most past research. The longest data base available is that from the ground-based Umkehr method of remote sensing which provides information on the vertical ozone profile up to 48 km, although several complications impact the accuracy of the technique. The geographic coverage obtained by the present Umkehr method is restricted. A long term data base covering on the order of two decades is available at some stations. Satellite systems are becoming operational which may meet the requirements for the study of long term changes in ozone. The data base presently available in this area is still relatively modest in its temporal coverage, although the coming decade will bring a continuing acquisition of satellite data relevant to the study of long term trends.

Attempts to infer the existence and character of long term trends in ozone from data obtained by the Umkehr method have led to an increased awareness of the difficulties involved in seeking small, statistically significant, changes in measurements whose quality is affected by factors beyond the

control of the analyst. Examination of the long term Umkehr record at selected stations shows occasional discontinuities in the measurements which are indicative of instrumental or procedural changes. Assembly of an internally consistent data set therefore requires inclusion of shifts in the tabulated numbers. More significant is the fact that, like any remotely sensed signal, the ultraviolet radiances measured in the Umkehr technique are related to ozone only through a fairly sophisticated theory of radiative transfer. The methodology routinely used in data reduction does not necessarily include all physical processes that impact the flow of radiation through the Earth's atmosphere. In fact, the presence of stratospheric aerosols and dust has an important effect on the ozone amounts inferred in the uppermost Umkehr layers, numbered 7, 8, and 9, covering the altitude range 34 to 48 km. Photochemical models predict the greatest reduction in ozone arising from fluorocarbon chemistry to occur in Umkehr layer 8, between 38 and 43 km, in the region where contamination by aerosols is significant. Clearly, analyses of the Umkehr record must account for the impact of these complicating processes on atmospheric transmission.

Early analyses that neglected the impact of aerosols on the Umkehr record generally concluded that any trend of the type predicted for CFC's was not evident in the measurements. However, in this methodology the atmospheric transmission, which clearly responds to the variable stratospheric dust loading associated with volcanic eruptions, acts to bias the results. Inclusion of this effect as a separate term in the regression model to account for changes in optical depth reveals the existence of a long term decrease in upper stratospheric ozone whose magnitude and altitude dependence are very similar to those predicted for a CFC-related depletion. Long term ozone trend results for Umkehr layer 7 (34-38 km), 8 (38-43 km), and 9 (43-48 km) are

$-0.22 \pm 0.17\%$ per year, $-0.30 \pm 0.16\%$ per year, and $-0.29 \pm 0.39\%$ per year respectively. The error bars define the 95% limits of confidence, and the results incorporate measurements from 13 Umkehr stations which have observations over periods extending from, typically, the early 1960's to 1980. Furthermore, the value of the regression coefficient deduced in the model, which multiplies the atmospheric transmission function, is consistent with theoretical calculations of this quantity.

Satellite instruments offer the best hope for studies of long term trends in ozone because of their continuous global coverage. Unfortunately, practical problems enter since a single instrument undergoes changes in sensitivity over long periods of operation. Analysis of tropical radiance data provided by the Nimbus 4 Backscatter Ultraviolet (BUV) experiment reveals a wavelength dependent drift which increases from approximately 1.1% per year at 292.2 nm to 1.6% per year at 255.5. These instrument artifacts are sufficiently large to overwhelm trends of the size predicted for CFC-related chemistry. The problem of instrument sensitivity changes is much less severe, although still present, on the Nimbus 7 Solar Backscatter Ultraviolet (SBUV) experiment which has been operating since late 1978.

IX. Future Developments

Several programs are being implemented, or are being planned, to enhance our understanding of the stratospheric system so that our predictions of future states can be made with greater confidence. New instrumentation is being developed that will allow measurements of many of the temporary reservoir species, such as HO_2NO_2 , ClONO_2 , N_2O_2 , and HOCl , for which adequate measurements do not presently exist. More in situ intercomparison campaigns are planned that will give us much greater knowledge of the accuracy of

various measurement techniques. Shuttle-borne instrumentation will also expand our measurement capability for stratospheric constituents.

The Upper Atmosphere Research Satellite Program (UARS) will give us much more complete measurements of the global distribution of important species in the stratospheric O_x , NO_x , and HO_x chemistry and will, for the first time, give measured global distributions of important species in stratospheric ClO_x chemistry. UARS will also give us directly measured stratospheric winds for the first time.

