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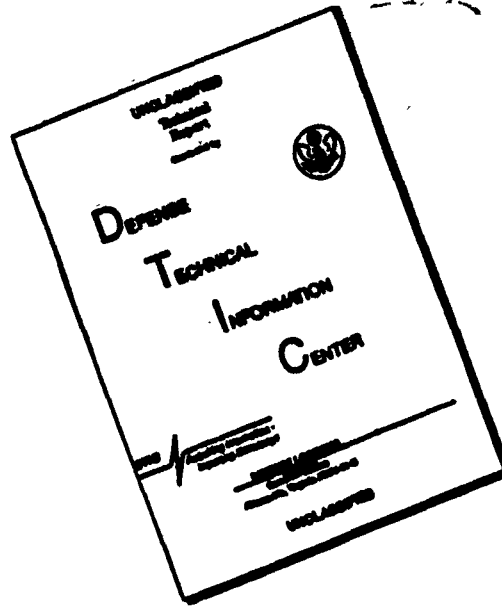
REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget/Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 4 June 1991	3. REPORT TYPE AND DATES COVERED Reprint	
4. TITLE AND SUBTITLE Handbook for MAP, Vol 32, Chapter 1 Structure and Composition			5. FUNDING NUMBERS PE 62101F PR 7601 TA 22 WU 02	
6. AUTHOR(S) J.M. Russell, III*, W. Swider			DTIC ELECTE JUN 21 1991 S C D	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Phillips Laboratory (PH) Hanscom AFB Massachusetts 01731-5000				
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER PL-TR-91-2128	
11. SUPPLEMENTARY NOTES *NASA/Langley Reprinted from Summary Report of the International Middle Atmosphere Program, Handbook for MAP, Vol 32, Part 1: MAP Summary, R.A. Vincent ed.			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; Distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) There is a very strong and complex interaction between the basic temperature structure, the neutral and ion composition, dynamics and transport, radiation, and chemistry of the middle atmosphere. In this chapter recent developments in our understanding of the structure and composition is summarized.				
14. SUBJECT TERMS Atmospheric Ion Composition, Atmospheric Ion Chemistry, Atmospheric Conductivity, D-region, Ionospheric Structure			15. NUMBER OF PAGES 20	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR	

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PROGRAM

HANDBOOK  
FOR MAP

Volume 32

- Part 1:  
MAP Summary
- Part 2:  
MAPSC Minutes, Reading, August 1989  
MAP Summaries from Nations
- Part 3:  
MAP Data Catalogue

Edited by  
R. A. Vincent, Part 1  
B. Edwards, Part 2  
I. Hirota, Part 3

January 1991

Published for the ICSU Scientific Committee on Solar-Terrestrial Physics (SCOSTEP) with financial assistance from the National Aeronautics and Space Administration under the 1988 Middle Atmosphere Program Management Contract and Unesco Subvention 1988-1989.

Copies available from SCOSTEP Secretariat, University of Illinois, 1406 W. Green Street, Urbana, Illinois 61801.

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91-02702



## STRUCTURE AND COMPOSITION

by J.M. Russell III, and W. Swider

There is a very strong and complex interaction between the basic temperature structure, the neutral and ion composition, dynamics and transport, radiation, and chemistry of the middle atmosphere. In this chapter recent developments in our understanding of the structure and composition is summarized, while progress in the other topics is dealt with in the following chapters.

1.1 Basic Temperature Structure

Knowledge of the basic structure of the middle atmosphere has improved significantly in the past decade. Measurements of thermal emissions made by a series of satellite-borne sensors, such as the downward looking SCR and PMR experiments and the limb-viewing measurements of the LIMS and SAMS sensors carried on various Nimbus satellites, have provided a global coverage of temperatures up to heights near 85 km, with height resolutions of between 3 and 10 km. Since 1978 stratospheric temperatures have been monitored by the Stratospheric Sounding Unit (SSU) on the NOAA series of operational weather satellites which has three 12-15 km thick weighting functions peaking in the 20-45 km altitude region. The instrument has provided daily measurements of the three-dimensional temperature field. These have been used for many studies of phenomena such as stratospheric warmings, long-term temperature trends, wave propagation and so on. In the next decade the SSU will be replaced by channels in the Advanced Microwave Sounder (AMSU) which will have a better vertical resolution of about 10 km.

The satellite observations have continued to be complemented by rocket measurements which provide not only 'ground-truth' for the satellite measurements but, because of their excellent height resolution, enable the fine structure due to tides and gravity waves to be studied. An important recent development has been the deployment of ground-based Rayleigh-scatter lidars which enable densities and temperatures to be measured at heights above 30 km with very high time (few minutes to hours) and height (~1 km) resolution.

The measurements, especially those made by satellites, have led to the production of improved climatologies and reference models for middle atmosphere structure, not only of temperature but also other important related parameters such as pressure, density and wind (e.g. see BARNETT and CORNEY (1985) and other references in the Handbook for MAP, volume 16). The almost global coverage provided has been especially valuable in allowing the structures of the northern and southern middle atmospheres to be intercompared; it is now clear that there are significant hemispheric differences in, not only the basic temperature structure, but also the planetary wave activity. The northern hemisphere winter stratospheric temperatures at high latitudes are warmer on average by some 5-10 K than the corresponding values in the southern hemisphere, except near the stratopause. The lower and middle stratosphere in the winter polar southern hemisphere is especially cold with temperatures falling as low as 180 K on average near 25 km altitude. Such low temperatures seem to be an important factor in the generation of stratospheric clouds which in turn appear to play a crucial role in the development of the Antarctic Ozone Hole (see 2.5.2, 5.3.2). In summer, the stratopause in the southern hemisphere is 5 K warmer than in the northern hemisphere.

Departures from zonal symmetry in the monthly means give information on the temperature structure of quasi-stationary waves. Penetration of waves with zonal wavenumbers 1 and 2 occurs most readily in winter with maximum wave

amplitudes being observed near the polar stratopause and decaying in the mesosphere. The peak amplitudes of wavenumber 2 ( $\sim 2-3$  K) are smaller than wave 1 ( $\sim 8-10$  K) in both hemispheres. Significant interannual variations may occur. There are also inter-hemispheric differences in wave amplitudes with the middle atmosphere in the northern hemisphere being more disturbed than the southern hemisphere, a characteristic caused by the differences in topography between hemispheres. The greater wave activity in the northern hemisphere probably accounts, at least in part, for the warmer wintertime stratospheric temperatures noted above.

The satellite measurements have also given a better picture of the day-to-day departures from the zonally-averaged structure. A number of these transient features in temperature and geopotential height have now been identified as manifestations of travelling atmospheric normal modes, which have well defined latitudinal structures and whose generation is not related to details of tropospheric forcing. Waves of various periods have been observed, amongst them a westward propagating wave of 5-day period and a 16-day oscillation which has especially large amplitudes in the northern hemisphere winter. There is some evidence that interference of this (and other travelling waves) with the quasi-stationary waves may play an important role in preconditioning the atmosphere prior to stratospheric warmings.

Rocket and recent satellite limb soundings have proved important for the study of low horizontal-wavenumber equatorial waves. Periodicities of several days have been observed with temperature variations of up to several degrees associated with vertical structures of  $\sim 5-40$  km. Spectral decomposition suggests that these disturbances are caused by eastward-propagating Kelvin waves; features due to westward-propagating Rossby-gravity waves have yet to be positively identified.

The temperature fluctuations produced by gravity waves are of too small a spatial scale to be resolved by satellites and so studies of their wave activity has relied mainly on the use of rocket soundings and more recently on lidar measurements. Amplitudes vary between  $\sim 1-5$  K in the stratosphere and  $\sim 10-20$  K in the mesosphere. From an analysis of meteorological rocket data HIROTA (1984) produced climatologies of wave activity which show an annual variation in activity in the high-latitude stratosphere with a winter maximum and a semi-annual variation (equinoctial maxima) in the sub-tropics.

The largest interannual variability is observed in the winter stratosphere. The most disturbed winters in the northern hemisphere tend to be associated with wavenumber 1 patterns and less disturbed winters with wave 2. Maximum variability in the southern hemisphere occurs in October and November at the time of the final warming, which occurs at a later time in the seasonal cycle than in the northern hemisphere.

