

# A Two-Dimensional Model of Ion Composition in the Stratosphere

## 2. Negative Ions

G. BEIG<sup>1</sup>

*Physical Research Laboratory, Ahmedabad, India*

S. WALTERS AND G. BRASSEUR

*National Center for Atmospheric Research, Boulder, Colorado*

A two-dimensional meridional model of negative ions in the stratosphere is presented. It indicates that  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  core ions with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  ligands are the most abundant negative ions in this region of the atmosphere. In accordance with observations at 44°N the model predicts a sharp changeover of  $\text{HSO}_4^-$  core ions over  $\text{NO}_3^-$  core ions at about 32 km. It also predicts a reverse changeover at 42 km above which  $\text{NO}_3^-$  core ions again become dominant. For other latitudes no comparison can be made due to the lack of observational data. The negative ion composition appears to be determined by sulfuric acid vapor and nitric acid concentrations. The sensitivity of the ion composition model to the concentration of these acids is discussed. Finally, the meridional distributions of major negative ions are presented. A companion paper on positive ions is presented by Beig et al. (this issue).

### 1. INTRODUCTION

The initial attempt to study the negative ion chemistry of the atmosphere was made by *Fehsenfeld et al.* [1967] when they measured in the laboratory the reaction rates for the loss processes of  $\text{O}_2^-$  ions under conditions encountered in the upper part of the middle atmosphere. They reported that the  $\text{NO}_3^-$  ion is very stable in the atmosphere. *Ferguson* [1969] reviewed the negative ion-molecular reactions for the ionosphere and emphasized the role of negative ion clustering reactions. *Mohnen* [1971] made the first attempt to predict the components of different ions below the stratopause. Later, *Ferguson* [1975] extrapolated the *D* region scheme down to the stratosphere with some additional reaction channels. The first in situ mass spectrometry measurement of the negative ions in the stratosphere was reported by *Arnold and Henschen* [1978] who confirmed the presence of  $\text{NO}_3^-$  core cluster ions and detected another type of cluster ion whose core is  $\text{HSO}_4^-$ . Thereafter, several negative ion composition measurements were carried out mainly by two groups: Belgian Institute for Space Aeronomy (BISA) [*Arijs et al.*, 1981, 1982, 1983, 1985] and Max Planck-Institut für Kernphysik, Heidelberg (MPIH) [*Arnold et al.*, 1981; *Arnold and Qiu*, 1984; *Schlager and Arnold*, 1987]. All these measurements were made at mid-latitudes (44°N), and as in the case of positive ions no attempt has been made so far to gather observational data for other latitudes. These measurements have established the existence of two dominant families of negative ions called  $\text{NO}_3^-$  core ions (represented as  $\text{NO}_3^- (\text{HNO}_3)_n$ ) and  $\text{HSO}_4^-$  core ions (represented

as  $\text{HSO}_4^- (\text{HNO}_3)_n$  and  $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_n$ ) having  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  as ligands. It has also become clear that a sharp changeover to  $\text{HSO}_4^-$  core ions predominating over  $\text{NO}_3^-$  core ions occurs somewhere between 30 and 35 km. In contrast, many in situ measurements of total negative ion density have been made all over the globe [*Widdel et al.*, 1977; *Rosen et al.*, 1985; *Beig et al.*, 1988].

After the above mentioned ion composition measurements, the theoretical studies on ion chemistry of stratosphere were accelerated. *Brasseur and Chatel* [1983] made the first attempt to make a detailed numerical model of stratospheric negative ion composition. They assumed the unknown reaction rates by adjusting them to fit the observed data at 35 km and reported the relative abundance of negative ions at other altitudes. Thereafter, a few more results based upon a steady state model of negative ions were reported by *Kawamoto and Ogawa* [1984, 1985]. However, these model studies were based on a limited knowledge of ion kinetics and several assumptions had to be made. Reaction rates of ion clusters having  $\text{NO}_3^-$  cores and  $\text{HSO}_4^-$  cores are poorly known, although the equilibrium constants among the  $\text{NO}_3^- (\text{HNO}_3)_n$  type of ions can now be calculated from the measurements of enthalpy and entropy changes [*Davidson et al.*, 1977; *Wlodek et al.*, 1980]. In the present paper we have taken a simplified approach to minimize the number of assumptions and substituted all the intermediate channels by a single channel whose equilibrium constant is suitably chosen.

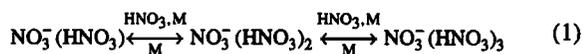
As discussed in a companion paper [*Beig et al.*, this issue], dynamics and latitudinal variations of neutral species density should be reflected in the ion composition data. In addition to other parameters discussed earlier, negative ion composition is highly influenced by the concentrations of nitric acid and sulfuric acid vapors. Several experimental and theoretical results on nitric acid density are available [World Meteorological Organization (WMO), 1981, 1985]. However, no direct measurements of  $\text{H}_2\text{SO}_4$  have been reported so far and the concentration of this compound has been deduced from the

<sup>1</sup>Now at Radio Science Division, National Physical Laboratory, New Delhi, India.

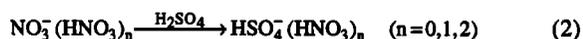
negative ion composition data. The profiles of  $\text{H}_2\text{SO}_4$  density obtained in this manner vary considerably from one another. The chemistry of  $\text{H}_2\text{SO}_4$  is complex and not properly understood. However, some theoretical attempts to provide a vertical profile of  $\text{H}_2\text{SO}_4$  have been made by *Turco et al.* [1981], *Arijs et al.* [1983], and *Ingels et al.* [1987]. *Arijs et al.* [1983] have calculated the vapor pressure of sulfuric acid from thermodynamic considerations, whereas *Turco et al.* [1981] considered different possible loss mechanisms for this acid. These models, however, could not fully reproduce the observed features of sulfuric acid density profile deduced from ion composition measurements. In the present work we have used the two-dimensional model to produce a meridional distribution of  $\text{H}_2\text{SO}_4$ , the details of which are discussed below.

