

# **VOLUME II**

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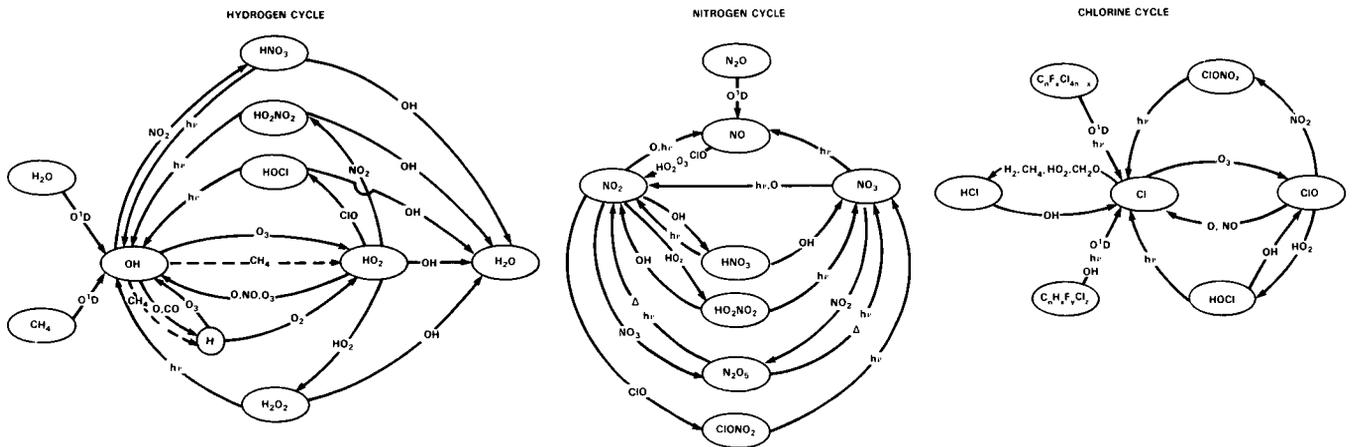
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# SPECIAL INTRODUCTION FOR CHAPTERS 8, 9, 10, and 11

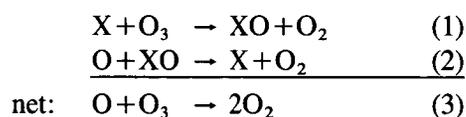


R.T. Watson

OXYGEN, HYDROGEN, NITROGEN,  
AND HALOGENATED SPECIES:  
OBSERVATIONS AND INTERPRETATION

Understanding the chemical composition and future behavior of the stratosphere cannot be achieved through laboratory simulation experiments because of the scale and complexity of atmospheric phenomena. The atmosphere is a complex chemical system with photochemical lifetimes of species ranging from nanoseconds to years, strongly influenced by dynamical and radiative processes. Consequently, at present and for the foreseeable future, heavy reliance must be placed on theoretical models. However, these models must be checked against atmospheric observations at every opportunity. A wide variety of in-situ and remote sensing techniques are now being used to determine the atmospheric concentrations of a large number of chemical species at a limited number of geographical locations from ground, aircraft, balloon, and rocket platforms. This type of data predominantly tests the radiative and chemical aspects of the models. A major advance in the last few years has been the demonstration of a capability to make global measurements of temperature and the concentrations of several species from satellites. Such new measurements are required to test the coupling of dynamics, chemistry, and radiation in the multidimensional models. In the longer term, future field and satellite programs will be needed to overcome our greatest limitation, which is a shortage of data. At present, the available measurements are inadequate for a complete test of the theoretical models.

The chemical processes controlling atmospheric ozone have already been described in detail in Chapter 2. Consequently, it is sufficient here to simply restate the key conclusion that atmospheric ozone is chemically controlled through a series of catalytic cycles involving members of the oxygen, hydrogen, nitrogen, chlorine, and to a lesser extent the bromine families. The chemical coupling that exists within and between the species of the HO<sub>x</sub>, NO<sub>x</sub>, and ClO<sub>x</sub> families can be simply illustrated as shown in Figures SI-1, SI-2, and SI-3. The classical catalytic cycle that destroys odd oxygen can be written:



where X=H, OH, NO, Cl, or Br.

