

2 Scientific Objectives

2.1 Summary

One of the most unique characteristics of the JEM/SMILES observation is its high sensitivity in detecting atmospheric limb emission of the submillimeter wave range. Molecular species to be observed by JEM/SMILES are: normal O₃, isotope O₃, ClO, HCl, HOCl, BrO, HO₂, H₂O₂ and HNO₃ (See Section 4.2.4). Thus, the JEM/SMILES mission is distinguished as that focusing on the detailed halogen chemistry related to ozone destruction. Spatial coverage is near global, but there is no observational chance at polar latitudes (See Section 3.2.2). In spite of this limitation, we expect high possibility to make measurements within the elongated polar vortex in the northern hemisphere. Vertical resolution is supposed to be about 3 km. Detectable range for each of the molecular species with height will be discussed in detail in Section 4.

In view of the above-mentioned status, we focus on the following scientific targets for the JEM/SMILES mission.

- Variation and its impact of radical species
- Isotopic composition of ozone

JEM/SMILES will make measurements on several radical species crucial to the ozone chemistry. Some of them have never be seen by any other satellite measurements, and the JEM/SMILES mission will be the first to detect them such as BrO. It would be very interesting to see the space-time variations in the polar vortex and even in the background situation. Overall observations of these radical species will provide us further insight into the ozone chemistry in the middle atmosphere.

Another possible scientific objective using the JEM/SMILES data is on the isotopic composition of ozone. Unusually high enrichment in most of the heavy ozone isotopomers has been puzzling problem and we still don't have a clear answer for this. The JEM/SMILES observation will provide us important findings to work out the puzzle of ozone isotope anomaly.

In the following, the background and detailed description for the JEM/SMILES scientific targets will be discussed.

2.2 Background

The earth system consisting of the atmosphere, the ocean, and the biosphere has been affected by natural and artificial perturbations. Resulting changes in the earth system become obvious in several places and in several parameters. Among those the middle atmosphere is one of the good places to sense such changes, since it has been known that there are some sensitive atmospheric parameters and minor species. In recent years we have found several important trends in the middle atmosphere, and now we need the synthetic understanding of these variations to project the future state of the earth system.

After the discovery of the Antarctic ozone hole in the mid 1980s, numerous observations from the ground, aircraft and satellites have been conducted to clarify the mechanism. One of the characteristic features is that the ozone hole is a typical phenomenon in the southern hemisphere where the polar vortex is stronger and the resulting temperature is colder than the northern hemisphere. However, in the 1990s, it has been reported that the late-winter ozone amounts in the Arctic have decreased significantly [*Newman et al.*, 1997].

Surrounding the Arctic ozone depletion, a decrease of lower stratospheric ozone at mid latitudes in the northern hemisphere has been noticed recently. In *WMO Scientific*

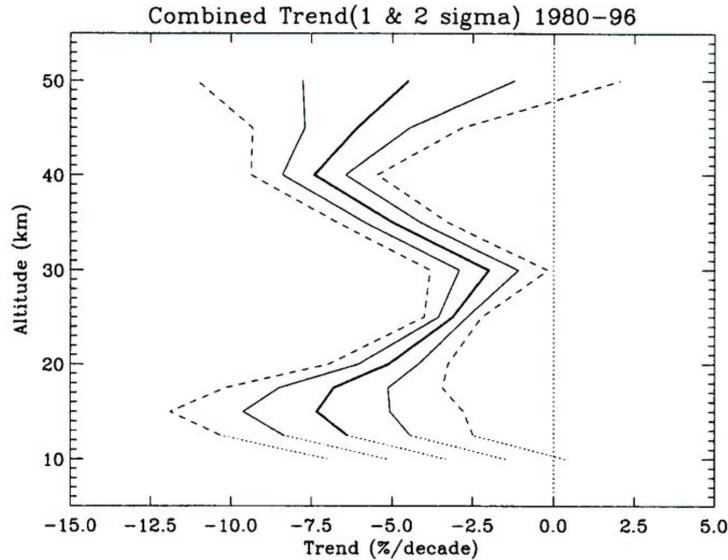


Figure 2.1 Estimate of the mean trend using all four measurement systems at northern mid-latitudes (heavy solid line). Combined uncertainties are also shown as 1σ (light solid line) and 2σ (dashed line) (After [WMO, 1999]).

Assessment of Ozone Depletion [1999, vertical distribution of the mean trend in the northern mid latitude is presented (Figure 2.1). This figure shows the lower stratospheric trend with 7.5 % decrease for decade, in addition to the upper stratospheric trend which is driven by the accumulation of anthropogenic chlorine. The lower stratospheric trend is also supposed to be contributed by the increased chlorine and bromine loading. However, the quantitative understanding about this mid latitude decrease is still uncertain. At the same time a cooling trend in the lower stratosphere has been observed. It is supposed to be due to the ozone decrease in the lower stratosphere [WMO, 1999]. The cooling trend may also contribute to the decreasing trend in ozone, but quantitative argument is not satisfactory yet.