## 2. SIMPLIFIED ION SCHEME

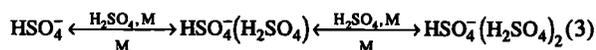
The simplified negative ion chemical scheme used in this work is shown in Figure 1 [Beig and Chakrabarty, 1992]. The first negative ion in the stratosphere is produced by the attachment of free electrons to oxygen molecules resulting in the primary ion  $\text{O}_2^-$ . The chemical evolution of negative ions in this region can be classified in three stages. In a first stage, the primary  $\text{O}_2^-$  ions are converted into  $\text{CO}_3^-$  and  $\text{CO}_4^-$  by reaction with relatively abundant trace gases such as  $\text{CO}_2$ , etc. The time scales for these reactions are very small. In a second stage, the  $\text{CO}_3^-$  and  $\text{CO}_4^-$  ions react with nitrogen oxides (such as  $\text{NO}$  and  $\text{NO}_2$ ) to form  $\text{NO}_3^-$  which is very stable due to its high electron affinity. In addition, clustering reactions of  $\text{NO}_3^-$  are possible, so that hydration resulting in  $\text{NO}_3^-(\text{H}_2\text{O})_n$  type ions should be fast. However, this latter process does not play a major role since  $\text{NO}_3^-(\text{H}_2\text{O})_n$  ions are weakly bonded ions. As a result, in a third stage, nitric acid and sulfuric acid replace  $\text{H}_2\text{O}$  [Fehsenfeld et al., 1975]. Reactions of  $\text{NO}_3^-$  ions with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are equally fast and compete with each other. Hence the products of stage 3 represent the most abundant negative ion species in the stratosphere. As shown in Figure 1, when  $\text{NO}_3^-$  combines with  $\text{HNO}_3$  then  $\text{NO}_3^-\cdot\text{HNO}_3$  is formed; this undergoes further clustering with  $\text{HNO}_3$  as follows:



Sulfate is introduced in the negative ion chemistry by reaction of nitrate core ions with  $\text{H}_2\text{SO}_4$  as



and clustering of  $\text{HSO}_4^-$  with sulfuric acid molecules, such as



The reaction rates of the ions represented in the first block of Figure 1 (up to  $\text{NO}_3^-$ ) are all based on experimental results and laboratory data. We have adopted the rates compiled and used by *Thomas* [1983]. The reaction rates of the conversion from  $\text{NO}_3^-$  to  $\text{HSO}_4^-$  cores reaching (2) were measured by *Viggiano et al.* [1982]. The majority of the remaining reaction rates are not properly known. Approximate values of these reaction rates based on some simple assumptions were used by the modelers in the past to develop a detailed model of

stratospheric ion composition [Brasseur and Chatel, 1983; Kawamoto and Ogawa, 1984, 1985]. For example, in the case of reaction (1) the forward reaction rates for the conversion of one cluster ion into the next cluster ion were assumed to be almost the same for each path. Similar is the case for reactions (2) and (3).

To minimize the number of assumptions, we have lumped all the reaction channels of (1), (2), and (3) into three different single reaction channels, as shown in Figure 1. In this figure,  $\text{NO}_3^-(\text{HNO}_3)_n$  represents the sum of all the  $\text{NO}_3^-$  core ions having  $\text{HNO}_3$  as ligand except  $\text{NO}_3^-\cdot\text{HNO}_3$ .  $\text{HSO}_4^-(\text{HNO}_3)_n$  and  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$  represent the sum of all the  $\text{HSO}_4^-$  core ions having  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  as ligands, respectively. The reaction rates for each of the above channels have been assumed to be identical, as done by earlier workers for one clustering to another. For the clustering reaction with  $\text{HNO}_3$  on  $\text{NO}_3^-(\text{HNO}_3)_n$  ( $n = 0, 1, 2$ ), no rate constant is available except for  $n = 0$  where *Viggiano et al.* [1985] and *Fehsenfeld et al.* [1975] indicated a value of about  $1 \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}$ . Therefore this value has been applied for the forward reaction channels of (1). For three reverse reaction rates, R2 and two of equation (1), measured thermodynamic values [Davidson et al., 1977; Wlodek et al., 1980] have been used to calculate the molecular equilibrium constants from which reaction rates have been calculated [Brasseur and Chatel, 1983; Kawamoto and Ogawa, 1984]. We have used the value of R2 as used by earlier workers and lumped the two remaining back reactions of (1) by a single reaction whose rate is taken as R11. All the values of reaction rates used in Figure 1 are listed in Table 1.

The net loss of negative ions at the stratospheric level is mainly by ion-ion recombination. In the present work the value of this coefficient is taken to be the same as the one used in the companion paper [Beig et al., this issue]. Similarly the associated ion production rate has been calculated by the parameterization given by *Heaps* [1978] for the solar maximum condition.

## 3. METHODOLOGY AND NEUTRAL FIELDS

The continuity equations of all the ions of Figure 1 are specified and solved simultaneously for the steady state conditions. Charge neutrality between positive and negative ions has been assumed. An updated version of the two-dimensional model [Brasseur et al., 1990] has been used to simulate the behavior of all the neutral species involved in negative ion chemistry. It extends from the surface to the mesopause and from the south to the north pole with a spatial resolution of  $5^\circ$  in latitude and 1 km in altitude. A brief description of this model is included in the companion paper [Beig et al., this issue]. The ion scheme shown in Figure 1 is added to the neutral model for the altitude range from 15 to 50 km. It involves 18 charged species, including the electron. The description of major neutral trace species affecting the chemistry of negative ions in the stratosphere is given below along with the corresponding model results.