Large temperature anomalies are caused by irregularly occurring wintertime stratospheric warmings which can have a major impact on the structure of the middle atmosphere. A number of studies have been made of both the large and small scale structure associated with warmings. A noteworthy international project was the Winter In Northern Europe campaign (MAP/WINE) of 1983/84 which combined observations using satellites, rockets and ground-based sensors located in a number of countries in the northern hemisphere and focussed on high-latitude regions of Europe. Preliminary results from MAP/WINE are introduced by VON ZAHN (1987) and discussed in accompanying papers. In the disturbed conditions associated with warmings, where sharp horizontal and vertical gradients in temperature are observed, the use of all available rocket, radiosondes and ground-based data proved crucial in the retrieval of temperatures from the satellite measured radiances. As far as the large scale

structure was concerned, the campaign revealed in detail the longitudinal variations of up to 50 K in temperature that can occur at a given latitude and height as well as the anti-correlation in temperature variations between the stratosphere and mesosphere. The high time resolution data from lidars and rockets revealed temperature fluctuations in the upper stratosphere on time scales of ~25 days which were related to a succession of minor warmings.

Although the generation of stratospheric warmings is not well understood, recent studies suggests a remarkable tendency for the occurrence of major warmings to be associated with solar cycles and the phases of the quasi-biennial-oscillation (QBO) in the tropical stratosphere. LABITZKE and VAN LOON (1988) show that in 3 solar cycles no major warmings occurred in the west phase of the QBO during solar minima whereas in east phases of the QBO major warmings tended to take place at the minima of the cycles.

## 1.2 Neutral Composition of the Middle Atmosphere

A dramatic improvement in our understanding of the middle atmosphere has taken place since the last MAP planning document was written. This has occurred primarily as a result of improved observational techniques being applied from ground, balloon, rocket, and satellite-based platforms. A series of satellite-experiments were launched during the MAP/MAC time period which used limb emission, occultation, and scattering methods to provide near global, collective data sets on temperature,  $O_3$ ,  $NO_2$ ,  $N_2O$ ,  $HNO_3$ ,  $CH_4$ ,  $CO$  and aerosols. These included flights of the SAMS, LIMS, SAM II, SAGE, SAGE II, SME, TOMS, and SBUV experiments. The major findings from these missions are summarized in World Meteorological Organization (WMO), 1982 and WMO, 1986. In addition to these measurements, two solar occultation experiments, the Grille Spectrometer and ATMOS, were launched on Spacelab 1 and 3, respectively, and have provided measurements of a host of minor gases at a few selected latitudes. An overview of these results follows with emphasis on outstanding problems and questions. The discussion is organized according to chemical family, including odd oxygen, odd nitrogen, odd chlorine, odd hydrogen and aerosols.

### 1.2.1 Odd Oxygen ( $O_y$ )

There are two odd oxygen gases of interest for middle atmosphere studies. The first, ozone ( $O_3$ ), is of central importance for a number of reasons including its role as a shield to Earth life from the extreme ultraviolet rays of the Sun and its effect on chemistry, radiation, and dynamical processes. The second is atomic oxygen which is important in atmospheric chemistry and energetics studies. A brief summary of current knowledge of the distributions of these gases, with discussion of future research needs, is included in the following paragraphs.

#### 1.2.1.1 Ozone ( $O_3$ )

Extensive satellite observations of the vertical ozone profile and the total ozone amount have provided a detailed picture of seasonal variation and changes with altitude, latitude, and longitude. The results confirm prior data showing that ozone is highly variable with maximum mixing ratios occurring at  $\approx 30$  km in the tropics. One of the key questions regarding ozone is what, if any, are the long-term changes in the ozone profile and integrated column amount? Satellite results from different experiments are not in agreement on vertical profile changes, with some showing definite decreases and others indicating little or no trend over a 7 year period. These data are the subject of a recent report by an ozone trends panel created by the NASA, NOAA, FAA, WMO, and UNEP organizations. Regarding the total ozone amount, the panel report noted, based on Dobson data, that ozone has decreased by 1.7 to 3 percent averaged over the

latitude range 30°N to 64° N between the years 1969 to 1986. It further points out that these changes are "broadly consistent" with model calculations. Wintertime decreases are much larger and are not consistent with model calculations. The Dobson network shows winter decreases of 2.3 percent between 30°N - 39°N, 4.7 percent between 40°N - 52°N, and 6.2 percent between 53° - 64°N. When satellite SBUV and TOMS data are normalized to the Dobson network and used to determine changes over the wider latitude range from 53°S to 53°N, the results show an ozone decline of about 2.5 percent over the 1978 to 1985 time period. This is the net change after corrections have been applied to the data for the effects of solar activity variations and the quasi-biennial oscillation.

The question of long-term ozone change is a critical one which should continue to be addressed both at selected ground sites and from satellites. Measurements should be made over a long time period using well-calibrated schemes that allow periodic updates with high accuracy.

Long-term observations are especially important in view of the recently discovered Antarctic ozone hole phenomenon which appears to be deepening each year in September and October. It is not unusual for column abundances to decrease to less than 30 percent of the long-term climatological average. In 1987, for example, amounts as low as 100 Dobson units were recorded - the lowest anywhere on the globe. Although evidence suggests that a likely cause of the "hole" is heterogeneous catalysed chlorine chemistry associated with extensive build-up of polar stratospheric clouds in the Antarctic winter (6.3.2), the phenomenon is poorly understood and the extent of the latitude spreading of this effect due to transport or dynamics/chemical mechanisms is unknown. It is a concern which needs to be addressed by well-understood observational techniques that provide sufficient sampling so that trends, or lack thereof, can be determined with confidence.

Another feature of the ozone distribution which is not understood at present is the lack of agreement between observed and calculated values in the upper stratosphere. Observations are 30-50 percent higher than model results above 35 km where the atmosphere is predominantly under photochemical control. Such large differences are surprising, and since independent measurements agree with one another to within 10 percent, it appears that there are fundamental problems with theory.

#### 1.2.1.2 Atomic Oxygen

Atomic oxygen is a critical gas in the odd oxygen photochemistry and is important in controlling ozone destruction. Its high reactivity and low concentration in the stratosphere makes it a challenging gas to observe by either in situ or remote-sensing methods. As a result, global observations have not been made, and only a small number of local stratospheric measurements has been made using balloon-borne sensing. Consequently, our state of knowledge of this constituent below about 65 km has not significantly advanced in recent years. A number of mesospheric and thermospheric measurements have been made from ground-based, rocket, and space platforms by a variety of techniques, including in situ resonance fluorescence, airglow emission using the 558 nm green line due to O(<sup>1</sup>D), the atmospheric O<sub>2</sub> band (caused by recombination of O), mass spectrometry, resonance scattering methods, and remote sensing based on O(<sup>3</sup>P) limb emission observations in the far infrared at 63 μm. As a result, the vertical distribution is better known now than before. There appears to be improved consistency among measurements which give a value of 10<sup>11</sup> to 10<sup>12</sup> cm<sup>-3</sup> concentration in the 90 to 100 km range, a rapid decrease to ≈ 10<sup>10</sup> cm<sup>-3</sup> at 80 km, and a continued daytime decline to about 10<sup>7</sup> - 10<sup>8</sup> cm<sup>-3</sup> near 27 km. There are photochemical diurnal changes above 80 km altitude, but at

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lower altitudes, atomic oxygen disappears at night through recombination processes. The chemical importance of this species, coupled with the lack of global data, highlights a critical need for a systematic observational program, especially in the upper stratosphere and lower mesosphere. These data could provide an important link in attempting to understand the reasons for the lack of agreement between observed and calculated ozone. It is important to note, for purposes of data interpretation, that observational and theoretical studies have demonstrated the importance of transport processes associated with breaking gravity waves in the mesosphere and lower thermosphere.

