

Recent Stratospheric Negative Ion Composition Measurements Between 22- and 45-km Altitude

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Ion spectra obtained during three balloon flights performed in June 1982, September 1982, and September 1983 are reported. The lower altitude limit of the measurements is imposed by the decrease of the instrument sensitivity and the upper limit by present ballooning techniques. At high altitudes the ion spectra are disturbed by contamination, whereas at low altitudes, ion cluster breakup is a severe problem. Nevertheless knowledge of relative abundances of the different negative ion mass peaks, mainly belonging to the $\text{NO}_3^-(\text{HNO}_3)_n$ and $\text{HSO}_4^-(\text{HNO}_3)_m(\text{H}_2\text{SO}_4)_l$ cluster families allows the derivation of concentrations of H_2SO_4 in the altitude region of 22-45 km. At 45 km an increased SO_2 mixing ratio, possibly due to volcanic activities, was estimated from the negative ion mass spectra. The data are discussed in terms of previous measurements and models. Special interest is given to the sulfur chemistry and the implications on aerosol formation.

1. INTRODUCTION

Although stratospheric ions play an important role in several processes such as atmospheric electricity and aerosol formation, ion composition measurements below 50 km have only been realized the last few years. Most of this recent experimental work has been reviewed by Arnold [1980] and more recently by Arijs [1983].

The first in situ mass spectrometric measurements of negative ions at about 35-km altitude made with balloon-borne instruments [Arnold and Henschen, 1978; Arijs et al., 1981] have shown the existence of two major negative ion families, namely, $\text{NO}_3^-(\text{HNO}_3)_n$ and $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m(\text{HNO}_3)_l$. The $\text{NO}_3^-(\text{HNO}_3)_n$ cluster ions had been predicted on the basis of earlier laboratory measurements [Fehsenfeld et al., 1975], whereas evidence for the formation of HSO_4^- clusters was only reported later by Viggiano et al. [1980, 1982].

During the last few years, several negative ion composition data, obtained between 15 and 45 km, have been published [Arnold et al., 1981a, 1982; Viggiano and Arnold, 1981a; McCrumb and Arnold, 1981; Arijs et al., 1982, 1983a; Viggiano et al., 1983], and the fractional ion abundances have been used extensively to derive sulfuric acid number densities in the stratosphere [Arnold and Fabian, 1980; Arnold et al., 1981b; Arijs et al., 1981, 1983a, b; Viggiano and Arnold, 1981b, 1983; Qiu and Arnold, 1984].

In this paper we would like to review and compare some results on stratospheric negative ion compositions obtained by our group during three recent balloon flights. The total data set covers the altitude range from 22 to 45 km and was obtained after the eruption of El Chichon (April 1982). Therefore special attention will be given in the discussion to sulfur chemistry and possible volcanic influences.

2. EXPERIMENTAL AND MEASUREMENTS

The measurements reported herein were performed during three balloon flights over southern France at about 44°N. A detailed description of the quadrupole ion mass spectrometer, used in the three flights, has been given elsewhere [Arijs et al., 1980; Ingels et al., 1978; Nevejans et al., 1982, 1985].

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The first flight (J-82), performed with a 100,000-m³ valve-controlled balloon on June 16, 1982, allowed us to take negative ion mass spectra between 34 and 25 km. In the second one (S-82), realized on September 25, 1982, a 1,000,000-m³ Wintzen balloon was used. A ceiling altitude of about 45.5 km was reached at about 1600 UT, and after sunset the balloon descended to 41.2 km at a rate of 1.3 m s⁻¹. A major part of the flight was devoted to positive ion measurements [Arijs et al., 1983c], and negative ion composition data were obtained only at float altitude and around 42.3 km.

Some results of these two flights have already been published [Arijs et al., 1983a, b, c].

The third flight (S-83) was performed on September 18, 1983. Again a 100,000-m³ valve-controlled balloon was used, and negative ion mass spectra were recorded between 32 and 22 km.

For the negative ion measurements, discussed below, a moderate resolution mode ($m/\Delta m \cong 17$) was used, adequate to resolve the major mass peaks. For minor mass peaks, however, the error on mass identification and peak height is rather large as discussed later on.

During the last two flights (S-82 and S-83) the gondola also contained an instrument for the detection of aerosols by means of photographic observations [Ackerman et al., 1981].