One of the most highlighted trends in the stratosphere is an increasing one in water vapor, though it is not directly related to the anthropogenic perturbation (*SPARC Assessment of Upper Tropospheric and Stratospheric Water Vapor* [2000]). The observations show that water vapor has increased at a rate of about 1 %/year (Figure 2.2). This increase may be attributed to an increase in methane entering the stratosphere, because water vapor in the stratosphere is produced by the methane oxidation. The increase in methane, however, is found to be far below what we expect from the observational increase in water vapor. Another idea to explain the water vapor trend is a control by the equatorial tropopause temperature, which can affect the concentration of water vapor entering the stratosphere, but this does not seem the case because the observations show the cooling trend in the equatorial tropopause temperature. Thus the mechanism of the water vapor trend has not been explained yet. Dvortsov and Solomon [2001] conducted a model calculation by taking account of the water vapor increase. They found that it can contribute to the cooling trend in temperature from the radiative aspect of water vapor and to the decreasing trend in ozone from the chemical role of it.

Associated with the mid latitude ozone depletion, the lower stratospheric ozone is sensitive to the volcanic aerosols. The Mt. Pinatubo eruption is a good natural experiment

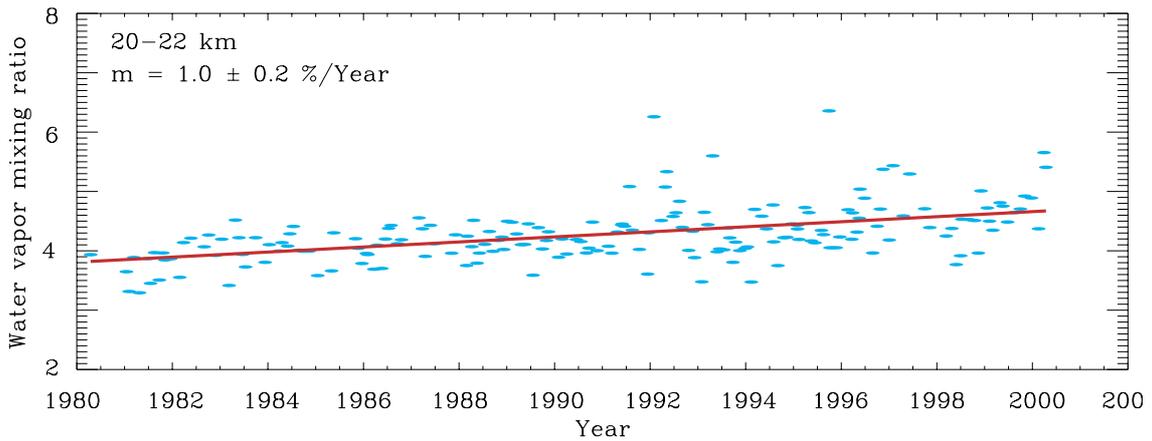


Figure 2.2 Time series of 20- 22 km layer averaged water vapor mixing ratio over Boulder. (After [SPARC, 2000]).

to learn its effect on the atmospheric dynamics and chemistry. After the eruption of Mt. Pinatubo in June 1991, significant total ozone decrease was observed. The eruption could modify the thermal structure of the atmosphere, then the general circulation, through the radiative effect. At the same time the increase of sulfuric aerosols may promote the heterogeneous chemistry around the tropopause region. Figure 2.3 shows a result from the two dimensional model with or without temperature variations and the aerosol effects

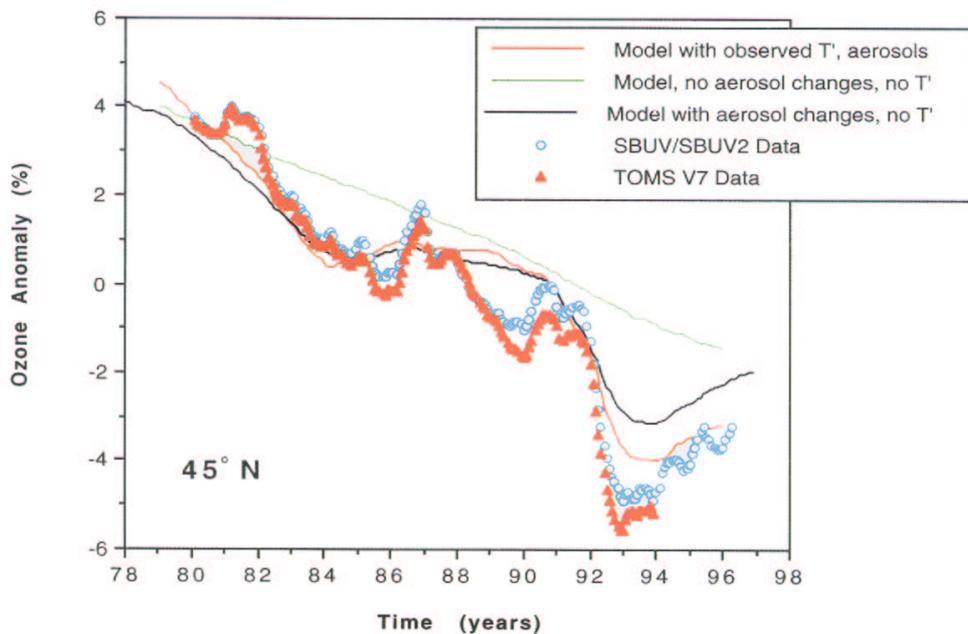


Figure 2.3 Observed and calculated total ozone anomalies from 1979 to 1997 at 45°N. (From [Solomon et al., 1997].)