In order to model quantitatively the roles of hydrogen-, nitrogen-, and chlorine-containing species in controlling the distribution of atmospheric ozone, it is vital to measure and understand their total budgets. In addition, it is essential to understand the photochemical partitioning between the active and inactive species within each family. Therefore, the key chemical constituents of importance in understanding the spatial and temporal distribution of atmospheric ozone include the source gases (H<sub>2</sub>O, CH<sub>4</sub>, N<sub>2</sub>O, and the halogenated alkanes) and the active and inactive inorganic species from the oxygen (O(<sup>3</sup>P), O(<sup>1</sup>D), and O<sub>3</sub>), hydrogen (H, OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>), nitrogen (N, NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, ClONO<sub>2</sub>, HO<sub>2</sub>NO<sub>2</sub>, and HNO<sub>3</sub>), and chlorine (Cl, ClO, HOCl, HCl, and ClONO<sub>2</sub>) families. Active species are defined as being those species which directly participate in the catalytic cycles which destroy odd oxygen, i.e. OH and HO<sub>2</sub> (HO<sub>x</sub>), NO and NO<sub>2</sub> (NO<sub>x</sub>), and Cl and ClO (ClO<sub>x</sub>). It should be noted that NO<sub>x</sub> plays the major role in controlling ozone throughout most of the stratosphere in today's atmosphere (see Figure 8-1). However, even if the emissions of CFC's do not increase but remain constant at the present level, ClO<sub>x</sub> will play an increasingly important, even dominant, role in controlling ozone in the middle and upper stratosphere as the concentration of ClO<sub>x</sub> approaches its steady state value.

Since the previous WMO assessment report in 1982 there has been a continued expansion of the atmospheric chemical composition data base, including the temporary reservoir species ClONO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>NO<sub>2</sub>. Therefore, we now have at least some measurements of most key species. While many of these observations have been isolated measurements of single species, they have provided a valuable

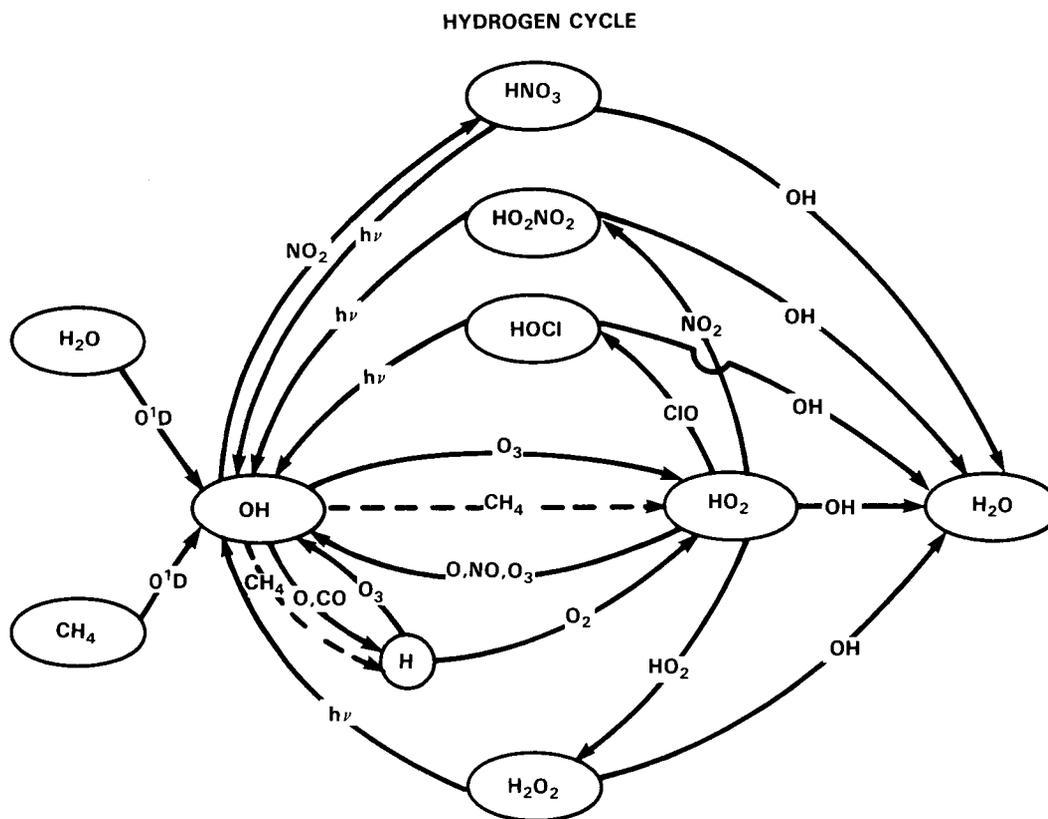


Figure SI-1. Schematic of the Hydrogen Cycle.

yet limited test of our knowledge of atmospheric photochemistry. However, 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. While there have been only a limited number of such simultaneous measurements to date, there is currently a growing emphasis to implement such a measurement strategy.