### 1.2.3 Odd Nitrogen (NO<sub>y</sub>)

The principal elements of odd nitrogen in the middle atmosphere include NO, NO<sub>2</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, ClONO<sub>2</sub>, HNO<sub>4</sub>, and NO<sub>3</sub>. Only NO<sub>2</sub> and HNO<sub>3</sub> have been observed on a global scale, in this case by the LIMS experiment. The others, however, have been observed during a shuttle mission by ATMOS, which provided the first simultaneous measurements of all the main elements of the odd nitrogen family. Even though nitrous oxide (N<sub>2</sub>O) is not considered part of the family, it is a source molecule, and is discussed in this section.

#### 1.2.3.1 Nitric Oxide (NO)

Data on the temporal and spatial variability of this key NO<sub>y</sub> molecule are sparse mainly because most observations have been made at specific locations using ground-based, balloon, aircraft, or rocket platforms. Recently, a limited set of data was collected from Space Shuttle at 47°S and 30°N. A variety of measurement approaches have been used, including chemiluminescence techniques, in situ optical and ion composition methods, and remote sensing using solar occultation. There is an indication from the data that NO is highly variable in the springtime mesosphere and that there is a vertical profile minimum of <10 ppbv near 75km as suggested by theory. The NO mixing ratio increases with decreasing altitude from that point reaching a peak on the order of 13 ppbv near 45km. It then declines to less than 1 ppbv at ≈ 20km. The mixing ratio increases with altitude above 75km to a value on the order of 1 ppmv at ≈ 105km. Data in this region are very sparse. Since NO is the dominant member of the NO<sub>y</sub> family above about 35-40km altitude, it is a critical factor in catalytic ozone destruction due to odd nitrogen and, therefore, its global distribution, temporal changes, and spatial variability need to be measured so that budget studies can be conducted.

#### 1.2.3.2 Nitrogen Dioxide (NO<sub>2</sub>)

The general characteristics of the global NO<sub>2</sub> distribution are now well known as a result of recent satellite observations. The largest NO<sub>2</sub> mixing ratio occurs in the tropics where, at night, it reaches a peak value of ≈ 18 ppbv at 4 mb (≈ 37km) decreasing to 1 ppbv or less at 15km and 55km. There is a large diurnal variation with the daytime peak reaching only ≈ 7 ppbv at 7 mb (≈ 32km). The diurnal change observed by LIMS in the northern terminator region in May shows very good agreement with theory, and it provides a good data base for evaluating the importance of including multiple scattering in photochemical model calculations. NO<sub>2</sub> varies greatly with altitude, latitude, and longitude. A sharp decline with increasing latitude is observed northward of ≈ 45°N in winter (NO<sub>2</sub> cliff), presumably due to conversion of NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub>. The nighttime NO<sub>2</sub> column sum decreases as much as a factor of 6 in 25° of latitude. Very large levels of NO<sub>2</sub> (≈ 175 ppbv) have been observed at about 70km in the northern polar night region, and it appears that this enhancement region in the mesosphere becomes a source for the stratosphere. Since these phenomena have been observed on a global scale in only one winter, more NO<sub>2</sub> data are needed, especially in the southern winter period and over a long time period so that an

$\text{NO}_2$  climatology can be built up for the stratosphere and mesosphere. Longer-time data sets from the SAGE, SAGE II, and SME satellites are available for sunrise, sunset, and mid-afternoon conditions, but these data have not been analyzed yet for determination of any multiyear trends that may be present.

#### 1.2.3.3 Nitric Acid ( $\text{HNO}_3$ )

Knowledge of the global distribution and variability of  $\text{HNO}_3$  has grown considerably since 1976 primarily as a result of satellite observations and additional balloon soundings. The data indicate that the  $\text{HNO}_3$  mixing ratio is always low in the tropics, with the peak value reaching 4 ppbv at 20 mb ( $\approx$  26km) but declining to very low levels ( $<1$  ppbv) at 45 and 15km, respectively. There is a hemispheric asymmetry with the largest mixing ratio (12 ppbv) occurring at  $\approx$  30 mb ( $\approx$  24km) in the winter polar night region. A secondary maximum occurs in the same region at the  $\approx$  5 mb ( $\approx$  36km) level. The observed asymmetry is poorly reproduced by theory and represents a key question the data have raised which needs to be better understood. A possible explanation is that an aerosol catalyzed reaction of  $\text{N}_2\text{O}_5$  with  $\text{H}_2\text{O}$  gives rise to the winter polar enhancement but little is known to confirm this suggestion. The temporal shift from maximum levels in the Northern Hemisphere to the Southern Hemisphere is slow and appears to be essentially in phase with the seasonal cycle. Only a limited 7½ month global data set exists on this key  $\text{NO}_x$  reservoir molecule, and it is essential that seasonal and longer-term data be collected.

#### 1.2.3.4 Nitrogen Trioxide ( $\text{NO}_3$ )

Although it is not an important component of odd nitrogen,  $\text{NO}_3$  is important because of the role it plays in the nighttime conversion of  $\text{NO}_2$  to  $\text{N}_2\text{O}_5$ . Optical observations of  $\text{NO}_3$  have been made from the ground and balloons. The measurements show maximum levels of  $1-2 \times 10^7 \text{ cm}^{-3}$  near 40km, which is in general agreement with theory. Broadband total column measurements suggest the presence of a possible scavenging reaction for  $\text{NO}_3$  in certain latitude bands and seasons, but the mechanism or the reality of the process has not been confirmed due to lack of sufficient data. The implication of this scavenging may be important in the  $\text{NO}_x$  budget.

#### 1.2.3.5 Nitrogen Pentoxide ( $\text{N}_2\text{O}_5$ ), Chlorine Nitrate ( $\text{ClONO}_2$ ) and Peroxynitric Acid ( $\text{HNO}_4$ )

These three molecules make up the remaining important elements of the  $\text{NO}_x$  family. Nitrogen pentoxide has been measured in the atmosphere only once, in this case by ATMOS using solar occultation measurements in the  $1240 \text{ cm}^{-1}$  and  $1720 \text{ cm}^{-1}$  bands. The presence of  $\text{N}_2\text{O}_5$  has also been inferred using balloon-based diurnal measurements taken in the same  $1240 \text{ cm}^{-1}$  band measured by ATMOS. The implied profile has a peak value of 1.6 ppbv at  $\approx$  5 mb (40 km). This value was obtained in the data analysis by assuming a profile shape and scaling the profile until the calculated band envelope matched the observed shape. No data exist on its spatial or temporal variability. The same is true of  $\text{ClONO}_2$  and  $\text{HNO}_4$ . The vertical profiles for these molecules have implied peak mixing ratios of 1.4 ppbv and 0.2 ppbv, respectively. The pressure levels of the peak mixing ratio for  $\text{ClONO}_2$  and  $\text{HNO}_4$  are  $\approx$  15 mb (28 km) and 24 mb ( $\approx$  26 km), respectively. It is important that global data be obtained on all three of these gases in order to evaluate their role in the total  $\text{NO}_x$  budget. This is especially true for  $\text{N}_2\text{O}_5$ , since it is believed to be of central importance in Antarctic  $\text{O}_3$  depletion reactions and to be a major factor in the chemistry of  $\text{NO}_2$  conversion and subsequent  $\text{HNO}_3$  formation in the polar night.

### 1.2.3.6 Total Odd Nitrogen ( $\text{NO}_y$ )

Total odd nitrogen is of critical importance in middle atmosphere photochemistry since it tends to buffer the effect of odd chlorine ( $\text{ClO}_y$ ) on ozone depletion. Using 1-D models, it has been calculated that for only a 20 percent increase above the 13 ppbv  $\text{NO}_y$  level used in the model, the predicted ozone steady-state decrease due to chlorine is reduced by a factor of two. Thus far, only one experiment, ATMOS, has provided nearly simultaneous data on all the main  $\text{NO}_y$  gases. The reported observations give peak  $\text{NO}_y$  levels of  $\approx 17$  ppbv at  $30^\circ\text{N}$  and  $47^\circ\text{S}$  with the peaks at each latitude occurring at 2 mb (43 km) and 5 mb (35 km), respectively. The mixing ratio decreases to  $\approx 2$  ppbv below  $\approx 100$  mb (16 km) and to  $\approx 8$  ppbv above 55 km.  $\text{NO}_y$  is in the form of only NO for the region above 50 km and outside of polar night regions. Data on the lower limit  $\text{NO}_y$  calculated from satellite observed sums of nighttime ( $\text{NO}_2 + \text{HNO}_3$ ) show that much larger  $\text{NO}_y$  values can be observed at certain times and locations. Values ranging from 17 ppbv to 26 ppbv are seen in the data at  $48^\circ\text{S}$  in May. These results highlight the need to collect more observations on  $\text{NO}_y$  over a wide latitude range and in different seasons in order to gain a better understanding of its distribution and variability.