[Solomon *et al.*, 1997]. This suggests that chemical effects owing to the aerosol loading play a significant role in perturbing the ozone anomalies.

From a dynamical point of view, understanding the meridional circulation in the stratosphere is also very important. Most long-live trace species are emitted in the troposphere as natural or anthropogenic perturbations. These are transported into the stratosphere and are deformed there. Methane is oxidized in the upper stratosphere and produces water vapor which is an important minor species to affect radiative balance of the atmosphere. CFCs are also destructed in the upper stratosphere, resulting in the production of chlorine species which affect the ozone layer especially in the lower stratosphere polar region during the spring time. Therefore, investigation of the atmospheric meridional circulation is a key issue to know temporal and spatial distributions of the minor species and their effects on the atmosphere.

Particularly the upper troposphere and lower stratosphere (UT/LS) is an important region for the dynamical processes such as transport and mixing, because the photochemical time scale of ozone in UT/LS is comparable or longer than that of the dynamical time scale. Of course the chemical processes such as heterogeneous reactions on PSCs are crucial to understand the ozone distribution and variation in the lower stratosphere in association with the ozone depletion. It has recently been recognized that the meridional circulation around UT/LS should be understood from the global view of dynamics (Figure 2.4). Holton *et al.* [1995] presented an idea that the upward motion at equatorial

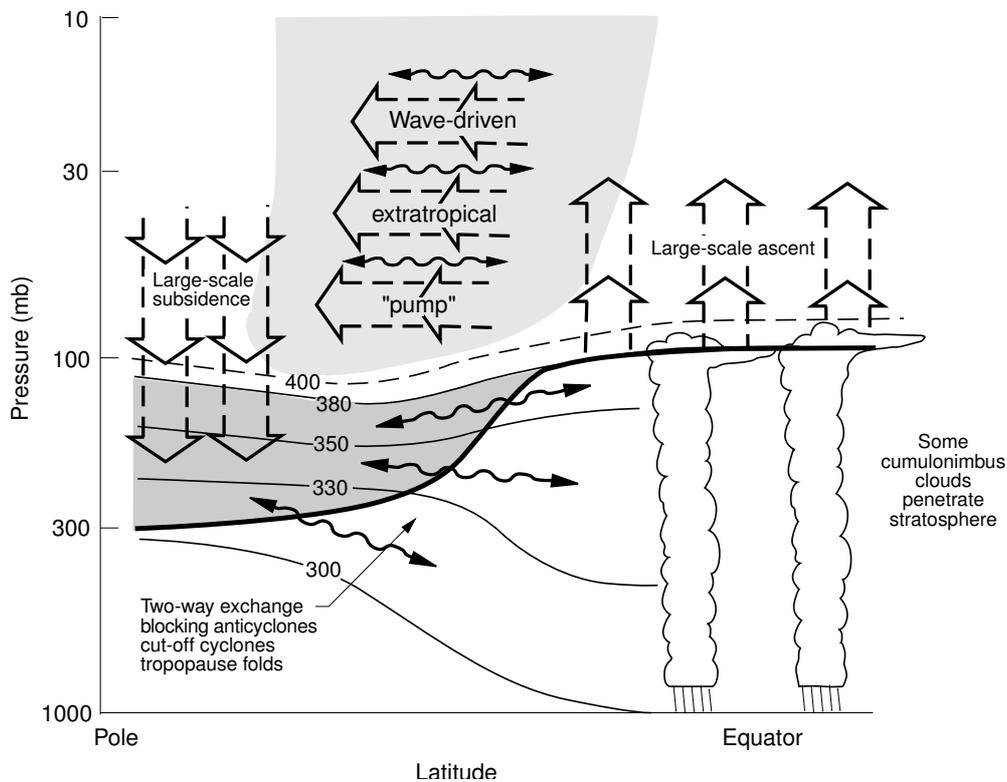


Figure 2.4 Dynamical aspects of stratosphere-troposphere exchange. The tropopause is shown by the thick line. Thin lines are isentropic or constant potential temperature surfaces labeled in kelvins. In detail, see Holton *et al.* [1995]

latitudes and the downward motion at mid- and high latitudes in the lower stratosphere are mainly driven by planetary wave induced torque. The meridional circulation is controlled by the strength of wave driving in the both hemispheres as the season goes by. At equatorial latitudes a modulation of the meridional circulation produces changes in the tropopause properties such as the tropopause height and the tropopause temperature. The manifestation of these combination is a recent finding of the so-called tape recorder signal in water vapor over the equator [Mote *et al.*, 1996].

All these factors affecting the earth's atmosphere system are closely connected with each other, but our recognition on these processes has just started; we don't know detailed inter-relation between the trends. We need comprehensive understanding of these variations to construct reliable models for the future earth system.