### 3.1 Sulfuric Acid Vapor

Sulfuric acid is believed to play a major role in the negative ion chemistry of the stratosphere. There is no direct measurement of  $\text{H}_2\text{SO}_4$  concentration, but the density of this compound has been derived from negative ion composition data [Arijs et al., 1985; Schlager and Arnold, 1987] which are available only for  $44^\circ\text{N}$ , from thermodynamic calculations

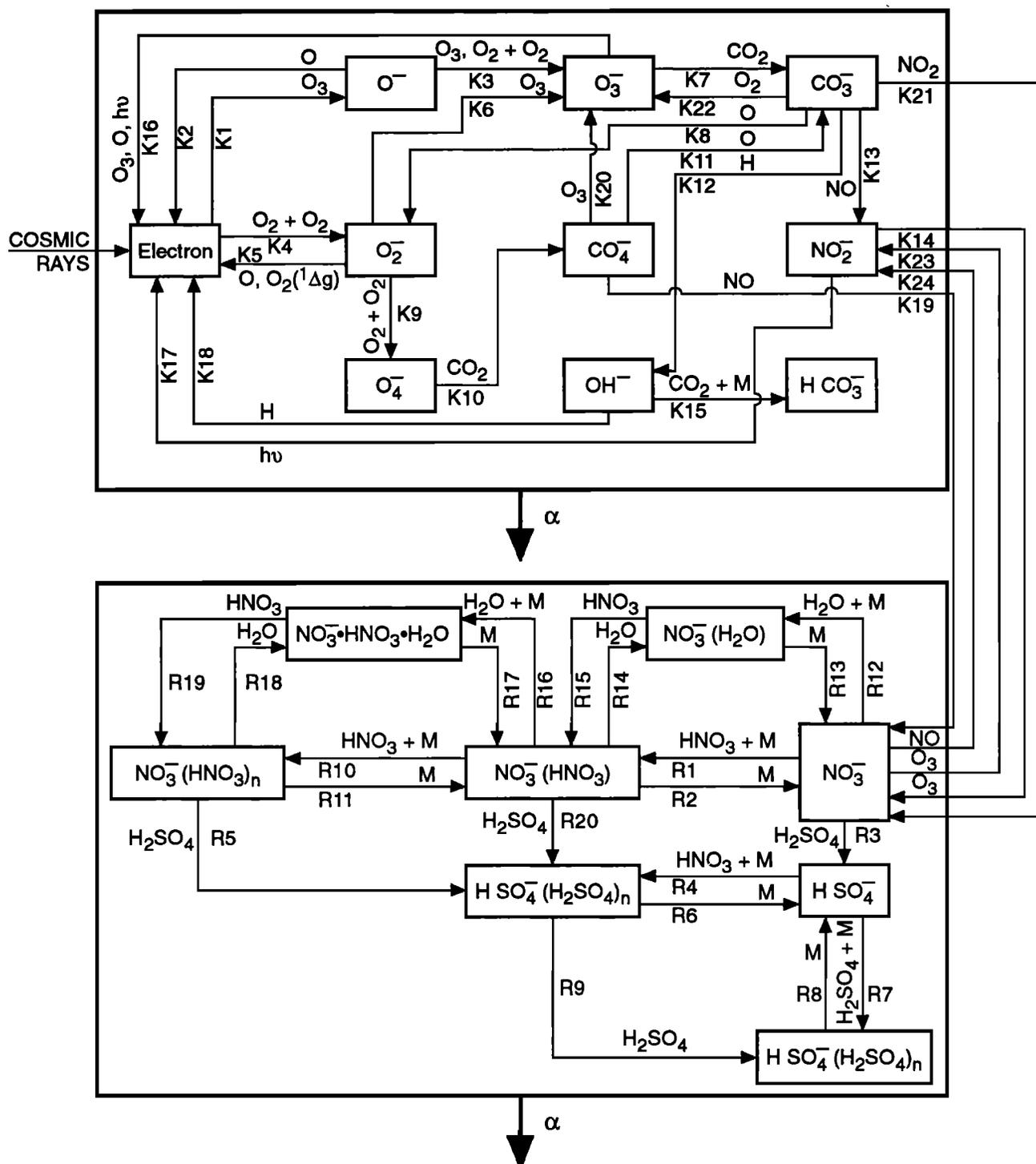


Fig. 1. Simplified negative ion chemical scheme adopted in this work.

based on vapor pressure considerations [Arijs *et al.*, 1983], and from model calculations [Turco *et al.*, 1981]. Large discrepancies exist between the concentrations obtained through these methods and even between the values derived from ion composition data [Ingels *et al.*, 1987]. The production mechanism of  $H_2SO_4$ , described by Viggiano and Arnold [1983] and Qui and Arnold [1984], has been adopted. However, the complete chemistry of  $H_2SO_4$  is not yet properly understood and, consequently, the chemical scheme adopted in the model probably represents an oversimplification. Major

discrepancies arise, for example, from uncertainties in the loss processes of sulfuric acid molecules. In recent years, Turco *et al.* [1981] have made a theoretical attempt to develop a one-dimensional model of  $H_2SO_4$ , considering various possible loss mechanisms. At low altitudes,  $H_2SO_4$  is primarily controlled by local photochemical production and heterogeneous removal by aerosol particles. Above about 28 km the  $H_2SO_4$  density can be calculated from the equilibrium saturation pressure of this acid over aerosols and hence is strongly temperature dependent. Above about 35 km,  $H_2SO_4$  is

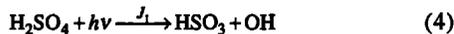
TABLE 1. Simplified Chemical Scheme for Sulfur Compounds Adopted in the Model

Reaction	Rate Constant*
$(\text{CH}_3)_2\text{S} + \text{OH} \xrightarrow{\text{O}_2} \text{SO}_2 + \text{products}$	$7 \times 10^{-12}$
$(\text{CH}_3)_2\text{S} + \text{O} \xrightarrow{\text{O}_2} \text{SO}_2 + \text{products}$	$1.3 \times 10^{-11} \exp(409/T)$
$\text{OCS} + h\nu \xrightarrow{\text{O}_2} \text{SO}_2 + \text{CO}$	J(OCS)
$\text{OCS} + \text{OH} \xrightarrow{\text{O}_2} \text{SO}_2 + \text{products}$	$1.1 \times 10^{-13} \exp(-1200/T)$
$\text{OCS} + \text{O} \xrightarrow{\text{O}_2} \text{SO}_2 + \text{products}$	$2.1 \times 10^{-11} \exp(-2200/T)$
$\text{SO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HSO}_3$	$3 \times 10^{-31} (300/T)^{3.3} [\text{M}]$
$\text{HSO}_3 + h\nu \rightarrow \text{SO}_2 + \text{OH}$	J(HSO <sub>3</sub> ) = J(HNO <sub>3</sub> )
$\text{HSO}_3 \rightarrow \text{H}_2\text{SO}_4(\text{g})$	$\tau = 20 \text{ days}$
$\text{H}_2\text{SO}_4(\text{g}) + h\nu \rightarrow \text{HSO}_3 + \text{OH}$	J(H <sub>2</sub> SO <sub>4</sub> ) = J(HNO <sub>3</sub> )
$\text{H}_2\text{SO}_4(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{aerosol})$	$\tau = 5 \text{ hours (below 24 km)}$
$\text{H}_2\text{SO}_4 + \text{washout (troposphere)}$	