3. RESULTS AND DISCUSSION

3.1. General

Figure 1 shows two typical spectra as recorded during flight S-83 in the moderate resolution mode and smoothed with a technique described before [Arijs et al., 1982]. Similar spectra of the J-82 and S-82 flights have been shown previously [Arijs et al., 1983a, b].

When comparing spectrum A taken at 31.8 km to spectrum B obtained at 21.6 km, some striking differences are noticed. First of all, spectrum A, being the sum of three scans of 160 s each, contains many more major mass peaks than spectrum B. The most intense peaks at 31.8 km are located at 125, 160, 188, 195, 223, and 293 amu. Some minor peaks at 143, 178, 206, 258, and 276 amu are detectable but can scarcely be seen on the reduced Figure 1. Below mass 125, several peaks occur, some of which have tentatively been identified before [McCrumb and Arnold, 1981; Arijs et al., 1982] but which are not pinned down here due to the low resolution used.

In view of previous high-resolution measurements [Arijs et

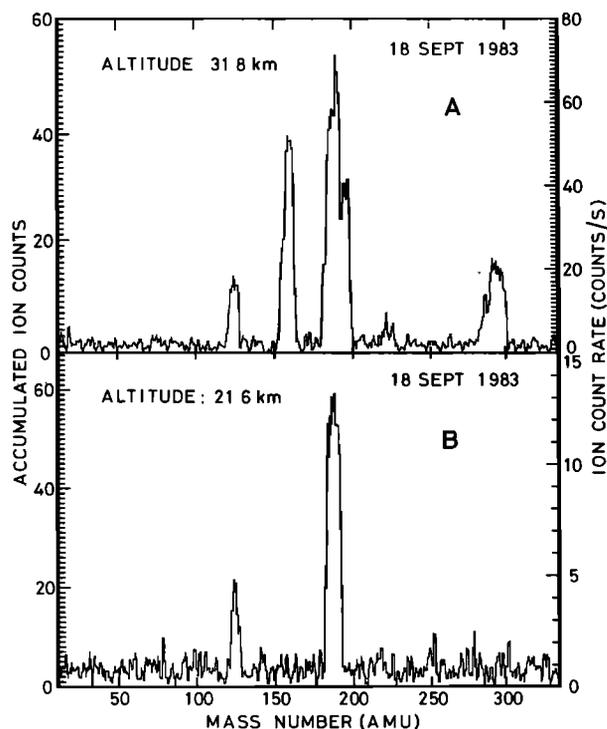


Fig. 1. Typical negative ion spectra obtained in the moderate resolution mode for the S-83 flight.

al., 1982] the major peaks of Figure 1a can be attributed to $\text{NO}_3^- (\text{HNO}_3)$, $\text{HSO}_4^- (\text{HNO}_3)$, $\text{NO}_3^- (\text{HNO}_3)_2$, $\text{HSO}_4^- (\text{H}_2\text{SO}_4)$, $\text{HSO}_4^- (\text{HNO}_3)_2$, and $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_2$. The minor peaks above mass 125 are probably hydrates of the previous ions, apart from 258 being $\text{HSO}_4^- \cdot \text{HNO}_3 \cdot \text{H}_2\text{SO}_4$ and 276 which has been interpreted as $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HSO}_3$ by Arnold *et al.* [1982]. Although it is the summation of 17 scans, spectrum B only shows two major mass peaks, namely, mass 125 ($\text{NO}_3^- \cdot \text{HNO}_3$) and 188 ($\text{NO}_3^- (\text{HNO}_3)_2$). This is of course due to a sharp decrease of the sulfuric acid concentration in the lower stratosphere, as will be discussed below. The mass numbers and the abundance of the minor peaks in this spectrum can only be determined with a considerable uncertainty. This explains the large error bars on the derived sulfuric acid number density at lower altitudes (see section 3.3).

Because of the restricted mass range of the instrument used, mass peaks beyond mass 330 amu could not be observed at moderate resolution. Measurements in the total ion mode, however, allowed an estimation of the heavy ion abundance [Arijs *et al.*, 1983d].