### 1.2.4 Nitrous Oxide ( $\text{N}_2\text{O}$ )

Nitrous oxide is the main source gas for middle atmosphere odd nitrogen. Reaction with  $\text{O}(^1\text{D})$  gives rise to nitric oxide, which is a catalyst in the odd nitrogen/ozone destruction cycle. This gas has now been measured extensively from in situ as well as satellite platforms. A mixing ratio of  $\approx 300$  ppbv is observed in the lower stratosphere up to 30 km, and it then drops off exponentially with altitude to less than 10 ppbv above 50 km. Zonal mean pressure versus latitude cross sections show that both single- and double-peaked distributions in latitude occur, depending on the month of the year. The latitude locations of the peaks vary considerably during the year, but they are concentrated mostly in the Tropics. This behavior is consistent with observed features in both methane and water vapor. The double peak phenomenon is seasonally dependent and does not appear in measured distributions for the last half of the year. Since  $\text{N}_2\text{O}$  has its source in the troposphere and a photochemical sink in the stratosphere, it is a good tracer molecule. Further observations are needed with higher space and time resolution to aid in dynamics studies and to better define the climatology.

### 1.2.5 Odd Chlorine ( $\text{ClO}_y$ )

Odd chlorine has become of central importance in the middle atmosphere because of its potential for catalytic ozone destruction. The main concern has been focused on the man-made fluorocarbons, F-11 and F-12, which carry chlorine into the middle atmosphere from below. The most important product gases after dissociation include Cl, ClO, HCl,  $\text{ClONO}_2$ , and HOCl. Other postdissociation by-products, HF and  $\text{COF}_2$ , are important as indicators of anthropogenic chlorine input to the middle atmosphere. The main natural source gas is methyl chloride ( $\text{CH}_3\text{Cl}$ ). This chemical family has been carefully studied in Antarctic ozone hole analyses, and a leading theory postulates that the hole is caused by chlorine catalyzed ozone destruction on aerosol surfaces.

The available chlorine data set is very limited and virtually no satellite observations exist. This gap will be partially filled when the Upper Atmosphere Research Satellite (UARS) is launched early in the next decade. Chlorine related gases to be measured by UARS experiments include ClO, HCl, HF, and  $\text{ClONO}_2$ . A brief summary of current knowledge follows.

### 1.2.5.1 Atomic Chlorine (Cl) and Chlorine Monoxide (ClO)

Atomic chlorine has been measured only twice and, in each case, the in situ resonance fluorescence technique was used. The measurements are very difficult to make because of low concentrations, and the observations have large error bars. The picture is much better for ClO, but it is still lacking in important details, especially concerning the spatial distribution. Chlorine monoxide observations have been made using in situ resonance fluorescence and remote techniques applied from the ground and balloons in both the millimeter and submillimeter regions. The mixing ratio distribution in the 20° to 30°N range varies from  $\approx 0.1$  ppbv at 27km to about 1 ppbv at 40km. Data taken from the ground during one of the recent Antarctic campaigns indicate much larger ClO mixing ratios in the lower stratosphere than were measured in the Tropics and mid-latitudes. The results at  $\approx 20$ km, for example, show levels which are two orders of magnitude higher than standard chemical predictions, suggesting that anomalous chemistry is taking place. The most plausible theory emerging from analyses of the body of data collected during two Antarctic campaigns is that heterogeneous chemical processes are occurring that lead to catalyzed ozone depletion by chlorine compounds. This idea is given further credence by OClO column amount measurements made at the same time which show levels 20 to 50 times higher than would be expected based on standard homogeneous chemistry. Also, the observed diurnal variation in OClO column amount is in good agreement with theory only when enhanced levels of ClO are used in the model (see Chapter 5 for further details).

The diurnal variation in ClO has been measured both from the ground, using millimeter-wave spectroscopy, and from a balloon in the microwave region. The observed temporal changes are in fair agreement with theoretical predictions. The day/night ratio of column amount above 30km has a value of about 6 and above 40km, it is about 2. The largest discrepancy with theory, again, occurs during Antarctic spring conditions. Observations there show more rapid low altitude diurnal changes than theory predicts and low-latitude observations show. More measurements of this important molecule are needed over various seasons, times and latitudes. Hopefully, much of these data will be provided by the UARS.

### 1.2.5.2 Hydrogen Chloride (HCl) and Hydrogen Fluoride (HF)

Each of these gases has been measured from ground-based, balloon and aircraft platforms using in situ methods and high resolution spectroscopy conducted against the solar background. In addition, a limited set of data was obtained by the Spacelab 3 ATOMS experiment at two latitudes (30°N and 47°S) in early May. All HCl results are in reasonable agreement and give a profile which is nearly constant at a level of 2 to 3 ppbv from 43km down to 35km and then the mixing ratio decreases to 0.3 ppbv at  $\approx 18$ km. The HCl column amount appears to be increasing at a rate of  $\approx 5$  percent per year presumably due to continued dissociation of chlorocarbons entering the stratosphere. Results from various methods for measurement of HF are also in reasonable agreement, and they give a vertical profile with a mixing ratio of 0.9 ppbv at 50km, 0.6 ppbv at 30km and 0.1 ppbv at 15km. The observed HF increase in column amount from ground-based and aircraft measurements is about 10 percent per year.

The ratio of HF to HCl is another parameter which should be monitored in order to evaluate the relative importance of natural and anthropogenic chlorine sources in the middle atmosphere. The value of this ratio from ground-based column amount measurements is  $\approx 0.2$ , which is in good agreement with theory. The measured profile of the ratio from satellite data gives a value of  $\approx 0.2$  below 25km and 0.29 above. Extended vertical profile observations of both of these gases are needed over several years time span and for various seasons and

latitudes. There are indications from limited measurements that the ratio of column HF to HCl for Antarctic springtime is much larger than what it is at other latitudes and times. This implies that either HCl is converted to some other form or else it is removed almost entirely. The prevailing theory regarding these observations is that HCl condenses and reacts with other compounds on polar stratospheric cloud surfaces. This process is believed to be a key factor in the springtime depletion of Antarctic ozone alluded to earlier. These kinds of observations, coupled with long-term data, will provide key information for study of ozone change effects. It is anticipated that these results will be forthcoming from the UARS.

#### 1.2.6 Methyl Chloride (CH<sub>3</sub>Cl) and Carbonyl Fluoride (COF<sub>2</sub>)

Methyl chloride is the most important natural halocarbon because of its role as a chlorine source molecule. It has been observed both in situ using cryogenic sampling methods and remotely from shuttle in solar occultation by ATMOS. The observed mixing ratio is  $\approx 0.6$  ppbv at 12km,  $\approx 0.3$  ppbv at 17km,  $\approx 0.1$  ppbv at 22km and 0.02 ppbv at 30km. The measurement error bars became large above about 25-30km altitude. Observations by more sensitive methods and over longer times, seasons and latitudes are needed for chlorine budget and trend studies.

Knowledge of the carbonyl fluoride mixing ratio distribution is important because of chemical partitioning questions which arise regarding the fate of the fluorine atom after the fluorocarbons are dissociated. If the COF<sub>2</sub> mixing ratio is comparable to HF, for example, then measurement of HF alone in combination with HCl would not be sufficient in studying the relative importance of anthropogenic and natural chlorine sources. ATMOS measured a peak COF<sub>2</sub> mixing ratio of  $\approx 0.1$  ppbv at  $\approx 33$ km which then declined to  $\approx 0.08$  ppbv at 40km and  $\approx 0.03$  ppbv at 20km. These results suggest that COF<sub>2</sub> is only a small consideration in chlorine source scenario studies, and above  $\approx 40$ km it can be neglected. Confirmation of these limited observations by ATOMS is needed.