2.3 Radical Species in the Stratosphere

2.3.1 Introduction

Recently it has been widely recognized that ozone abundance in the lower stratosphere has crucially decreased. The Antarctic ozone hole has been observed since 1980's, the Arctic ozone depletion is another one over the past decade, and the mid latitude decrease trend in the northern lower stratosphere is slowly but certainly emerging. Current observational evidences and their understandings are summarized in detail in *WMO Scientific Assessment of Ozone Depletion* [1999]. What we have learned about the scenario of the ozone depletion is that the chlorine chemistry is crucial even in the lower stratosphere when the chemical processes such as heterogeneous reactions on PSCs occur.

One of the most successful results from the satellite was brought by the Microwave Limb Sounder (MLS) onboard the Upper Atmosphere Research Satellite (UARS). The MLS measurements provided the first global maps of stratospheric ClO, which should be observed when ozone is destructed by reactive chlorine chemistry. Figure 2.5 shows such enhancement of ClO and low abundance of O₃ even in the northern hemisphere of the lower stratosphere.

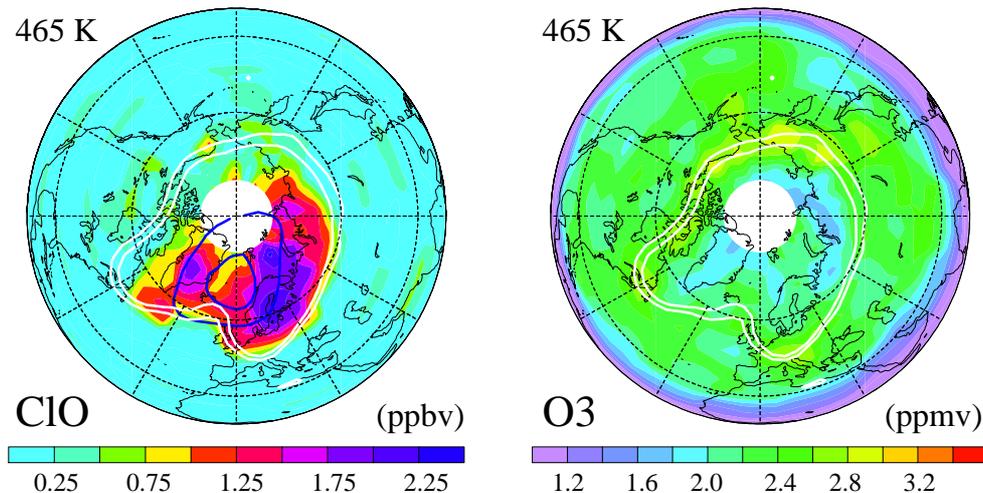


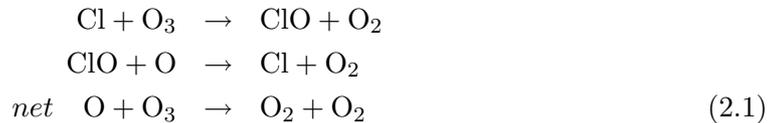
Figure 2.5 UARS MLS measurements of ClO and O₃ for February 20, 1996 for the northern hemisphere (After Manney *et al.* [1996]).

The decrease of ozone in the upper stratosphere has also been noticed on the basis of recent satellite observations (e.g. Figure 2.1). This decreasing trend is also understood in terms of the accumulation of anthropogenic chlorine. Especially in the upper stratosphere not only ClO_x cycle, but also NO_x , BrO_x and HO_x cycles become very important.

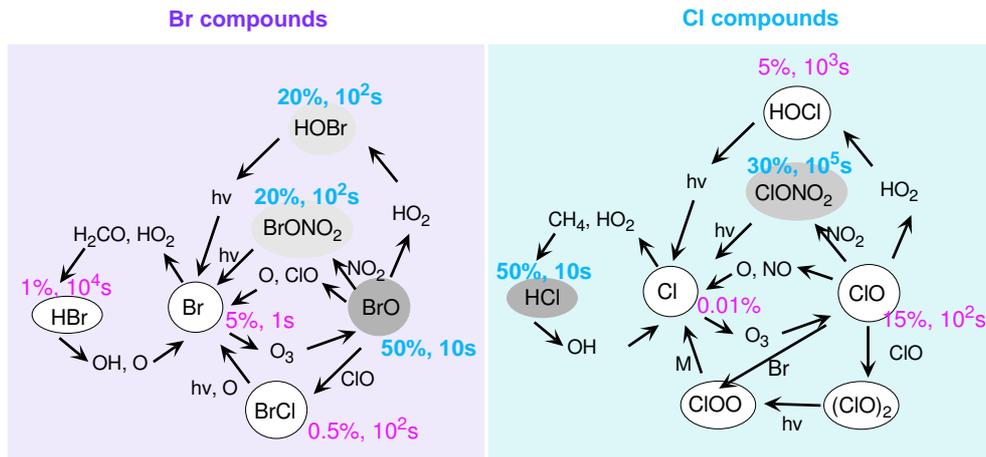
Here we will briefly see such reactions in association with the ozone destruction processes.