As can be seen in Figure 1b, both signal to background ratio and signal strength are rather low. The latter is due to scattering of ions in the instrument, which is more effective at lower altitudes because the internal pressure is proportional to the ambient pressure. This phenomenon imposes a lower limit of about 20 km to the measurement range with our present mass spectrometer. Using a smaller inlet orifice would shift this lower limit to lower altitude, but would also imply lower high-altitude signal strength.

When compared with the S-83 data, the spectra of J-82 are very similar. However, spectra obtained during the S-82 flight, where an altitude of 45.5 km was reached, were quite different. Many of the features of these data have been reported previously [Arijs *et al.*, 1983b], and therefore only those related

to sulfur chemistry will be discussed here. It should be pointed out, however, that contamination is suspected to have influenced the S-82 data, especially during measurements taken at float altitude. For this reason, valve-controlled balloons were used for all other measurements, and spectra were taken during the descent portion of the flights. Apart from minimizing possible contaminating influences, valve-controlled balloons also offer the advantage of allowing a controlled descent at about 1 m s^{-1} , which permits a longer measuring time at a given altitude level than during ascent.

We will now turn to the discussion of the abundances of the different ions of the $\text{NO}_3^- (\text{HNO}_3)_n$ and the $\text{HSO}_4^- (\text{H}_2\text{SO}_4)_m (\text{HNO}_3)_l$ families as measured in the different balloon flights.

3.2. NO_3^- Cluster Ions

As seen in Figure 1, the main ions observed belonging to the $\text{NO}_3^- (\text{HNO}_3)_n$ family are $\text{NO}_3^- (\text{HNO}_3)$ at mass 125 and $\text{NO}_3^- (\text{HNO}_3)_2$ at mass 188. Mass 63 (NO_3^-) and mass 251 ($\text{NO}_3^- (\text{HNO}_3)_3$) are present as minor mass peaks only. In principle, it is possible to deduce with the so-called equilibrium method the HNO_3 mixing ratio from the relative abundances of these ions [Arnold *et al.*, 1980]. This method is based on the formulas

$$[\text{NO}_3^- (\text{HNO}_3)_{n+1}] = K_{n,n+1} [\text{NO}_3^- (\text{HNO}_3)_n] [\text{HNO}_3] \quad (1)$$

and

$$-RT \ln K_{n,n+1} = \Delta H_0 - T \Delta S_0 \quad (2)$$

where square brackets denote number densities.

For $n=1$, ΔH_0 and ΔS_0 are known from laboratory measurements [Davidson *et al.*, 1977] and $[\text{HNO}_3]$ can be deduced from the relative abundances of mass 125 and mass 188. In order to assess the validity of the method, throughout the altitude range 35–20 km we have calculated $[\text{NO}_3^- (\text{HNO}_3)_2] / [\text{NO}_3^- \cdot \text{HNO}_3]$ using formulas (1) and (2) and a compilation of nitric acid measurements, recently reported [World Meteorological Organization, 1981]. The results are compared with the $[\text{NO}_3^- (\text{HNO}_3)_2] / [\text{NO}_3^- \cdot \text{HNO}_3]$ values in Figure 2, as measured in the J-82 and S-83 flights. Agreement between measurements and calculations is only reasonable above 32 km. Below this altitude the measured $[\text{NO}_3^- (\text{HNO}_3)_2] / [\text{NO}_3^- \cdot \text{HNO}_3]$ ratios are much too low. The explanation for this phenomenon is that the measured abundance of mass 125 is partly (and below 32 km mainly) due to cluster breakup of mass 188. This cluster breakup is taking place just behind the inlet hole, where the sampled ions are accelerated in the ion lens and where the pressure is still high enough to allow many collisions with neutrals. In fact a marked increase of this cluster breakup effect is noticed as a function of altitude, and the fraction of $\text{NO}_3^- (\text{HNO}_3)_2$ converted into $\text{NO}_3^- \cdot \text{HNO}_3$ is roughly varying from 1/8 to 1/2 between 30 and 20 km.

It should be emphasized that cluster breakup strongly depends on the sampling orifice diameter and on the instrumental arrangement. Therefore the altitude above which fragmentation can be neglected may vary from flight to flight. The value of 32 km stated here is typical for the S-83 experiment, where a sampling aperture of about 0.2 mm was used.