A major limitation in our ability to critically compare atmospheric observations with theoretical predictions at the time of writing the previous WMO assessment report (1982) was our lack of knowledge of the accuracy and precision of the atmospheric chemical composition measurements. Differences between measurements of the same species made at different times and places could be ascribed either to atmospheric variability or to measurement inaccuracies. Consequently, a major effort has been expended during the last four years to determine the accuracy and precision of atmospheric chemical composition measurements by conducting a series of international intercomparison balloon campaigns where chemical constituents were measured using a variety of observational techniques simultaneously in time and space. The intercomparison campaigns performed to date include:

- (a) a series of three campaigns, employing both *in-situ* and remote sensing balloon and rocket-borne instruments, to measure ozone.
- (b) two campaigns utilizing remote sensing balloon-borne instruments (13 on the first, and 18 on the second), using eight different techniques including grating spectrometers, radiometers, and Fourier transform

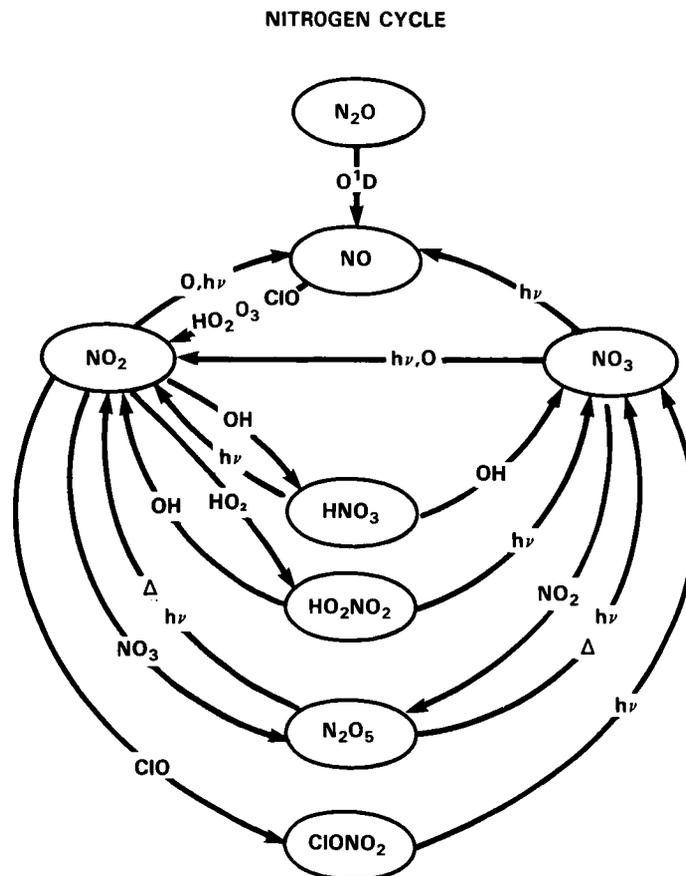
interferometers, to measure several key atmospheric constituents including  $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{OH}$ . These sensors covered the visible, infrared, far-infrared, and microwave region of the electromagnetic spectrum in both absorption and emission.

(c) three campaigns employing *in-situ* and remote sensing balloon-borne instruments to measure water vapor.

(d) *in-situ* cryogenic grab sampling techniques to measure source gases such as  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and chlorofluorocarbons (including  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ ).

The data from these intercomparison campaigns which is described more fully in Appendix C is currently in the final stages of analysis. The results have shown that some of our current measurements, such as those for  $\text{O}_3$ , are accurate to better than ten percent. Others are accurate to no better than a factor of two, e.g. those for  $\text{NO}_2$ .