2.3.2 Chlorine and Bromine Chemistry

Over the Earth's lifetime, natural processes have regulated the balance of ozone in the stratosphere. In the past two decades, however, human production of halogen-containing compounds, such as chlorofluoro-carbons (CFCs), has brought an additional force to destroy ozone. Once in the stratosphere, the CFC molecules break up due to UV radiation and release their chlorine atoms. The free chlorine atoms then react with ozone molecules taking one oxygen atom to form chlorine monoxide as shown in Eq. (2.1).



The reaction cycle happens over and over again as called catalytic reaction, allowing a single atom of chlorine to destroy many of ozone. Fortunately, chlorine atoms do not remain in the stratosphere forever. When a free chlorine atom reacts with gases such as methane (CH_4), it produces molecule such as hydrogen chloride (HCl). This Chlorine cycle is illustrated in Figure 2.6 (right).



1 dimensional simulation
height = 30km, mid latitude spring, Time = 12:00

Figure 2.6 Ozone depletion reaction (% and lifetime) (After *Lary* [1996, 1997]).

Bromine-related chemistry in the stratosphere has become an important issue since the halons and methyl bromide have been suspected as ozone-depleting substances more powerful than the CFCs. Bromine is estimated to be about 50 times more efficient than Cl in destroying stratospheric ozone on a per-atom basis. Methyl bromide, which represents

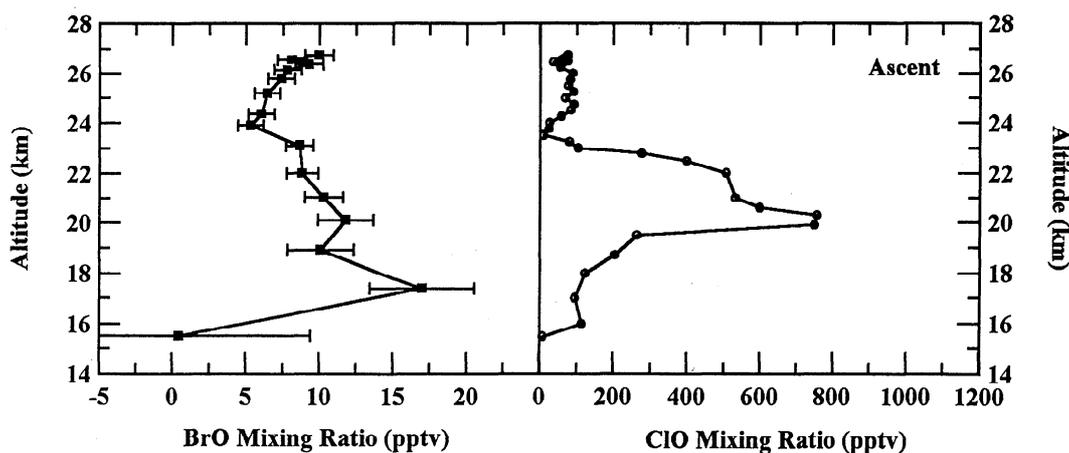


Figure 2.7 Profile of BrO mixing ratios (left panel); ClO mixing ratios from *Pierson et al.* [1997] (After [McKinney et al., 1997]).

the major source of bromine in the stratosphere, is used as an agricultural fumigant, and is an interesting compound in the context of stratospheric ozone depletion because it has significant natural sources and also has a very short lifetime in the troposphere.

Br photo-chemistry is believed to be basically similar to that of Cl, but the lifetime of radicals and reservoirs is completely different from that of Cl. In the Br chemistry, HBr and BrONO₂ do not work as reservoirs, as shown in Figure 2.6. In contrast to chlorine species, there have been few measurements of bromine compounds in the stratosphere. No observation has been reported for the thermal emission in the frequency region of the infrared and sub-millimeter. Almost the only in situ observation of BrO in the stratosphere is plotted in Figure 2.7 [McKinney et al., 1997].

2.3.3 HO_x Chemistry

Reactions of HO_x family (OH, HO₂, H₂O₂) are also considered to play an important role in the whole stratosphere. In spite of the fundamental importance of HO_x family, the observational data remains one of the poorest in the atmosphere. Global measurements of the latitudinal, seasonal, and diurnal variation in the HO_x family and related species, ClO_x, BrO_x, H₂O, CH₄, H₂ and O₃ are needed to address this deficiency. The JEM/SMILES observation will enable us to obtain the global data for HO₂, H₂O₂, HOCl, HOBr, ClO, BrO and O₃. Figure 2.8 summarizes ozone loss mechanism by the HO_x catalytic cycle, and we will see details in the following.

(a) HO_x reactions destroying the odd oxygens

The odd oxygen, O and O₃, are destructed by the activated hydrogen through a variety of catalytic cycles. In Figure 2.8, the reactions destroying the odd hydrogen in a direct manner are represented by the straight blue line. Water vapor molecule can be transformed into two OH radicals via the reaction of water vapor with the first electronically excited oxygen atom.