The derivation of HNO_3 number densities from (1) and (2) for $n=2$ poses some severe problems because a rather large error exists on the measurement of the abundance of mass 251. The latter is only observed as a minor ion at lower alti-

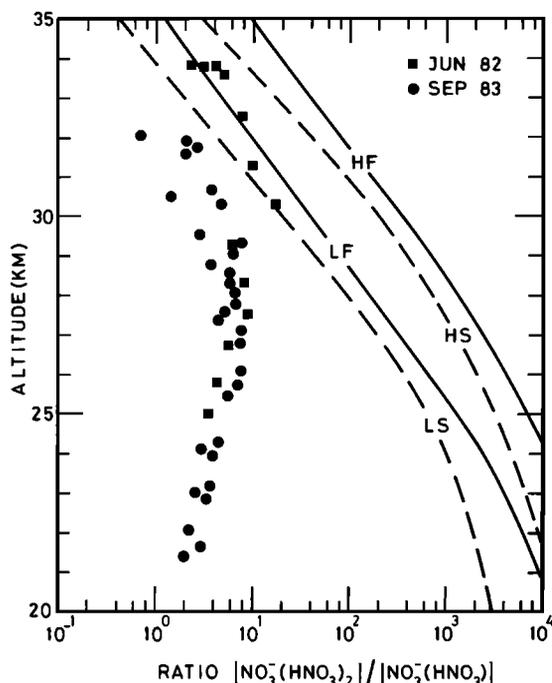


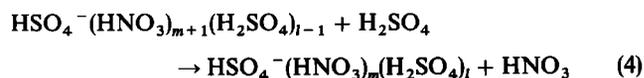
Fig. 2. Abundance ratio $[\text{NO}_3^-(\text{HNO}_3)_2]/[\text{NO}_3^-(\text{HNO}_3)]$ as measured in the J-82 and S-83 flight. For comparison, theoretically deduced abundance ratios are also shown. LF and HF are calculated for a spring-fall temperature profile and low and high HNO_3 mixing ratio, respectively. LS and HS are for summer temperature conditions.

tudes, indicating that the $\text{NO}_3^-(\text{HNO}_3)_3$ ion is also strongly affected by cluster breakup.

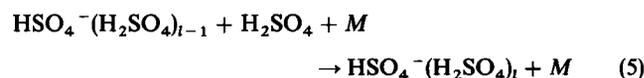
It is evident that in order to use the relative abundances of the $\text{NO}_3^-(\text{HNO}_3)_n$ ions to derive HNO_3 number densities, the cluster breakup effects must be either avoided or be understood very well so that they can be corrected for. Therefore modifications of our present instrument as well as laboratory studies are needed.

3.3. HSO_4^- Cluster Ions and Sulfur Chemistry

Apart from the NO_3^- cluster ions a second family of major ions, represented by $\text{HSO}_4^-(\text{HNO}_3)_m(\text{H}_2\text{SO}_4)_b$, is detected in the stratosphere. They result from a set of ion molecule reactions, such as



and



Unfortunately, very few kinetic or thermochemical data are available about these reactions. Only for switching reactions of type (3) rate constants have been reported for $n = 0, 1$, and 2 [Viggiano *et al.*, 1980, 1982].

As pointed out recently [Arnold *et al.*, 1982], other sulfur-containing gases, such as HSO_3 , may contribute to the formation of HSO_4^- cluster ions.

One of the most appealing applications of negative ion composition measurements is the derivation of the number

density of H_2SO_4 and other sulfur-bearing compounds in the stratosphere, using the steady state equation

$$k[n_N^-][\text{H}_2\text{SO}_4 + \text{HSO}_3] = \alpha[n^+][n_s^-] \quad (6)$$

Here k is the reaction rate coefficient for the ion-molecule switching reactions of NO_3^- cluster ions (represented by n_N^-) and sulfur compounds, such as H_2SO_4 and HSO_3 . The resulting HSO_4^- cluster ion number density is denoted by $[n_s^-]$; $[n^+]$ is the total positive ion density, and α is the ion-ion recombination coefficient. It is assumed in this steady state treatment that all product ions are lost by recombination and that no reverse reactions from n_s^- type ions to n_N^- type ions occur. Furthermore, the values of k and of α are taken common for all ion-molecule and all ion-ion reactions involved.