Within the last four years, several newly developed *in-situ* and remote sensing techniques have been demonstrated for species for which there had been inadequate measurements, e.g.  $\text{OH}$ . In addition, some existing techniques have been improved which will result in greater sensitivity for a number of species, e.g.  $\text{ClO}$  and  $\text{O}_3$  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 understanding of atmospheric photochemistry. Techniques that have been demonstrated within the last four years include:



**Figure SI-2. Schematic of the Nitrogen Cycle.**

### CHLORINE CYCLE

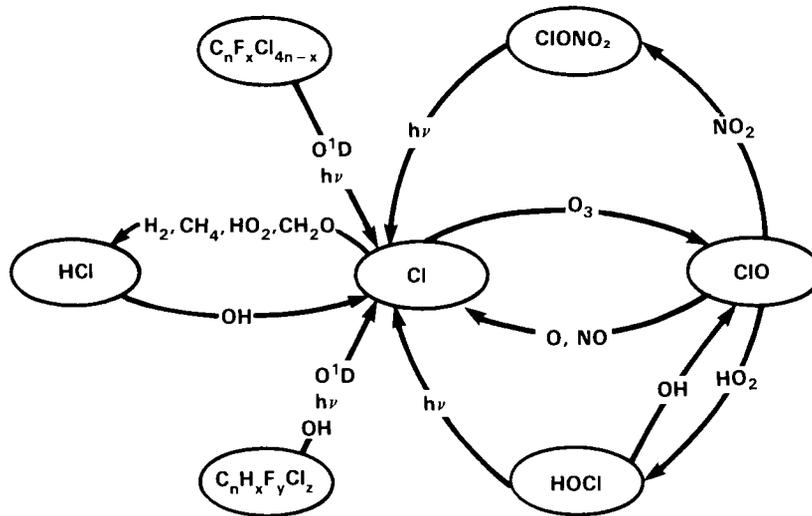


Figure SI-3. Schematic of the Chlorine Cycle.

- Two balloon-borne far-infrared emission interferometers for remote sensing detection of OH;
- Balloon-borne laser induced fluorescence systems for *in-situ* and range resolved detection of OH;
- A balloon-borne laser diode absorption system for *in-situ* detection of NO and NO<sub>2</sub>;
- A shuttle-borne high resolution infrared absorption interferometer (ATMOS) for detection of a wide range of chemical constituents including several of the temporary reservoir species, e.g. ClONO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>NO<sub>2</sub>;
- A ground-based microwave emission system for remote detection of species including ClO, HO<sub>2</sub>, and O<sub>3</sub>;
- A balloon-borne cryogenic matrix isolation technique for *in-situ* detection of HO<sub>2</sub> and NO<sub>2</sub>;
- Ground-based lidar systems for remote detection of O<sub>3</sub> and temperature.

As stated earlier, the single greatest advance during the last four years has been the analysis, validation and release of data obtained by instruments flown on the Nimbus 7, Applications Explorer II (AEM-2), and Solar Mesospheric Explorer satellites. These data includes seven months of Limb Infrared Monitor of the Stratosphere (LIMS) (HNO<sub>3</sub>, NO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, temperature); four years of Stratospheric and Mesospheric Sounder (SAMS) (CH<sub>4</sub>, N<sub>2</sub>O, temperature), four years of Solar Backscatter Ultraviolet/Total Ozone Monitoring System (SBUV/TOMS) (O<sub>3</sub> (column and vertical distribution) and solar flux); three years of Stratospheric Aerosol and Gas Experiment (SAGE) (O<sub>3</sub>, NO<sub>2</sub>, aerosols); and Solar Mesospheric Explorer (SME) (O<sub>3</sub>, NO<sub>2</sub>, aerosols, solar flux). In addition, five years of polar stratospheric aerosol data are available from the SAMS II experiment. These data have now been processed and archived at the National Space Science Data Center in Greenbelt, Maryland, USA.

A brief description of each of these satellite instruments will now be presented:

(1) The Limb Infrared Monitor of the Stratosphere (LIMS):