#### 1.2.7 Hydrogen (HO<sub>y</sub>)

Odd hydrogen gases are important in ozone destruction scenarios both directly and indirectly. The hydroxyl radical OH, for example, directly affects formation of the NO<sub>y</sub> sink HNO<sub>3</sub> and the ClO<sub>y</sub> sink HCl. Hydroperoxyl (HO<sub>2</sub>) has an indirect affect on NO<sub>y</sub> through reaction with NO<sub>2</sub> to form a reservoir gas HNO<sub>3</sub> which, thereby, slows down the NO<sub>y</sub> catalytic ozone destruction cycle. A third main HO<sub>y</sub> element, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), is a major HO<sub>y</sub> sink molecule. The primary source gases for HO<sub>y</sub> are H<sub>2</sub>O and CH<sub>4</sub>.

##### 1.2.7.1 Hydroxyl Radical (OH)

The hydroxyl radical has been observed by a variety of methods using in situ resonance fluorescence, balloon-borne laser radar scunding and balloon remote sensing using far infrared emission. The results exhibit a wide range of variability. This is due in part to the diurnal variability of OH, low signal-to-noise and probable spatial variations. Mixing ratios range from 0.3 to 0.1 ppbv at 40km, 0.03 to 0.2 ppbv at 35km and  $\approx 0.01$  ppbv at 25km altitude. There have been attempts to determine the global distribution of OH through calculations using LIMS NO<sub>2</sub> and HNO<sub>3</sub> distributions based on current photochemical understanding. However, no global direct measurements exist. Such data are needed over extended time periods and seasons.

##### 1.2.7.2 Hydroperoxyl (HO<sub>2</sub>) and Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)

The vertical hydroperoxyl profile has been observed in a series of balloon flights using in situ resonance fluorescence and cryogenic sampling coupled

with the matrix isolation technique. The results show a profile that increases with altitude from 0.03 ppbv at 16km, to 0.1 ppbv at 25km and 0.2-0.3 ppbv at 35km. The HO<sub>2</sub> column amount above ≈ 35km has also been observed from the ground using millimeter wave emission measurements. The in situ results appear to give significantly more HO<sub>2</sub> than is indicated from ground-based observations. The reasons for this are not understood.

Hydrogen peroxide measurements are very scant. The only reported observations were obtained using far infrared spectroscopy from a balloon platform. The measured mixing ratio obtained was 0.4 ppbv at 38km, 0.09 ppbv at 32km and 0.06 ppbv at 28km. These mixing ratio values are much less than model predictions at these altitudes and, at the same time, the HO<sub>2</sub> values obtained by cryogenic sampling are much greater than predictions. Therefore, there appears to be an important flaw in theoretical understanding if the reported HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> concentrations are representative of the mean atmosphere. Because of the key role HO<sub>2</sub> plays in removal of the OH radical and the importance H<sub>2</sub>O<sub>2</sub> has as an HO<sub>x</sub> sink for the middle atmosphere, it is essential that more data be collected from ground, balloon and aircraft platforms. The goal of future observations should be to measure the global distributions of these gases from a satellite so that detailed HO<sub>x</sub>-O<sub>x</sub> studies can be conducted.

### 1.2.7.3 Water Vapor (H<sub>2</sub>O) and Methane (CH<sub>4</sub>)

Water vapor observations in the middle atmosphere have been made for many years. It has been only recently, however, that a general consensus has been formed about the magnitude and shape of the vertical profile in the stratosphere. This has occurred as a result of development and application of improved observational techniques from balloons, rockets and more recently, satellites. The most comprehensive data base thus far has come from the LIMS experiment launched on Nimbus 7. More data have been collected since then by SAGE II on the ERBS satellite, but the results are not yet public.

The stratospheric H<sub>2</sub>O mixing ratio is essentially constant with altitude for mid- and high latitudes at a value of about 4.5 ppmv. In the Tropics, there is an increase as a function of altitude which is consistent with the methane oxidation theory as a water vapor source. The tropical peak mixing ratio of ≈ 6.5 ppmv occurs at or just above the stratopause. A hygropause, or region of low mixing ratio is present just above the tropopause and persists during the 7-1/2 months the LIMS data spans; but it occurs primarily in the Tropics. A daily zonal mean pressure versus latitude cross-section shows regions of low water vapor that extend in the Tropics to the mid-stratosphere. At times, there are double minima that coincide in latitude with the N<sub>2</sub>O double maxima referred to earlier. There also appears to be a wintertime H<sub>2</sub>O enhancement in the 18-20km range at high latitudes poleward of 50°, where the mixing ratio reaches ≈ 6.5 ppmv. Unfortunately, this rather detailed view of the H<sub>2</sub>O distribution and its variability exists only for the 7½ months of the LIMS data, from November 1978 to May 1979. Hopefully, the SAGE II results will significantly enhance this data base, but SAGE II data will probably not extend down to hygropause levels. Global data are needed over a several year time span so that a better climatology can be constructed. Also, global mesospheric measurements are needed in order to study important HO<sub>x</sub>-O<sub>x</sub> processes that are unique to that atmospheric region. There is only a limited amount of mesospheric water vapor data available. Measurements have been made from the ground using microwave observations and from rockets using in situ positive ion measurements, N<sub>2</sub> measurements and remote infrared and far infrared observations. Also, a few measurements have been made from the space shuttle platform using solar occultation in the infrared. The data indicate that there is a variable but strong, decreasing, water vapor gradient in the 55 to 80km range. Many more observations are needed to confirm this feature and to better characterize it.

Methane measurements have been made by a variety of techniques using both in situ and remote sensing approaches. The most extensive data set is the multiyear data base provided by the Nimbus 7 SAMS experiment. These results show  $\text{CH}_4$  variations with time which are very similar to the  $\text{N}_2\text{O}$  changes discussed earlier. The zonal mean pressure versus latitude cross-sections for various months show that in January, for example, there is a single peak in the mixing ratio contour plot tilted to the south which gradually changes to double peaked in March and then single peaked in May and tilted to the north by June. Like  $\text{N}_2\text{O}$ , the double peaks do not appear in the last half of the year. The mixing ratio varies from  $\approx 1.2$  ppmv at 22km to  $\approx 0.7$  ppmv at 40km and 0.2 ppmv at 55km.

The zonal mean pressure versus latitude cross sections for  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$  in any single month have features that are well correlated. There is very good agreement, for example, in the location of the  $\text{CH}_4$  and  $\text{N}_2\text{O}$  double maxima and the  $\text{H}_2\text{O}$  double minima. These and other correlations support the idea that  $\text{CH}_4$  and  $\text{N}_2\text{O}$  rich air from the tropical tropospheric source region is carried upward by the net circulation along with  $\text{H}_2\text{O}$  poor air from the tropical "dry reservoir" hygropause region in the lower stratosphere. More observations for a longer time period are needed so that the implications of the data for study of the general stratospheric circulation can be evaluated.

### 1.2.8 Aerosols

The flights of the SAM II, SAGE and SAGE II satellite experiments are providing an evolving global aerosol climatology picture. In general, five major zones are evident in the data base. There are three regions of relative aerosol maxima in the 75°S to 40°S, 20°S to 20°N and 40°N to 75°N range and two areas of relative minima in aerosol loading in the 40°S to 20°S and 20°S to 40°N range. The observed global background aerosol load for nonvolcanic conditions appears to be  $\approx 0.5 \times 10^9$  kg. The long-term trend in stratospheric aerosols is governed by volcanic perturbations with the altitude and latitude of the eruption being the important parameters that determine when and to where material is mixed after an eruption. The polar regions show a large variability in aerosol amount depending on the stratospheric polar vortex location and temperature. Aerosol tracer studies have shown that the polar vortex restricts aerosol motion and tends to entrain the aerosol preventing transport to regions outside the vortex. Polar stratospheric clouds (PSC's) have been identified and are observed to be a localized phenomenon that occurs only in the cold winter polar vortex of both hemispheres. These PSC's have become ever more important recently in view of theories for Antarctic ozone hole formation which invoke heterogeneous chemistry arguments. A typical value for aerosol extinction for nonvolcanic loading conditions is on the order of  $10^{-6} \text{ km}^{-1}$  in the range from the tropopause to about 25km altitude. This value can be many times larger after a volcanic eruption. It is important that monitoring of aerosol conditions of the middle atmosphere continue well into the future. Such data are needed in radiation and chemistry studies and they are required for reduction of data from other remote sensing experiments that are affected by aerosol contamination in the spectral regions being used. Unfortunately, there are no aerosol satellite experiments planned for launch after the current SAGE II experiment is terminated.