J(x) is the photolysis frequency (s<sup>-1</sup>) of species X;  $\tau$  is the conversion time.

\*Rate constants are in cm<sup>3</sup> s<sup>-1</sup>.

believed to be in the gas phase and its major loss is assumed to be photolysis. We have thus ignored a possible removal by the OH radical or a heterogeneous destruction by "meteor smoke particles." This latter mechanism has been proposed by *Turco et al.* [1981] but questioned by *Qiu and Arnold* [1984]. We have also considered a loss of H<sub>2</sub>SO<sub>4</sub> by washout in the troposphere and a conversion of gas phase sulfuric acid into the stratospheric aerosol layer with a constant aerosol loss coefficient equal to  $5.5 \times 10^{-5} \text{ s}^{-1}$  (conversion time of 5 hours) up to about 24 km. Above this level the loss of H<sub>2</sub>SO<sub>4</sub> has been assumed to decrease exponentially with a scale height of about 6 km. The rate of the photochemical reaction



is not yet known. In the present work the photodissociation coefficient ( $J_1$ ) was assumed to be equal to that of HNO<sub>3</sub>. This reaction contributes to the production of HSO<sub>3</sub>, which is also assumed to be rapidly photolyzed, resulting in the formation of SO<sub>2</sub>. The major source of H<sub>2</sub>SO<sub>4</sub> in the stratosphere is provided by photolysis of carbonyl sulfide (COS) and subsequent oxidation mechanisms involving SO<sub>2</sub>. Table 1 shows the chemical scheme adopted in the model with the corresponding reaction rate constants or conversion times ( $\tau$ ).

Figure 2a shows the vertical profile of sulfuric acid vapor obtained at 45°N. All the available observational data (44°N) as reported by two groups, i.e., MPIH [e.g., *Schlager and Arnold* [1987]] and BISA [e.g., *Ingels et al.* [1987]], are also shown in this figure along with one-dimensional model results of *Turco et al.* [1981]. Both models and observations suggest that the number density of H<sub>2</sub>SO<sub>4</sub> is nearly constant with altitude below about 25 km and increases with height above this level to attain a maximum value ( $\approx 2 \times 10^6 \text{ cm}^{-3}$ ) at about 34 km. Above this height, the concentration of H<sub>2</sub>SO<sub>4</sub> decreases. With the assumptions made, our results agree very well with the experimental data of the BISA group represented by the shaded area (4) in Figure 2a. Present results are also in reasonably good agreement with the experimental results of the MPIH group (represented by circles) above about 30 km. However, below 30 km altitude, present values of H<sub>2</sub>SO<sub>4</sub>

number densities are higher than the MPIH values. It can be mentioned here that the BISA data are consistently higher than the MPIH data. *Viggiano and Arnold* [1983] have commented that one cannot at this moment conclude whether this represents a real difference due to seasonal or other variations or a systematic difference. The details of the one-dimensional model profiles (1, 2, and 3) are mentioned by *Turco et al.* [1981]. Our model profile is close to profile 3 of *Turco et al.* [1981] which also includes an additional loss mechanism of H<sub>2</sub>SO<sub>4</sub> by "meteoric smoke" particles. However, the

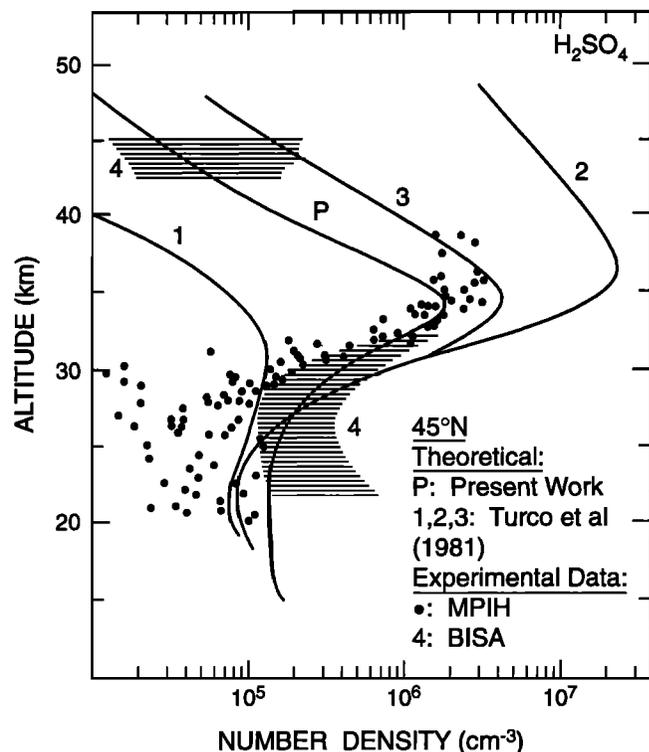


Fig. 2a. Comparison of vertical distribution of sulfuric acid vapor number density (cm<sup>-3</sup>) calculated at 45°N by our two-dimensional model with available observational data. One-dimensional model profiles of *Turco et al.* [1981] are also shown.