The LIMS instrument is a six channel limb scanning infrared radiometer that was launched on the Nimbus 7 spacecraft in a circular Sun synchronous polar orbit on October 24, 1978. LIMS scanned across the Earth's limb, and measured the radiation emitted by the atmosphere as a function of height above the surface. The radiances measured in two channels at  $15\ \mu\text{m}$  were used to derive vertical temperature distributions as a function of pressure. These were then used with radiances measured by channels centered at  $9.6$ ,  $6.7$ ,  $11.3$ , and  $6.2\ \mu\text{m}$  to retrieve the vertical distributions of  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , and  $\text{NO}_2$ , respectively. The instrument's detectors were cooled to  $63\text{K}$  by subliming solid methane cryogen in order to achieve high radiometric signal-to-noise with a narrow field of view. The cryogen system was designed for a seven month lifetime, so LIMS data spanned the period October 1978 - May 1979. Each retrieval provides a profile with a vertical resolution of about  $2\ \text{km}$  for temperature,  $\text{O}_3$ , and  $\text{HNO}_3$ , and  $4\ \text{km}$  for  $\text{NO}_2$  and  $\text{H}_2\text{O}$ . The profiles extend from  $10$  to  $65\ \text{km}$  for temperature and  $\text{O}_3$ , and  $10$  to  $50\ \text{km}$  for  $\text{NO}_2$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{O}$ . Retrievals were performed every  $4$  degrees of latitude from  $64^\circ\text{S}$  to  $84^\circ\text{N}$ , resulting in about  $7000$  profiles per day. The local times of overpass were close to  $1\ \text{PM}$  and  $11\ \text{PM}$  over a wide range of latitudes, but changed rapidly at high latitudes near the terminator.

(2) The Stratospheric and Mesospheric Sounder (SAMS):

The SAMS instrument is a multichannel infrared limb-scanning radiometer using both conventional and pressure modulation techniques, in the emission mode, to measure atmospheric temperature (using the  $15\ \mu\text{m}$   $\text{CO}_2$  band) and the abundances of a number of minor atmospheric constituents including  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ .  $\text{CH}_4$  and  $\text{N}_2\text{O}$  were measured using a common optical chain and detector at  $7.8\ \mu\text{m}$ . Consequently, these gases could not be measured simultaneously and were observed on alternative  $24$  hour periods.  $\text{H}_2\text{O}$  was measured at  $6.3\ \mu\text{m}$  but no data has yet been archived due to retrieval difficulties. The instrument flew aboard the Nimbus 7 satellite and operated successfully for more than four years providing profiles from  $20\ \text{mbar}$  ( $\sim 28\ \text{km}$ ) to  $0.3\ \text{mbar}$  ( $\sim 58\ \text{km}$ ) with a vertical resolution of approximately  $8\ \text{km}$  every  $10$  degrees from about  $50^\circ\ \text{S}$  to  $70^\circ\ \text{N}$ . As with the LIMS instrument, the local times of overpass were close to  $1\ \text{PM}$  and  $11\ \text{PM}$  at all but high latitudes.

(3) The Solar Backscatter Ultraviolet/Total Ozone Monitoring System (SBUV/TOMS):

The SBUV and TOMS instruments were launched on the Nimbus 7 satellite and are still operating. Consequently, they have so far provided a continuous  $7$  year data set starting in October 1978 for the vertical distribution and total column content of  $\text{O}_3$  from  $80^\circ\ \text{N}$  to  $80^\circ\ \text{S}$ . The SBUV instrument is a nadir-viewing double monochromator, with a field of view of  $200$  by  $200\ \text{km}$ , which measures the radiances backscattered from the atmosphere at  $12$  discrete wavelengths from  $255$  to  $340\ \text{nm}$  with a  $1\ \text{nm}$  bandpass, and continuously scans wavelength ranging between  $160$  and  $400\ \text{nm}$ . Radiances between  $255$  and  $306\ \text{nm}$  are used in the  $\text{O}_3$  profile inversion, while radiances between  $312$  and  $340\ \text{nm}$  are used to calculate total  $\text{O}_3$ . In order to calculate backscattered albedo, the ratio of backscattered radiance to extraterrestrial solar irradiance must be measured daily by employing a diffuser plate. The retrieved  $\text{O}_3$  profiles extend from about  $25$  to  $55\ \text{km}$  with an altitude resolution of approximately  $8\ \text{km}$ .

The TOMS instrument is similar in concept to the SBUV instrument but has two distinct differences i.e., it has only  $6$  discrete wavelength channels, and incorporates a side scan feature with approximately  $50$  by  $50\ \text{km}$  field of view. These differences result in the TOMS instrument being limited to total  $\text{O}_3$

measurements only, but with true global daily coverage and a significantly enhanced capability to observe small spatial scale features. As the SBUV and TOMS measurements are restricted to the sunlit portion of the Earth this means that continuous spatial coverage throughout the year is from 60°N-60°S, with coverage to the poles by TOMS only in the summer season.