### 1.3 Ion Composition and Ion Chemistry

Great strides have been made in our knowledge of the ion composition and ion chemistry of the middle atmosphere since MAP's inception. In fact, there were no in-situ stratospheric data prior to MAP. This progress is briefly reviewed here. Most advances concern measurements in the stratosphere and troposphere, although there has been some progress at mesospheric altitudes. Important

uncertainties remain, mainly in regard to the identities of the negative ions in the mesosphere and their chemistry.

### 1.3.1 Positive Ions

The positive ion composition and chemistry is fairly well understood. When air is ionized the principal ions generated are normally  $O_2^+$  and  $N_2^+$ . Since the latter ions rapidly charge transfer with  $O_2$ , one may assume the initial ions are all  $O_2^+$  ions. The main exception pertains to the quiet daytime mesosphere (D-region) where a window in  $O_2$  absorption allows the 10.2 eV H Ly  $\alpha$  line to ionize the NO in the D-region. However, the pioneering work of Narcisi and Bailey found that cluster ions of the type  $H_3O^+(H_2O)_n$  were prevalent in the D-region rather than  $NO^+$  or  $O_2^+$  ions, the principal ions of the E-region. At first, there was some concern that these rocket measurements may have been contaminated by water vapor, a notorious out-gassing component. However, additional measurements by Narcisi and co-workers plus similar results by scientists at NASA, Univ. of Bern and the Max-Planck Inst. at Heidelberg, left no doubt that hydronium ions or proton-hydrate ions (PH) were the dominant ions of the D-region. These cluster ions can be dissociated in the sampling process by the electric draw-in field and by their passage through the shock wave normally present during rocket flight. The latter problem is especially exacerbated in the lower D-region where the rocket's speed and the ambient gas concentration are substantial.

In general, for the quiet D-region, the transition from simple ions ( $O_2^+$  and  $NO^+$ ) to hydronium ions take place near 82 km by day and 86 km by night (NARCISI, 1973). REID (1977) demonstrated the influence of high and low temperatures and/or water vapor mixing ratios upon the positive ion composition of the quiet D-region. However, detailed comparisons of models and actual measurements are rare and undoubtedly such comparisons would show the need for additional rate coefficient measurements. Many of the three-body rate coefficients in the lengthy transition scheme from  $NO^+$  ions to  $H_3O^+(H_2O)_n$  ions have never been measured. This fact is troublesome, especially as some temperature dependences are appreciable.

A case in point is the NO-enhanced winter anomaly of the D-region where, for at least one event,  $NO^+$  was recorded to be the dominant ion down to a rather low altitude, 71 km. Detailed comparisons of disturbed D-region measurements with a model lead to the conclusion (SWIDER and NARCISI, 1983) that  $NO^+$  ions are depleted too rapidly if the conventional  $NO^+$  clustering chemistry is assumed.

For the disturbed D-region, where  $O_2^+$  is the precursor ion, the transition altitude from  $NO^+$  and  $O_2^+$  ions to hydronium ions is lower than for quiet conditions. This situation may be attributed to the fact that  $O_2^+$  ions change to  $H_3O^+(H_2O)_n$  ions at a rate somewhat slower than for  $NO^+$  ions, and because for a disturbed event (higher electron concentrations) dissociative recombination of  $O_2^+$  and  $NO^+$  is more probable relative to their transition chemistry.

There are few ion composition measurements in the lower D-region where sampling problems can be severe. ARNOLD and VIGGIANO (1982) have made mass spectrometric observations down to near 55 km in a weak aurora. Fortunately, the positive ion composition appears to be well-determined (SWIDER, 1984) simply from thermodynamic relationships below about 65-70 km. This is especially fortunate since there are no data whatsoever between about 55 km and 40 km, the highest altitudes attained by balloons. From about 40 km to 70 km the dominant positive ions appear to be  $H_3O_3^+$  and  $H_3O_4^+$ . There appears to be sufficient water vapor at these altitudes so that the relative distribution of hydronium ions appears



to be dependent mainly upon temperature. Lower temperatures favour heavier ions (less collisional dissociation).

No ion composition measurements of the stratosphere existed prior to MAP. Under the leadership of Arijs and his co-workers at the Belgium Institute for Spatial Aeronomy, and Arnold and his colleagues at the Max-Planck Institute for Kern-Physik in Heidelberg, enormous progress has been made.

The situation in the stratosphere is relatively simple, even though the actual chemical rate equations involve a substantial number of terms. Hydronium ions are important but the principal ions are mostly hydronium ions with one or two water molecules replaced by acetonitrile ( $\text{CH}_3\text{CN}$ ) molecules. Thus, although the positive ion chemistry becomes more complex, the data can be modelled reasonably by assuming that the unmeasured reactions proceed at their kinetic rate. ARIJS and BRASSEUR (1986) calculate  $\text{H}_3\text{O}_4^+$  to be the dominant ion in the upper stratosphere (40 to 50 km) with  $\text{H}^+\cdot\text{CH}_3\text{CN}\cdot(\text{H}_2\text{O})_3$  dominant below this region down to about 20 km followed by a mix of ions below this height. From ground level up to about 6 km (EISELE and McDANIEL, 1986; ZIEREIS and ARNOLD, 1986)  $\text{NH}_4^+(\text{H}_2\text{O})_n$  are major ions. Other ions near ground level include species whose origin is associated with the terrestrial vegetation (EISELE and McDANIEL, 1986).

### 1.3.2 Negative Ions

Our knowledge of negative ions and their chemistry is less satisfactory, especially in the mesosphere (D-region). First of all, Narcisi and co-workers (e.g., NARCISI et al., 1983) consistently have observed a layer of heavy negative ions centred near 85 km. These observations are supported by the data of ARNOLD et al. (1982). Gas phase chemistry cannot be the source of these ions. The latter authors suggest meteoric dust may be responsible. This layer may explain the commonly observed "ledge" of electron density in the upper D-region, i.e., a very strong positive gradient,  $d[e]/dz$ , near 85 km. Other factors which may contribute to this "ledge" include a sharp decrease in NO near this altitude and a transition from  $\text{NO}^+$  and  $\text{O}_2^+$  ions to hydronium ions. The latter ions recombine 3-5 times faster with electrons than do either  $\text{NO}^+$  or  $\text{O}_2^+$  ions. GANGULY (1984) reported large negative ion layers at 85-90 km for one-third of the evenings studied with the Arecibo backscatter radar.

Negative ions are thought to be important below about 70 km by day and 80 km by night, i.e., the altitudes where  $\lambda = 1$ , ( $\lambda$  being the ratio of electrons to negative ions). The principal negative ions of the D-region are believed to be species like  $\text{HCO}_3^-$ ,  $\text{CO}_3^-$  and  $\text{NO}_3^-$  with perhaps an attached water molecule or two, although the hydrates of  $\text{HCO}_3^-$  and  $\text{CO}_3^-$  are probably less abundant than the core ions in the mesosphere (KEESEE et al., 1979). The identities of the negative ions and their abundance are very important in the daytime mesosphere where considerable detachment of electrons from negative ions takes place. Although the unhydrated eight-negative ion scheme of SWIDER et al., (1978) is undoubtedly inexact, their model reproduces well the electron distribution for an SPE-disturbed D-region. No significant difference in ion chemistry should occur in going from the quiet to the disturbed D-region (SWIDER, 1988a) just as in the more simple case of the disturbed and quiet E region. The total ion concentration is always far less than the total neutral particle population.