In assessing the effects of tropospheric chemical sources on stratospheric composition, a very important factor is our understanding the transport processes by which tropospheric and stratospheric air are exchanged. Major new aircraft measurement programs will be carried out to investigate the physics of these processes. This, together with newly available satellite data, should put our understanding of troposphere-stratosphere exchange processes on a much firmer basis.

The SBUV instrument is being deployed on operational NOAA spacecraft to give us well calibrated satellite measurement of the global O_3 distribution so that better O_3 trend determinations can be made.

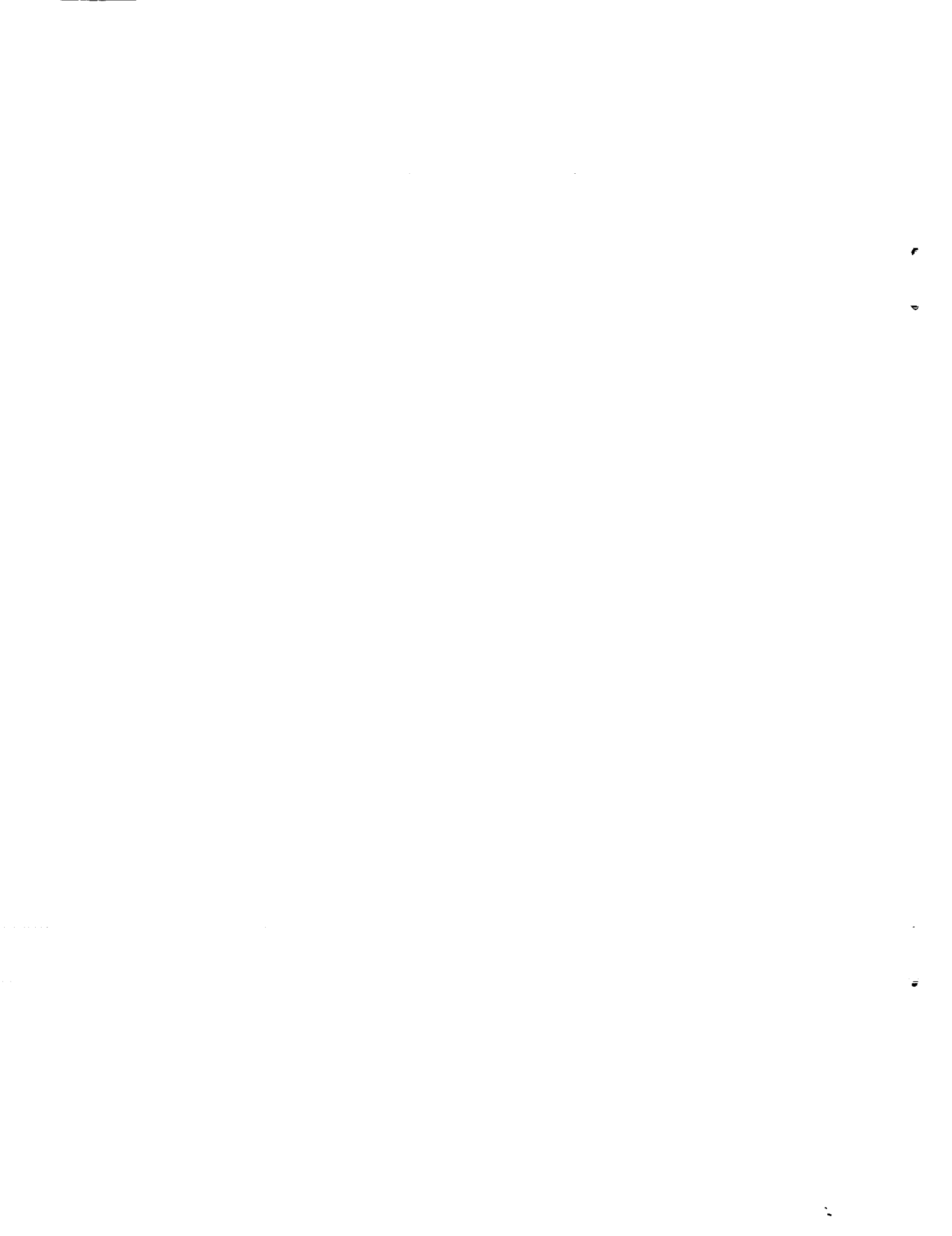
Finally, theoretical modeling and laboratory investigations are being carried out that will continue to put our study of the stratosphere on an even firmer basis.

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