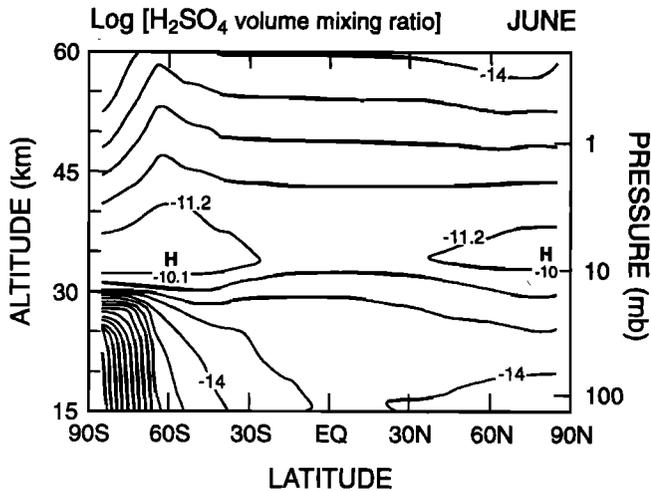


Fig. 2b. Meridional distribution of sulfuric acid vapor volume mixing ratio (logarithmic scale) derived by the two-dimensional model. June conditions.

experimental data of the MPIH group fall between our model profile and profile 3 in the 35- to 40-km altitude region.

The meridional distribution of sulfuric acid vapor volume mixing ratio is shown in Figure 2b. It is found that the value of  $\text{H}_2\text{SO}_4$  is maximum at tropical latitudes and minimum at the south pole below 30 km. A maximum of the  $\text{H}_2\text{SO}_4$  occurs at about 34 km for low and mid-latitudes, whereas for high latitudes, maximum values are somewhere between 30 and 33 km.

### 3.2. Nitric Acid and Other Neutral Species

In addition to  $\text{H}_2\text{SO}_4$ , several other neutral species take part in the negative ion chemistry (see Figure 1). The distribution of all these species has been calculated using two-dimensional models, as discussed by Brasseur *et al* [1990]. However, the concentration of these species do not play any major role in negative ion chemistry except in the case of  $\text{HNO}_3$ . The meridional distribution of  $\text{HNO}_3$  volume mixing ratio is shown in Figure 3 from which it is clear that  $\text{HNO}_3$  volume mixing ratio is higher toward the poles. It has a

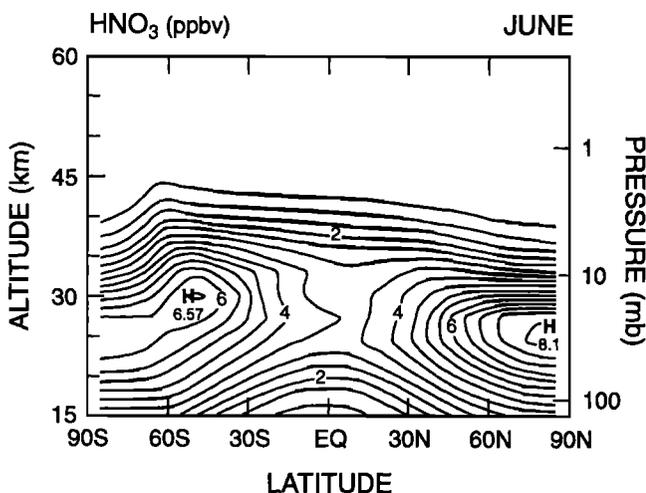


Fig. 3. Meridional distribution of nitric acid volume mixing ratio calculated in the model. June conditions.

maximum value at 50°S and at 80°N. The volume mixing ratio of  $\text{HNO}_3$  increases with height and attains a maximum around 27 km, above which it again starts decreasing. The maximum latitudinal variation in  $\text{HNO}_3$  occurs between 20-km and 33-km altitudes. It should be noted that heterogeneous conversion of  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  on the surface of sulfate aerosol particles in the lower stratosphere should enhance the concentration of nitric acid, particularly at high latitudes. Due to uncertainties in the rate of this conversion this latter process has not been included in the present model calculations. The distributions of major neutrals  $\text{O}_2$  and  $\text{N}_2$  along with temperature have also been calculated in the model [Brasseur *et al.*, 1990].

## 4. ION MODEL RESULTS AND DISCUSSION

Model results of negative ion composition show that in the stratosphere the concentrations of ions represented in the first block (left-hand side in Figure 1) are negligible compared to the ions of block 2 (right-hand side). Ions  $\text{NO}_3^- \cdot \text{H}_2\text{O}$  and  $\text{NO}_3^- \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$  are also found to be of minor importance for stratospheric altitudes. The dominant ions are the  $\text{NO}_3^-$  core ions (includes  $\text{NO}_3^-$ ,  $\text{NO}_3^- \cdot \text{HNO}_3$ , and  $\text{NO}_3^- (\text{HNO}_3)_n$ ) and  $\text{HSO}_4^-$  core ions (includes  $\text{HSO}_4^-$ ,  $\text{HSO}_4^- (\text{HNO}_3)_n$ , and  $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_n$ ).

Figure 4 shows the percentage abundance of  $\text{NO}_3^-$  core and  $\text{HSO}_4^-$  core ions at 45°N. Present model results are shown by profiles 1 and 2, whereas the hatched area (3 and 4) shows the experimental data available for 44°N latitude as obtained by two groups, i.e. MPIH and BISA. The crossover point of  $\text{NO}_3^-$