The identity of the ions is somewhat less important in the stratosphere where attachment completely overwhelms detachment. Negative ions appear to be most massive near 35 km where sulphuric acid leads to complex ions like  $\text{HSO}_4^-$ ,  $(\text{H}_2\text{SO}_4)_n$  and  $\text{HSO}_4^-\cdot(\text{HNO}_3)_n$  (Arijs et al., 1982). On one particular flight, ARNOLD and QIU (1984) observed that just two ions,  $\text{HSO}_4^-\cdot(\text{H}_2\text{SO}_4)_2$  and  $\text{HSO}_4^-\cdot(\text{H}_2\text{SO}_4)_3$ , comprised more than half of the total negative ion population. Below

35 km,  $\text{NO}_3^-(\text{HNO}_3)_n \cdot (\text{H}_2\text{O})_n$  ions are important (VIGGIANO et al., 1983), even at ground level (EISELE and McDANIEL, 1986). The major negative ion from about 33 km down to at least 15 km is  $\text{NO}_3^-(\text{HNO}_3)_2$ .

The chemistry of negative ions in the middle atmosphere is rather incomplete in regards to measured rate coefficients. BRASSEUR and CHATEL (1983) listed more than 150 processes. Much more than half required an estimate value. Fortunately, most ionic rates proceed near the kinetic collision rate and hence model results are in reasonable accord with the measurements irrespective of the enormous (uncertain) algebra involved. However, derivation of minor neutral species from a comparison of a model with data must be viewed with caution.

#### 1.3.4 Summary of Ion Composition.

Figure 1.1 depicts the principal ions and mean ion masses as derived from both models and mass spectrometric data from ground level to 70 km (from SWIDER, 1938b). Our knowledge of the positive ions appears to be more certain than for the negative ions.

At the top of the homosphere, not shown in the figure,  $\text{NO}^+$  and  $\text{O}_2^+$  are the principal positive ions down to near 86 km at night and 82 km by day. Three-body processes and switching reactions convert these ions to hydronium ions,  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$  with decreasing height below these altitudes. In the lower D-region, the relative composition of the hydronium ions is determined well through their thermodynamic criteria (temperature and absolute water vapor concentration must be known). Near and below 40 km, acetonitrile,  $\text{CH}_3\text{CN}$  replaces one or more water molecules in the hydronium ion. In the lower troposphere, there is sufficient ammonia for  $\text{NH}_4^+$  to be the core ion.

The chemistry of the positive ions, as implied by the above, is reasonably well understood although many ionic rate coefficients are unmeasured. One troublesome area arises in regard to the conversion of  $\text{NO}^+$  to hydronium ions. In two instances where a model is compared in detail to disturbed D-region data (SWIDER and NARCISI, 1983),  $\text{NO}^+$  is found to cluster less rapidly than thought. In particular,  $\text{NO}^+ + \text{CO}_2 + \text{N}_2 \rightarrow \text{NO}^+ \cdot \text{CO}_2 + \text{N}_2$  appears to be more effective than  $\text{NO}^+ \cdot \text{N}_2 + \text{N}_2 \rightarrow \text{NO}^+ \cdot \text{N}_2 + \text{N}_2$ . This problem probably relates to an uncertainty in key processes including certain intermediate reactions which are only estimated to date.

The negative ion population and chemistry is certainly less well understood. The more serious problem would appear to be at mesospheric heights where an exact knowledge of the individual negative ions are important since detachment by photo and chemical processes has a major impact upon the electron population. (The influence of electrons and negative ions upon electromagnetic wave propagation is inversely proportional to their masses of course.)

There is some evidence that a cloud of fairly heavy negative ions persists near 85 km. Their origin may be attachment to meteoric debris since their existence is not possible through gas-phase chemistry. The prevalence of these ions is somewhat uncertain but if they are significantly abundant they may be at least partly responsible for the so-called D-region "ledge" in electron density at these altitudes.

In the stratosphere, the negative ion mean mass maximizes at 400 amu (Figure 1) near 35 km. This heavy mass is a result of the relatively high sulphur oxide concentrations in this region. Major negative ions near 35 km include  $\text{HSO}_4^-$  ( $\text{H}_2\text{SO}_4$ )<sub>2</sub> and  $\text{HSO}_4^- \cdot (\text{H}_2\text{SO}_4)$ <sub>3</sub> with masses of 293 and 391 amu, respectively.

Nitrites become prominent with decreasing altitude and  $\text{NO}_3^-(\text{HNO}_3)_2$  at 188 amu

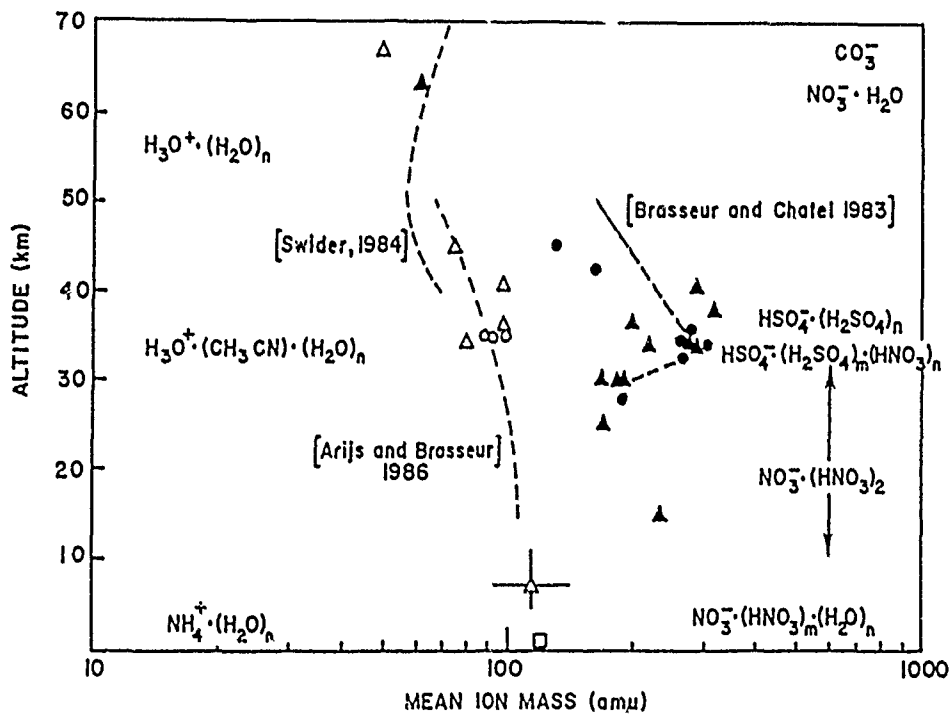


Figure 1.1

appears to be a major negative ion from about 35 km down to 15 km with hydrated forms of this ion becoming significant with a further decrease in altitude.

Gerdian condenser results have led to claims of both much lighter and much heavier ions. Such conclusions have been challenged by MEYEROTT et al., (1980) on the basis of experimental problems. The discussion here and more fully elsewhere (SWIDER, 1988b) basically supports their argument. Claims of very light mobilities, as associated with  $H_3O^+$  ions are compatible with both the mass spectrometric observations and theory. Claims of very heavy ions,  $\sim 1000$  amu, appear to be suspect also, although a limited number might not easily be detected by the mass spectrometers, nor play any great role either. It is significant that stratospheric aerosols have little influence over the total ion concentration (ROSEN et al., 1985). Some correlation between narrow layers of condensation nuclei and positive ion concentrations were noted. Hence, perhaps rather massive ions may exist from time-to-time over narrow height intervals.