OH radical reacts with O₃ to form HO₂, and HO₂ radical reacts with O to produce OH

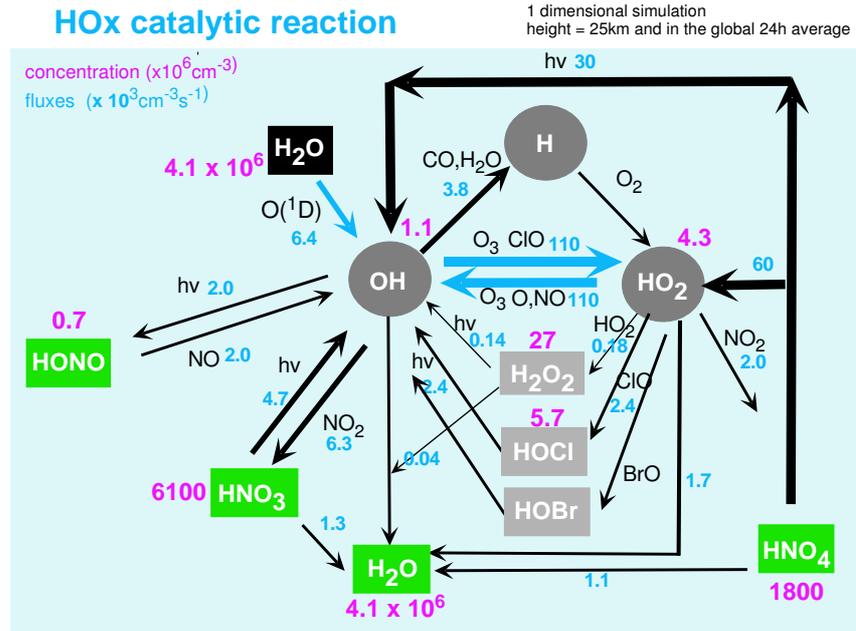
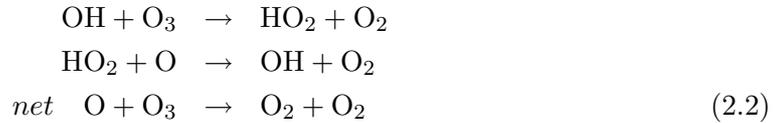


Figure 2.8 Gas phase reaction of HO_x in the stratosphere (Based on Brasseur [2000]).

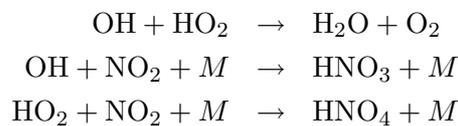
radical. The sum of reactions is written as follows.



It should be noticed that the net effect of the reactions is simply a conversion of two odd oxygens into two O₂ molecules.

(b) *Reservoir molecules*

The reservoir molecules are able to remove HO_x through catalytic reactions. In Figure 2.8, reservoir molecules are written by using green letters (i.e., H₂O, HNO₃, and HNO₄). These molecules are produced by the reaction such as,

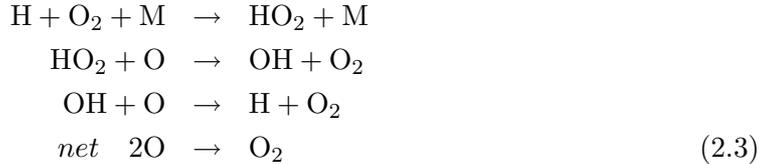


As these reservoir molecules are stable chemical compounds and have very long lifetimes, they are transported into the troposphere. They have an important role of removing HO_x from the stratosphere altogether.

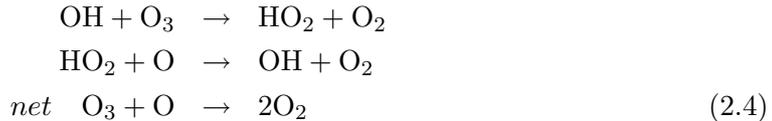
(c) *Reactions in the upper stratosphere*

In the upper stratosphere, where O atoms are relatively plentiful, the HO_x catalytic cycle outlined above is fairly effective. Two other reactions are also important in the upper stratosphere. The first one involves a free H (hydrogen) atom as an intermediate compound. This reaction is described in the upper part of Figure 2.8. Two O atoms are

converted into a single diatomic oxygen molecule.

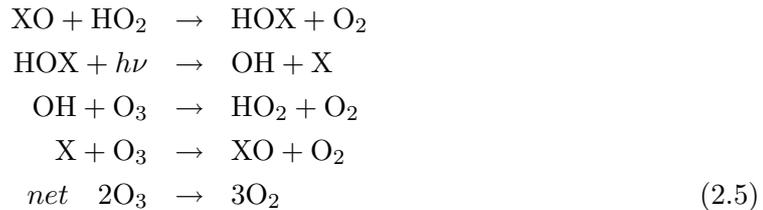


The second reaction involves the loss of two odd oxygens. The two odd oxygens are converted into two diatomic oxygen molecules.



(d) *Reactions in the lower stratosphere*

The HO_x cycles interacting with the chlorine or bromine cycles are important in the lower stratosphere. This is the most complicated one of the catalytic cycles, but yields the similar catalytic destruction of odd oxygen as we have seen so far. In these reactions, X can be either chlorine or bromine:



These two cycles are shown in the lower part of Figure 2.8.