Application of formula (6) to the data of the three flights considered here leads to the results pictured in Figure 3. The recombination coefficient α and the total positive ion number density $[n^+]$ were derived as described before [Arijs *et al.*, 1983a]. For the rate coefficient k of the reaction of sulfuric acid with $\text{NO}_3^-(\text{HNO}_3)_2$ a value of $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was found by Viggiano *et al.* [1982]. Since the most abundant peak among n_N^- type ions in the J-82 and S-83 flight was mass 188, this k value was used for the appropriate data. For the S-82 flight, however, the most abundant NO_3^- cluster ion was $\text{NO}_3^-(\text{HNO}_3)$, and thus k was put equal to $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in agreement with the data of Viggiano *et al.* [1982].

For comparison, some recent derivations of Qiu and Arnold [1984], reduced with the same α and $[n^+]$ values as used here have also been indicated in Figure 3. Furthermore, different modeling results are shown. Curves A, B, C, and D are taken from a model by Turco *et al.* [1981], wherein $[\text{H}_2\text{SO}_4]$ is calculated for different cases. All curves take into account heterogeneous reactions of H_2SO_4 with aerosol particles and metallic species from meteoric debris. Curve A (dashed line) results from a model with zero H_2SO_4 vapor pressure. Curves B, C, and D are calculated for a metal flux of 1×10^6 , 5×10^6 , and zero $\text{cm}^{-2} \text{ s}^{-1}$, respectively. Below 30 km these three models result in the same H_2SO_4 concentration represented by the dashed line B.

Curve G (dash-dot line) is a model of $[\text{HSO}_3]$ by Turco *et al.* [1979].

Curve E (solid line) represents $[\text{H}_2\text{SO}_4 + \text{HSO}_3]$ as given by A + G. Curves FB, FC, and FD represent $[\text{H}_2\text{SO}_4 + \text{HSO}_3]$ as given by G + B, G + C, and G + D, respectively. Again these three curves merge into one (curve F) below 30 km.

The dashed line (H) in Figure 3 is a vapor pressure calculation of H_2SO_4 using a temperature profile as measured in flight S-83 and a procedure explained in detail before [Arijs *et al.*, 1983a].

In comparing the derivations of $[\text{H}_2\text{SO}_4 + \text{HSO}_3]$ from ion composition measurements with the different model calculations, three distinct altitude regions can be treated.

The first one extends from about 28 to 33 km. As seen in Figure 3 the $[\text{H}_2\text{SO}_4 + \text{HSO}_3]$ measurements of the S-83 flight in this altitude region are in good agreement with the calculated H_2SO_4 vapor pressure. As shown before, the same holds for the J-82 data [Arijs *et al.*, 1983a] if the appropriate temperature profile is used. An estimation of $[\text{HSO}_3]$ with a method described by Arnold and Bührke [1983] indicates that in this altitude region H_2SO_4 is the major sulfur component of $[\text{H}_2\text{SO}_4 + \text{HSO}_3]$. It is concluded that in the altitude region 28–33 km the H_2SO_4 vapor is mainly controlled by the evapo-

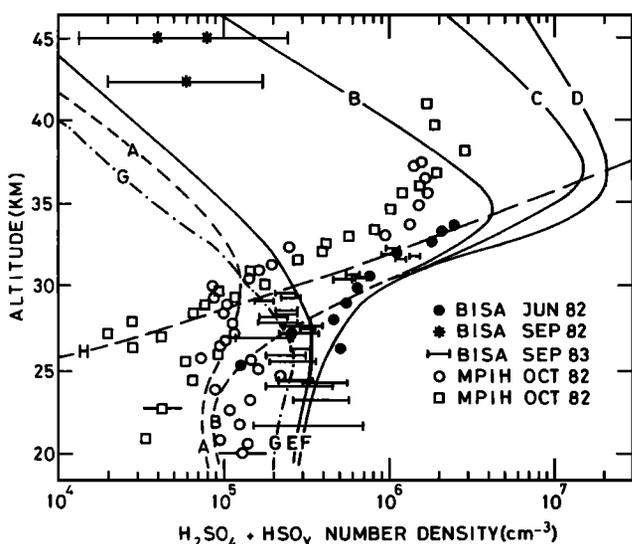
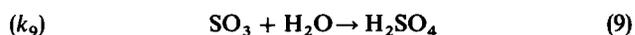