#### 1.4 Recommendations

##### 1.4.1 General Recommendations

The body of data collected on the middle atmosphere thus far emphasizes the fact that it consists of a coupled system involving interactions among processes (i.e. chemistry, radiation and dynamics/transport) and atmospheric regions (i.e., thermosphere, mesosphere, stratosphere and troposphere). Consequently, simultaneous measurements of various processes in these different regions should be a goal of future observational programs. It is clear, for example, that adequate understanding of ozone changes due to chemistry requires simultaneous measurements of key elements in the main chemical families controlling ozone (i.e.  $NO_y$ ,  $ClO_y$  and  $HO_y$ ). Also, because ozone and other gases are further controlled by transport processes in some regions, temperature and thus derived or observed dynamical quantities (e.g. winds, potential vorticity and Eliassen-Palm flux - see Chapter 2) are required for proper data interpretation. One example of chemistry/dynamics interaction noted in Section 1.2.1.1 is the rapid decline of  $NO_2$  column amount with latitude at high winter latitudes. This occurs presumably because of chemical conversion of  $NO_2$  to  $N_2O_5$ , which is either slowed down or accelerated depending on the time an air parcel spends in polar night or sunlight. This is controlled by the strength and location of the circumpolar vortex. It is essential, therefore, that the capability for simultaneous observations of chemical and dynamical processes be included in future measurement system designs and observational campaigns.

Another general requirement is the need to make global long-term (multi-year) observations, especially of ozone and key parameters which influence its distribution (e.g. temperature, solar flux and selected constituents). This requirement places stringent bounds on long-term calibration system stability for absolute measurement approaches (e.g. limb emission, limb scattering, or backscattering approaches), which is difficult to achieve. The problem is greatly alleviated when the occultation method is used, but there are still challenges to be overcome.

It is recommended that the current program of ground-based, rocket, aircraft and balloon observations be continued. These programs serve valuable purposes which have already been demonstrated (e.g. discovery of the Antarctic ozone hole was made using a Dobson instrument, MST radar has provided a significant data base for study of gravity waves, ground-based microwave observations have provided the most extensive data set available on mesospheric  $H_2O$ ; and virtually all chemical data in the Antarctic has been collected using ground-

and aircraft-based platforms). Such systems have also been shown to yield valuable scientific data in major campaigns, with MAP/WINE being a prime example. Finally, these platforms provide the opportunity to explore new measurement methods; to pursue difficult observations such as measurement of tenuous radical species (e.g. HO<sub>2</sub> gases); to conduct comprehensive chemistry studies, especially from balloon platforms; and to test and prove methods that can be used for validation of satellite observations.

The last general recommendation is that agencies emphasize application of small Explorer class satellites, in addition to large observatories (like the Upper Atmosphere Research Satellite). This approach will allow more rapid response to changing scientific needs and will provide a way to fill the data gaps that exist between the operational periods of larger spacecraft missions.

#### 1.4.2 Specific Recommendations

##### Temperature

Despite the advances made in MAP, many of the statements made in the corresponding section in the MAP Planning Document still apply and bear repeating. For example, on the need for continuing measurements the document stated "The importance of the continuation of the current effort in temperature measurement cannot be overemphasized. The need exists to distinguish between climatic trends and cycles of temperature changes of one degree or less over several years. For these purposes it is essential that measurement standards be retained and intercomparisons made between the data from different types of sensors". The closing of meteorological rocket stations over widely different latitudes and the consequent reduction of firings is a particularly serious problem as rocket data are crucial for calibration of satellite measurements both in order to correct for drift and to facilitate retrievals during disturbed conditions. This problem may be partly alleviated by a more extensive network of Rayleigh-scatter lidars to provide "ground-truth", especially if they are operated on a more continuous basis.

The poor height resolution of the current generation of satellite borne instrumentation in the 70-120 km region means that this region is still not well understood as far as temperature structure is concerned, with most data coming from relatively infrequent rocket and lidar soundings. The expansion of lidar facilities to a wider range of locations will be an important factor in improving understanding of the mesosphere and lower thermosphere. The position regarding satellite data should improve greatly in the 1990s with the launch of UARS, currently planned for 1991. This will carry instruments to observe middle atmosphere and lower thermosphere temperature, constituents (both using limb sounders) and winds (directly by measuring Doppler shifts), as well as energy input from the magnetosphere and the sun. A coordinated ground-based and in situ campaign is being planned and should provide excellent opportunities for cross validation between various methods, and for studying any given phenomena in much greater depth.

##### Neutral Composition

Specific recommendations for measurements of each gas were noted in the above. The following comments are provided to amplify on these measurement needs where appropriate.

##### 1.4.2.3 Odd Oxygen

The apparent decline in total ozone reported by the Dobson network in the Northern Hemisphere and the observed ozone year-to-year decreases in Antarctica

during springtime highlight the critical need for continued and intensive observations of ozone both from the ground and from orbit. It is important to collect sufficient data over a wide geographic range, preferably globally and over a long time period (years) so that more information regarding trends can be assessed. The goal should be to develop global maps of monthly means and variances of total ozone and ozone mixing ratio on selected pressure surfaces. A critical need also exists for global measurements of atomic oxygen from the mid-stratosphere to the thermosphere because of the strong chemical role this constituent plays throughout the middle atmosphere. Measurements using both in situ and remote methods are needed.

#### 1.4.2.4 Odd Nitrogen

While much has been learned about the odd nitrogen distribution using balloon, rocket and satellite techniques, the data only points to the need for more extensive observations. It is especially important to make simultaneous measurements of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ,  $\text{ClONO}_2$  and  $\text{HNO}_4$  in polar regions during polar night and early spring to study partitioning of the  $\text{NO}_y$  family, to evaluate heterogeneous chemistry scenarios and to assess the importance of high altitude production of  $\text{NO}_y$  as a source for the stratosphere. Such observations are also needed on a global scale over a long time period to develop a climatology, to define the morphology of these constituents and to provide an appropriate data base for  $\text{NO}_y$  budget studies.

#### 1.4.2.5 Odd Chlorine

Little is known about the global distribution of the  $\text{ClO}_y$  gases  $\text{Cl}$ ,  $\text{ClO}$ ,  $\text{HCl}$ ,  $\text{HOCl}$ ,  $\text{CH}_3\text{Cl}$  and  $\text{HF}$ . It is important, therefore, that programs be initiated to determine the global morphology and changes in the mixing ratios of these gases over a long time period so that a climatology can be developed to delineate seasonal, latitudinal and temporal variations. Measurements should be made using ground, balloon, rocket and satellite methods, where possible. The observations of enhanced chlorine in Antarctica, recent evidence of elevated chlorine levels ( $\text{HOCl}$ ) in the Arctic and compelling data suggesting that the Antarctic ozone hole is caused by chlorine catalyzed chemistry emphasize the need for these observations.

#### 1.4.2.6 Odd Hydrogen

Essentially no information is available on the latitudinal, seasonal, or temporal changes in the odd hydrogen gases  $\text{OH}$ ,  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$ . Global observations are required, as well as measurements at selected latitudes by balloon techniques or other means so that the character and variability of the profiles can begin to be defined. Measurements of the source gases,  $\text{H}_2\text{O}$  and  $\text{CH}_4$ , also need to be continued in order to confirm observed features and to develop a climatology.

#### 1.4.2.7 Aerosols

The importance of aerosol observations as a tracer of motions in the atmosphere, for use in heterogeneous chemistry studies and for application in stratospheric radiation budget studies is now clearly established. There is a strong need for continued global observations of aerosols from satellites over a long time period, especially in the polar regions where heterogeneous chemistry is important. Aerosol observations are also needed for use in interpretation of channel contaminant effects in remote sensing of gases.

Ion-Composition

A host of problems pertain to a rather narrow altitude regime, 85-90 km, including the D-region ledge, NLC, and a layer of rather heavy negative ions. Transport is ill-defined here, and hence the distributions of  $H_2O$ ,  $NO$ ,  $O$ ,  $O_3$  and  $O_2$  ( $1\Delta$ ), gases important to the D-region and prominent airglow features ( $O_1$  at 557.7 nm,  $NaI$  at 589.3 nm, OH Meinel Bands). An intense co-ordinated study is needed, preferably at high latitudes for both warm (winter) and cold (summer) temperatures. Super Camp is planned for the latter case.

Very few observations of negative ions and electrons exist for the lower half of the D-Region, 50-70 km. This lack of data leads to substantial uncertainties in modelling this region where electrons, although few in number, are still significant to electromagnetic propagation at low frequencies. Precision measurements would be very welcome. (AFGL workers will attempt to measure electrons in this region by first converting them to  $SF_6^-$  ions).