2.3.4 Targets

JEM/SMILES will make measurements on several radical species crucial to the ozone chemistry. Some of them have never been seen by any other satellite measurements in the stratosphere, and the JEM/SMILES mission will be the first to detect them such as BrO. Especially in the lower stratosphere it would be very interesting to see the space-time variations of these species. Though there is a limitation of latitudinal coverage of the JEM/SMILES observations, we expect high possibility to make measurements within the elongated polar vortex in the northern hemisphere. Also we hope JEM/SMILES has a capability to observe such species even in the background situation.

The upper stratosphere is another interesting field to investigate from the viewpoint of the ozone budget. By the use of the JEM/SMILES data we may try to estimate the decreasing trend of ozone affected by the anthropogenic chlorine and bromine loading. As to the HO_x reaction cycle, for example, the volume mixing ratios of HO₂ and H₂O₂ become large in the upper stratosphere and the mesosphere. This region is still unknown considering the distribution of HO_x species.

2.4 Observation of Ozone Isotopes

2.4.1 Introduction

A problem in molecular and atmospheric physics has puzzled scientists for almost two decades: the unusually high enrichments in most of the heavy isotopomers of ozone have

been observed in the troposphere and stratosphere [Thiemens, 1999]. In general, by combining the observed isotopic compositions with knowledge of the rates and isotope effect of each of the process producing and removing a given molecule in a system, one should be able to validate them with each other. Alternatively, if the isotopic composition and either the isotope specific production or loss rates are known, the other may be inferred from the available observations using a simple model on the basis of the corresponding chemistry of the molecule. Despite the extensive laboratory studies and atmospheric observations have been made, a convincing physical explanation of the processes to result in the heavy ozone isotope enrichment is still missing.

The oxygen isotope distribution in the Earth’s atmosphere is well defined. The three stable isotopes have the following abundance: $^{16}\text{O} = 0.9976$, $^{17}\text{O} = 0.00037$, and $^{18}\text{O} = 0.00204$. Besides the dominant form of ozone, $^{48}\text{O}_3$, the isotopomers produced by single replacement of ^{16}O to ^{17}O or ^{18}O are of any significance in the atmosphere, namely $^{49}\text{O}_3$ and $^{50}\text{O}_3$, respectively. The abundance ratios of these isotopomers are statistically calculated to be 900 and 163 for $^{48}\text{O}_3/^{49}\text{O}_3$ and $^{48}\text{O}_3/^{50}\text{O}_3$, respectively. The degree of the ozone isotope enrichment is defined as $\delta^M\text{O} = ({}^M R_{obs}/{}^M R_{std} - 1) \times 1000$ [‰], where ${}^M R_{obs}$ is the observed abundance ratio of the heavy isotopomer with mass number M , and ${}^M R_{std}$ is the standard ratio described above [Kaye, 1987]. Isotope fractionation in chemical reaction is usually explained in terms of its mass-dependence. For example, the isotope ratios in a three-isotope system are an approximate linear function of the differences in the reciprocal masses of the isotopic species. In the case of ozone isotopes, mass-dependent fractionation is given by $\delta^{17}\text{O} \approx 0.5\delta^{18}\text{O}$. Thus, 2 ‰ enrichment in ^{18}O is accompanied by 1 ‰ fractionation of ^{17}O . The “mass-independent isotopic compositions,” or simply “isotope anomaly” are now known to be pervasive in a range of atmospheric molecules, including O_3 , CO_2 , N_2O and sulfate aerosols, which awaits for thorough understanding of the mechanism.

2.4.2 Atmospheric Observations and Laboratory and Theoretical Studies

The first observational evidence of the ozone isotope anomaly was found during a balloon flight using an in-situ airborne mass spectrometer (AMS) in 1981 [Mauersberger, 1981]. Their study showed the stratospheric ozone is greatly enriched in $^{50}\text{O}_3$, as high as $\delta \approx 400$ ‰ at 32 km, with approximately equal $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ enrichments. Hereafter, heavy isotope enrichments in stratospheric ozone have been confirmed by various techniques as reviewed by Johnson *et al.* [2000] (Figure 2.9). The first ground-based FT-IR measurements were made in 1985 and could discriminate between the two isotopomers of $^{50}\text{O}_3$ while mass spectrometric measurements cannot. The higher column enrichment in asymmetric isotopomer of $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ than symmetric one $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ was observed. The Atmospheric Trace Molecule Spectroscopy (ATMOS) Grille Spectrometer has flown four times on the Space Shuttle since 1985. The zonal mean profiles of $^{18}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ retrieved showed no statistically significant variation with latitude, altitude, or time. The FIRS-2 FTIR spectrometer also made measurements during seven balloon flights, which took place between 1989 and 1997.