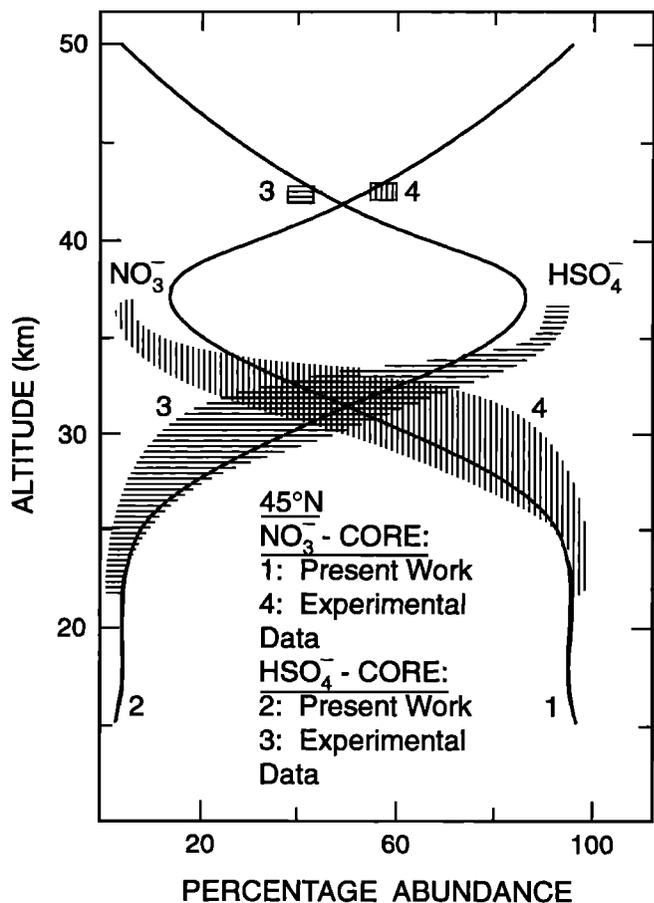


Fig. 4. Percentage abundance of  $\text{NO}_3^-$  core and  $\text{HSO}_4^-$  core ions as a function of altitude at 45°N. Model results are compared with available experimental data.

core and  $\text{HSO}_4^-$  core ions occurs at about 31.5 km. Below this altitude,  $\text{NO}_3^-$  core ions dominate, while above this level and up to 40 km it is the  $\text{HSO}_4^-$  core ions that dominate. A reverse changeover occurs at about 42 km where the concentration of both type of ions become equal. Near the stratopause,  $\text{NO}_3^-$  core ions again become most abundant. This result confirms the observational finding of *Arijs et al.* [1983]. Our model results agree very well with the experimental data except between 34 and 37 km where the calculated densities of  $\text{NO}_3^-$  core ions are slightly overestimated. However, not many experimental data on ion composition are available above 35 km, so that the comparison between models and observations is not straightforward.

Figure 5 shows the meridional distribution of the percentage abundance of  $\text{NO}_3^-$  core ions calculated in the model. It is clear from this figure that the relative abundance of  $\text{NO}_3^-$  core ions is very high at low altitudes and decreases with altitude to become 50% at about 32 km. This is true for almost all the latitudes. Above about 32 km,  $\text{NO}_3^-$  core ions remain in minority up to a certain height and then again start to dominate. This decrease in  $\text{NO}_3^-$  core ion abundance is due to the sharp increase in  $\text{H}_2\text{SO}_4$  concentration in this height region, which makes the conversion of  $\text{NO}_3^-$  core ions to  $\text{HSO}_4^-$  core ions faster. However, it does not persist at higher altitudes and as the concentration of  $\text{H}_2\text{SO}_4$  decreases at higher altitudes, the reappearance of  $\text{NO}_3^-$  core ions become prominent. This reverse changeover phenomenon (when  $\text{NO}_3^-$  core ions again become dominant) occurs at about 45 km for the tropical region, whereas for other latitudes it occurs around 42 km.

The  $\text{HSO}_4^-$  core ions considered in the present chemical scheme (Figure 1) consist of  $\text{HSO}_4^-$ ,  $\text{HSO}_4^-(\text{HNO}_3)_n$ , and  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$ . The concentration of  $\text{HSO}_4^-$  ion is negligible compared to the other two. The height distributions of the remaining two prominent  $\text{HSO}_4^-$  core ions are shown in Figures 6 and 7. Figure 6 shows as a function of altitude and latitude the percentage abundance of  $\text{HSO}_4^-(\text{HNO}_3)_n$  ions, which is low below about 30 km and above about 45 km. The percentage abundance of these types of ions increases with height. These ions appear to be the most dominant  $\text{HSO}_4^-$  core ions between 40 and 44 km. The meridional distribution of these ions show the maximum abundance at tropical latitude with a maximum near the equator where the relative contribution of these ions

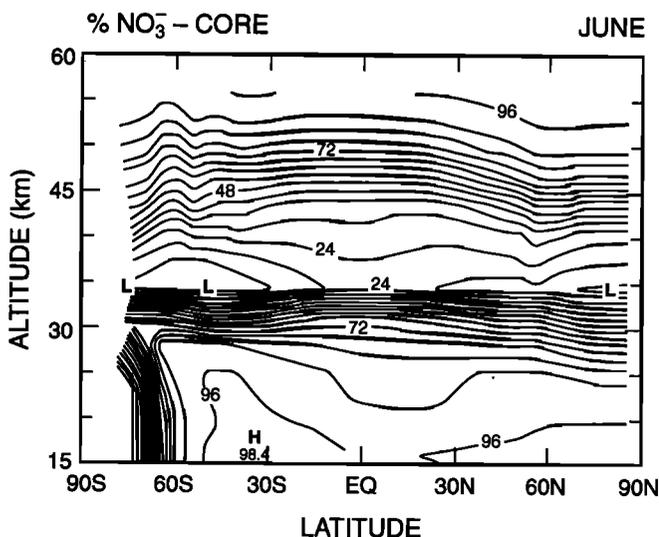


Fig. 5. Meridional distribution of the percentage abundance of  $\text{NO}_3^-$  core ions obtained in this work.