Fig. 3. $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ concentrations as obtained for different in situ measurements. Data labeled MPIH are those reported by Qiu and Arnold [1984] and obtained by the group of the Max Planck Institute of Heidelberg during balloon flights on October 4 (circles), and October 17 (squares), 1982. Measurements labeled BISA JUN 82, SEP 82, and SEP 83 are the J-82, S-82, and S-83 results reported here. The error bars for the S-83 flights are due to uncertainties in ion abundance measurements. The error bars indicated for the S-82 flights result from uncertainties in kinetic data.

ration equilibrium between aerosol droplets and the vapor phase.

Below 28 km, however, the $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ values are much larger than those derived from vapor pressure calculations. In this region, H_2SO_4 and HSO_3 are formed by photochemical conversion of SO_2 , COS, and other sulfur-bearing gases, which are injected into the stratosphere [Turco et al., 1979]. The major production paths to H_2SO_4 and HSO_3 are assumed to be

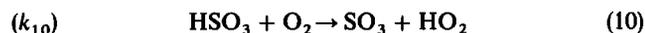


The main loss processes for sulfuric acid below 30 km are believed to be heterogeneous reactions with aerosol particles.

In comparing the $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ data of the J-82 and S-83 flights with the models, it seems difficult to draw conclusions for the J-82 experiment because of the large scattering of data points below 28 km. The S-83 results, however, show a more pronounced behavior. Between 25- and 30-km altitude the values of $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ deduced from the S-83 flight are considerably lower than those derived from J-82. This is probably due to the increase of sulfuric acid in June 1982 as a result of the El Chichon eruption. An inspection of the Lidar profiles obtained by Reiter et al. [1983] shows that in June 1982 the El Chichon cloud was over central Europe around 25-km altitude. The excess of SO_2 induced by this cloud would result in an enhanced H_2SO_4 production. According to Capone et al. [1983] the conversion of SO_2 to H_2SO_4 should have been completed well before September 1983, so that one would not expect an enhanced H_2SO_4 concentration in the S-83 data. The results of the S-83 flight seem to be in better agreement with curve F than with curve B below 25 km, suggesting that most of the $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ consists of HSO_3 in this altitude region.

Although this seems to be an experimental support for the model of Turco et al. [1979, 1981], care should be taken with this interpretation for different reasons. First of all, the error bars on the S-83 $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ data below 25 km are rather large, due to possible incomplete counting statistics for the HSO_3^- ion signals, which are rather low in this altitude region. These errors may in fact partially explain the difference between the results of Qiu and Arnold [1984] and ours. Second, it should be kept in mind that apart from the experimental errors indicated in Figure 3 for S-83, a systematic error of a factor of 3 (as shown, e.g., for S-82 in Figure 3) due to uncertainties in α , k , and $[n^+]$ should be added.

Finally, the HSO_y species may consist of other sulfur compounds (such as HSO_2) not taken into account in Turco's model. In fact, if the conversion of HSO_3 to H_2SO_4 would proceed according to



Followed by reaction (9), as suggested by Stockwell and Calvert [1983], the existence of HSO_3 in any detectable amounts in the stratosphere becomes very questionable as well as the recent HSO_3 derivation of Qiu and Arnold [1984]. More information on the atmospheric sulfur chemistry is therefore needed before the data can be fully exploited.

Above 35 km, two data points for $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ were obtained in the S-82 flight. At 45.1 km a number density between $4 \times 10^4 \text{ cm}^{-3}$ and $8 \times 10^4 \text{ cm}^{-3}$ is found. As explained before [Arijs et al., 1983b], the uncertainty is caused by the difficult ion identification. At 42.3 km a value of $6 \times 10^4 \text{ cm}^{-3}$ is derived for $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$. When comparing these data points in Figure 3 with the results obtained in October 1983 by Qiu and Arnold [1984], a large discrepancy emerges. Some remarks, however, need to be made here. In our calculations a value of $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was used for the reaction rate coefficient k between n_N^- type and n_s^- ions, because $\text{NO}_3^- \cdot \text{HNO}_3$ (mass 125) was the dominant n_N^- ion observed in the S-82 flight, whereas Qiu and Arnold put $k = 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. An inspection of the spectra from which the data of Qiu and Arnold were obtained [Arnold and Qiu, 1984] shows that mass 125 represents about 75% of the NO_3^- core ions and mass 188 about 25%. Therefore an effective k value of 1.75×10^{-9} should be applied. Consequently, the data of Qiu and Arnold corresponding to 40-km altitude as plotted in Figure 3 should be reduced by a factor of 1.75.