The extent of the enrichments observed are in good agreement except that AMS measurements showed systematically larger enrichments in ^{18}O compared to cryogenic sampling (CS), ATOMS, and FIRS results. Meanwhile, observed variation of the enrichments with latitude, altitude, or time are not consistent with each other where the statistically significant variability was seen in AMS and CS measurements while it was not seen in spectroscopic observations. One possible explanation of the discrepancy is that the small variability may not be detected with the limited precision of the remote sensing mea-

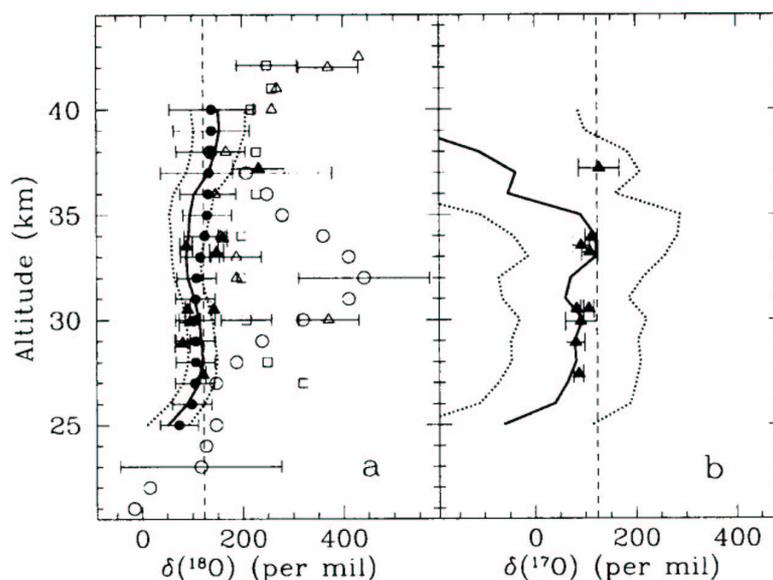


Figure 2.9 Comparison of published results of measurements of heavy ozone enrichment. (a) Enrichment for $^{50}\text{O}_3$. Enrichment for $^{49}\text{O}_3$. (From *Johnson et al.* [2000]).

measurements. Very recently, *Mauersberger et al.* [2001] have made a critical review for the stratospheric ozone isotope data, whose samples were cryogenically collected in the past. They concluded that the data indicated $^{50}\text{O}_3$ enrichment ranging from 70 to 90 ‰ in the middle stratosphere, in which the enrichments were in good agreement with results from laboratory studies, and suggested to abandon several measurements showing very high enrichments due to unidentified measurement errors.

Since pioneering work of atmospheric observations by *Mauersberger* [1981], the dedicated laboratory experiments have emerged to explain the ozone isotope anomaly occurred in the stratosphere. The relative recombination rate coefficients for ozone production from various combinations of atomic and molecular oxygen isotopes have been evaluated through mass spectrometric and tunable diode laser spectroscopic experiments [for example *Mauersberger et al.*, 1999]. Those studies suggest that, for example, the rate coefficient of the recombination $^{16}\text{O} + ^{18}\text{O}^{18}\text{O}$ is about 50 ‰ larger than that of the standard $^{48}\text{O}_3$ formation. Such laboratory data have been applied to model the enrichments of symmetric and asymmetric $^{50}\text{O}_3$ and $^{49}\text{O}_3$ in the stratosphere [*Johnson et al.*, 2000]. Laboratory experiments also motivated quantum chemical treatment of the kinetic isotope effects in the recombination processes [*Gao and Marcus*, 2001].

2.4.3 Targets

The inability to account for the stratospheric ozone isotope anomaly and variability represents a significant inadequacy in our understanding of the chemical transformation and/or transport of stratospheric and tropospheric ozone. The magnitude of the heavy isotope enrichment at times far exceeds that expected on the basis of laboratory measurements and theoretical studies as shown in Figure 2.9. Further improvement of precision, spatial and temporal coverage of the measurement are required to get a firm picture of the enrichments in stratospheric $^{50}\text{O}_3$ and $^{49}\text{O}_3$, which will provide vital information for the

sound understanding of the mechanism of the isotopic fractionation. Global and quantitative measurements may elucidate hitherto unobserved chemical processes related to the heavy isotope enrichment of ozone, by making a comparison with the experimental and theoretical studies. The JEM/SMILES observations will cover polar, mid latitude and tropical region (from 38°S to 65°N) in the latitude range between 10 and 60 km with all 5 isotopes of mono-substituted ozone; $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, $^{18}\text{O}^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{17}\text{O}^{16}\text{O}$, and $^{17}\text{O}^{16}\text{O}^{16}\text{O}$. The first simultaneous observation of ozone isotopic species reduces systematic errors due to the difference of the observational methods as previously. We propose that the new tool JEM/SMILES observation will provide us important findings to work out the puzzle of ozone isotope anomaly

It is worth while commenting that ozone molecule is believed to be the principal source of mass-independent fractionation in other atmospheric molecules and its anomaly can transfer to other species either through direct reaction or via reaction with the ozone photolysis products. For example, precise measurements of the ozone isotopomer distributions are crucial to investigate the oxygen isotope distributions of stratospheric and mesospheric CO_2 by means of a photochemical model calculation [Barth and Zahn, 1997]. This is because the CO_2 isotope anomaly is thought to be related to the ozone isotope anomaly through the reaction of CO_2 with $\text{O}(^1\text{D})$ generated via UV photolysis of ozone. More recently a photochemical equilibrium model for short-lived radical species such as ClO , HO_x , and NO_x , has been constructed to calculate their amounts of mass-independent fractionations under mid-latitude conditions [Lyons, 2001]. Thus the JEM/SMILES observations of ozone isotopomer would also be incorporated in the studies of isotope anomalies of other atmospheric species.

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