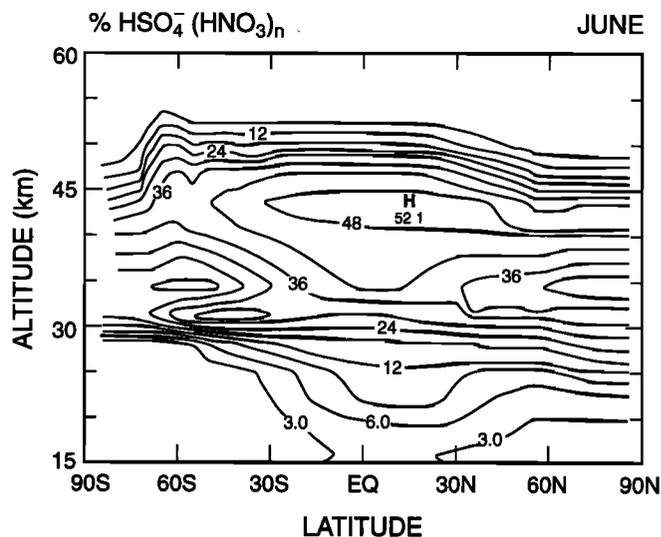


Fig. 6. Meridional distribution of the percentage abundance of  $\text{HSO}_4^-(\text{HNO}_3)_n$  ions calculated in the model.

reaches about 50% of the total negative ions. It is interesting to note in Figure 6 that  $\text{HSO}_4^-(\text{HNO}_3)_n$  ions show a strong vertical gradient for high and middle latitudes between 30 and 40 km. Below about 30 km and above 45 km where these ions are in minority, the distribution is almost uniform with latitude.

Figure 7 shows the meridional distribution of the percentage abundance of  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$  ions. Below 30 km the concentration of these type of ions is negligible, but above this level and up to 40 km altitude they are present in considerable quantity. These ions are the most abundant negative ions in high and middle latitudes for this height region. The maximum percentage abundance of  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$  ions is found to be at around 34 km at about  $80^\circ\text{N}$  and  $50^\circ\text{S}$ . In this region the concentration of these ions is highly variable. A comparison of Figures 6 and 7 shows that wherever the abundance of  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$  is lower (e.g., at the tropics), the abundance of  $\text{HSO}_4^-(\text{HNO}_3)_n$  is higher and vice versa. This shows that within this region there is a fast exchange of these two types of ions which produces the high-gradient region, especially at high and mid-latitudes. The total concentration of

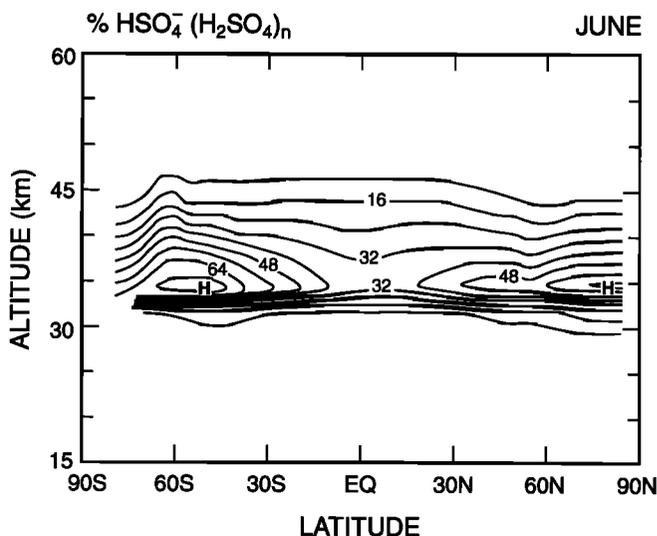


Fig. 7. Meridional distribution of the percentage abundance of  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$  ions calculated in the model.

both types of ions (which are major components of  $\text{HSO}_4^-$  core ions) do not exhibit the variability or a gradient seen in the concentration of the individual ions and the distribution becomes almost uniform with latitude.

### 5. CONCLUSIONS

The meridional variations of the fractional abundance of negative ions between 15 and 50 km were obtained using a simplified negative ion chemical scheme. The typical profiles of neutral species and temperature were calculated using a two-dimensional model. In order to reduce the number of assumptions on reaction rates and to simplify the negative ion scheme, unknown reaction channels were lumped together.

Our ion model results represent the main features of ion composition observed at middle latitudes. However, these need to be confirmed by measurements at other latitudes which are not yet available. Present model results indicate the dominance of  $\text{NO}_3^-$  core ions in the stratosphere except for the altitude range from about 30 to 42 km altitude where  $\text{HSO}_4^-$  core ions dominate. Interestingly, a high-gradient region is found in different  $\text{HSO}_4^-$  core ions for the altitude range of 30 to 40 km, particularly for high and mid-latitudes. Model results also predict a reverse changeover phenomenon between 42 to 45 km from  $\text{HSO}_4^-$  core ions to  $\text{NO}_3^-$  core ions. More in situ ion composition measurements are required especially above 40 km to elucidate and confirm these findings.

The negative ion composition is determined by nitric and sulfuric acid concentrations. No direct measurements of  $\text{H}_2\text{SO}_4$  are available. Sophisticated techniques have enabled the sulfuric acid density to be derived from ion composition data with greater accuracy than in the past. However, it is desirable that sulfuric gases  $\text{H}_2\text{SO}_4$  and other sulfur compounds be measured directly. In addition, laboratory studies of  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3$  reactions and photolysis are required to investigate the removal of  $\text{H}_2\text{SO}_4$  in the upper stratosphere.

*Acknowledgments.* The National Center for Atmospheric Research is sponsored by the National Science Foundation. One of the authors (G. Beig) is indebted to D. K. Chakrabarty (PRL) for the encouragement during the course of this work.