#### 4) The Stratospheric Aerosol and Gas Experiment (SAGE):

The SAGE instrument is a four channel Sun photometer that measures atmospheric attenuation during each solar occultation (sunrise or sunset). SAGE was launched on the AEM-2 satellite during February 1979 with an orbital inclination of 55 degrees. It operated for 34 months but due to a battery problem SAGE sunrise measurements were terminated in August 1979 and only sunset measurements were continued. The four spectral channels were centered at 1000, 600, 450, and 385 nm. The four wavelength transmission profiles are inverted to produce vertical profiles of aerosol extinction, O<sub>3</sub>, and NO<sub>2</sub>. The vertical resolution is 1 km for O<sub>3</sub> and aerosol extinction measured at 1000 nm, and the vertical resolution is 3 km for NO<sub>2</sub> and aerosol extinction measured at 450 nm. The vertical ranges of O<sub>3</sub>, NO<sub>2</sub>, and aerosol extinction measurements were 10-50, 20-40, and 2-35 km, respectively (the lower limit for O<sub>3</sub> and aerosol profiles was normally limited by the cloud top height) with a latitude coverage of about 80° S to 80° N over a two week period.

An improved version of the SAGE instrument, SAGE 2, was recently launched on the Earth Radiation Budget Experiment satellite (ERBE). SAGE 2 has 7 channels and will measure H<sub>2</sub>O in addition to O<sub>3</sub>, NO<sub>2</sub>, and aerosol extinction.

#### (5) The Solar Mesospheric Explorer (SME):

The SME satellite was launched in October 1981 in a Sun synchronous polar orbit. It has four limb scanning instruments that are used to measure O<sub>3</sub>, the O<sub>3</sub> photodissociation rate, temperature, H<sub>2</sub>O, thermal emission, and NO<sub>2</sub>. In addition it has two instruments to measure the solar ultraviolet radiation and to detect solar proton events. The satellite spins at a rate of 5 rpm enabling the limb scanning instruments to obtain vertical profiles every 12 seconds along its orbit track. The local equator crossing time is approximately 3 PM. The duty cycle of the instruments is about 30% which results in complete latitudinal coverage, but incomplete longitudinal coverage, with most of the data being taken over the North American Continent.

O<sub>3</sub> density is measured between 50 and 70 km altitude with an ultraviolet spectrometer which detects solar radiation scattered by the atmosphere at 265 and 297 nm. Differential absorption by O<sub>3</sub> at these two wavelengths produces an absolute measurement of the O<sub>3</sub> density along the line of sight of the limb viewing instrument. An onion peeling inversion algorithm converts the observed Rayleigh scattered sunlight including O<sub>3</sub> absorption into O<sub>3</sub> density as a function of altitude with a vertical resolution of approximately 3.5 km.

O<sub>3</sub> density is also determined with a near infrared spectrometer which measures the airglow at 1270 nm. This emission is the result of the photodissociation of O<sub>3</sub> which produces O<sub>2</sub> in excited states. Vertical profiles of O<sub>3</sub> densities can be deduced from 50 to 90 km from these data.

NO<sub>2</sub> densities can be measured between 20 and 40 km altitude with a visible spectrometer detecting solar radiation scattered by the atmosphere in the spectral region of the spectrum near 440 nm. Differential absorption by NO<sub>2</sub> in this spectral region produces an absolute measurement of NO<sub>2</sub> in a manner similar to O<sub>3</sub>. The El Chichon eruption of April 1982 injected a large number of scattering particles into the

atmosphere, interrupting NO<sub>2</sub> observations for almost two years. Algorithms are currently being developed to retrieve NO<sub>2</sub> in the two year period following the El Chichon eruption.

H<sub>2</sub>O and temperature measurements were to be made using an infrared spectrometer operated in the emission mode at 6.3 and 15 μm respectively. Unfortunately no data has yet been archived because of difficulties in retrieving atmospheric temperatures due to low signal-to-noise ratios caused by the high operating temperature of the instrument.

The next four chapters review, and compare to both one-dimensional and two-dimensional model descriptions of the present day stratosphere, the stratospheric measurements of oxygen, hydrogen, nitrogen, and halogen containing species obtained from ground, aircraft, balloon, rocket, shuttle, and satellite-based instruments.