### REFERENCES

- Arijs, E., D. Nevejans, P. Frederick, and J. Ingels, Negative ion composition measurements in the stratosphere, *Geophys. Res. Lett.*, **8**, 121–124, 1981.
- Arijs, E., D. Nevejans, P. Frederics, and J. Ingels, Stratospheric negative ion composition measurements, ion abundances and related trace gas detection, *J. Atmos. Terr. Phys.*, **44**, 681–694, 1982.
- Arijs, E., D. Nevejans, J. Ingels, and P. Frederick, Negative ion composition and sulfuric acid vapor in the upper stratosphere, *Planet Space Sci.*, **31**, 1459–1464, 1983.
- Arijs, E., D. Nevejans, J. Ingels, and P. Frederick, Recent stratospheric negative ion composition measurements between 22 and 45 km altitude, *J. Geophys. Res.*, **90**, 5891–5896, 1985.
- Arnold, F., and G. Henschen, First mass analysis of stratospheric negative ions, *Nature*, **275**, 521–522, 1978.
- Arnold, F., and S. Qiu, Upper stratosphere negative ion composition measurements and inferred trace gas abundances, *Planet. Space Sci.*, **32**, 169–177, 1984.
- Arnold, F., R. Fabian, E. E. Ferguson, and W. Joos, Mass spectrometric measurements of fractions ion abundances in the stratosphere, 2. Negative ions, *Planet. Space Sci.*, **29**, 195–203, 1981.
- Beig, G., and D. K. Chakrabarty, On modelling stratospheric positive ions, *J. Atmos. Chem.*, **6**, 175–183, 1988.
- Beig, G., S. Walters, and G. Brasseur, A two-dimensional model of ion composition in the stratosphere, 1. Positive ions, *J. Geophys. Res.*, this issue.
- Brasseur, G., and A. Chatel, Modelling of stratospheric ions: A first attempt, *Ann. Geophys.*, **1**, 173–185, 1983.
- Brasseur, G., M. H. Hitchman, S. Walters, M. Dymek, E. Falise, and M. Pirre, An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere, *J. Geophys. Res.*, **95**, 5639–5655, 1990.
- Davidson, J. A., F. C. Fehsenfeld, and C. J. Howard, The heat of formation of  $\text{NO}_3^-$  and  $\text{NO}_3^-$  association complexes with  $\text{HNO}_3$  and  $\text{HBr}$ , *Int. J. Chem. Kinet.*, **9**, 17–29, 1977.
- Fehsenfeld, F. C., C. J. Howard, and A. L. Schmeltekopf, Gas phase ion chemistry of  $\text{HNO}_3$ , *J. Chem. Phys.*, **63**, 2835–2841, 1975.
- Fehsenfeld, F. C., A. L. Schmeltekopf, H. I. Schiff, and E. E. Ferguson, Laboratory measurements of negative ion reactions of atmospheric interest, *Planet. Space Sci.*, **15**, 373–379, 1967.
- Ferguson, E. E., Negative ion-molecular reactions, *Can. J. Chem.*, **47**, 1815–1820, 1969.
- Ferguson, E. E., *The Natural Stratosphere of 1974*, CIAP Monogr. 1, Dept. of Transport., Climatic Impact Assessment Program, DOT-TST-75-51, pp. 5–43 to 5–55, 1975.
- Heaps, M. G., Parameterization of cosmic ray ion-pair production rate above 18 km, *Planet. Space Sci.*, **26**, 513–517, 1978.
- Ingels, J., D. Nevejans, P. Frederick, and E. Arijs, Acetonitrile and sulfuric acid concentrations derived from ion composition measurements during the MAP/GLOBUS 1983, *Planet. Space Sci.*, **35**, 685–691, 1987.
- Kawamoto, H., and T. Ogawa, A steady state model of negative ions in the lower stratosphere, *Planet. Space Sci.*, **32**, 1223–1233, 1984.
- Kawamoto, H., and T. Ogawa, Minor species of negative ions in the lower stratosphere, *Res. Lett. Atmos. Electr.*, **5**, 1–6, 1985.
- Mohnen, V. A., Discussion of the formation of major positive and negative ions up to the 50 km level, *Pure Appl. Geophys.*, **84**, 141–153, 1971.
- Qiu, S., and F. Arnold, Stratospheric in-situ measurements of  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3$  vapors during a volcanically active period, *Planet. Space Sci.*, **32**, 87–95, 1984.
- Rosen, J. M., D. J. Hofmann, and W. Gringel, Measurements of ion mobility to 30 km, *J. Geophys. Res.*, **90**, 5876–5884, 1985.
- Schlager, H., and F. Arnold, Balloon-borne composition measurements of stratospheric negative ions and inferred sulfuric acid vapor abundances during the MAP/GLOBUS 1983 campaign, *Planet. Space Sci.*, **35**, 693–701, 1987.
- Thomas, L., Modelling of the ion composition in the middle atmosphere, *Ann. Geophys.*, **1**, 61–73, 1983.
- Turco, R. P., O. B. Toon, P. Hamill, and R. C. Whitten, Effects of meteoric debris on stratospheric aerosols and gases, *J. Geophys. Res.*, **86**, 1113–1128, 1981.
- Viggiano, A. A., and F. Arnold, Stratospheric sulfuric acid vapor: New and updated measurements, *J. Geophys. Res.*, **88**, 1457–1462, 1983.
- Viggiano, A. A., R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, Stratospheric negative ion fraction rates with  $\text{H}_2\text{SO}_4$ , *J. Geophys. Res.*, **87**, 7340–7342, 1982.
- Viggiano, A. A., F. Dale, and J. F. Paulson, Measurements of some stratospheric ion-molecule association rates: Implications for ion chemistry and derived  $\text{HNO}_3$  concentrations in the stratosphere, *J. Geophys. Res.*, **90**, 7977–7984, 1985.
- Widdel, H. U., G. Ross, and R. Bochers, Payload B-III, an instrument package for the measurement of conductivity, concentration and mobility of positive and negative ions in the mesosphere, *J. Geophys.*, **44**, 179–188, 1977.
- Wlodek, S., Z. Luczynski, and H. Wincel, Stabilities of gas-phase  $\text{NO}_3^-(\text{HNO}_3)_n$ ,  $n \leq 6$ , clusters, *Int. J. Mass Spectr. Ion Phys.*, **35**, 39–46, 1980.
- World Meteorological Organization (WMO), The stratosphere 1981, WMO global ozone research report, *WMO Rep. 11*, Geneva, 1981.
- World Meteorological Organization (WMO), Atmospheric ozone 1985, WMO global ozone research and monitoring project report, *WMO Rep. 16*, vol. 2, Geneva, 1985.

G. Beig, Physical Research Laboratory, Navrangpura, Ahmedabad, now at National Physical Laboratory, New Delhi, India.

G. Brasseur and S. Walters, National Center for Atmospheric Research, ACD, P. O. Box 3000, Boulder, CO 80307-3000.

(Received March 19, 1992;  
revised March 31, 1993;  
accepted April 1, 1993.)