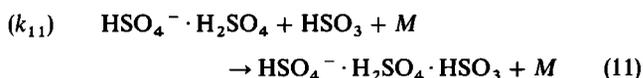
In addition it seems that the reported maximum altitude in the Qiu and Arnold data of October 1982 may be overestimated by about 1.5 km (F. Arnold, private communication, 1984).

Taking into account the previous remarks, the discrepancies become less dramatic. In fact, the data then suggest an $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ profile similar to the model curve B of Turco et al. [1981], where an additional loss for H_2SO_4 is assumed to be reaction with "smoke" particles, caused by a downward metal flux of $1 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ from meteoric debris.

It would be premature, however, to conclude that the model therefore represents a good representation of reality. In fact instead of assuming a loss of $[\text{H}_2\text{SO}_4 + \text{HSO}_3]$ through reaction with smoke particles, a similar fitting might be obtained by introducing a larger photodissociation frequency for H_2SO_4 . This will be demonstrated by the following considerations.

From the relative abundances of the $\text{Cl}^- \cdot \text{SO}_2$ and $\text{Cl}^- \cdot \text{H}_2\text{O}$ ions, detected as contaminant ions in our S-82 flight, an SO_2

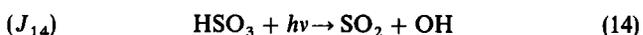
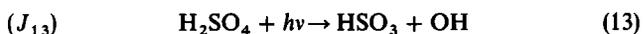
mixing ratio of about 3 ppb was deduced at about 45 km [Arijs *et al.*, 1983b]. This value, probably subject to a considerable error, is about 100 times larger than the values obtained from model calculations under normal atmospheric conditions. Such high SO₂ concentrations, probably due to volcanic activities (El Chichon) would imply a rather high H₂SO₄ concentration through reactions (7), (8), and (9). In a previous report on the S-82 flight, we identified mass 276 as HSO₄⁻ · HNO₃ · H₂SO₄ · H₂O [Arijs *et al.*, 1983a]. In view of the low signal at mass 258, being the nonhydrated precursor of mass 276, and considering the high number of ligands which occur in the previous tentative identification, it might be more attractive to attribute mass 276 to HSO₄⁻ · H₂SO₄ · HSO₃ as suggested by Arnold *et al.* [1982]. Accepting that mass 276 is formed through



and assuming that product ions are lost by recombination, the HSO₃ number density can be calculated with steady state equation

$$k_{11}[\text{HSO}_3][\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4] \\ = \alpha[\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HSO}_3][n^+] \quad (12)$$

Taking the same k_{11} value as for the association of H₂SO₄ to HSO₄⁻ · H₂SO₄, [HSO₃]/[H₂SO₄] can be derived in a first approximation from the abundance ratio of mass 276 and 293. It turns out that at 42.3 and 45.1 km HSO₃ represents about 80% of the H₂SO₄ content. These high HSO₃ concentrations and the high SO₂ mixing ratio indicate a much larger photodissociation of H₂SO₄ than used in previous model calculations. Assuming that photolysis occurs according to



steady state considerations about HSO₃ and H₂SO₄, combining (7), (8), (9), (13), and (14) lead to

$$J_{13}[\text{H}_2\text{SO}_4] = k_8[\text{HSO}_3][\text{OH}] \quad (15)$$

and

$$J_{14}[\text{HSO}_3] = k_7[\text{SO}_2][\text{OH}][M] \quad (16)$$

Accepting an upper limit for k_8 of 10⁻¹¹ cm³ s⁻¹ as proposed by Turco *et al.* [1979] and taking for k_7 , 3 × 10⁻³¹(300/T)^{2.9} cm⁶ s⁻¹ as reported by De More *et al.* [1982], the values of [SO₂], [HSO₃], and [H₂SO₄] derived from ion composition measurements lead to $J_{13} \cong 1.6 \times 10^{-4}$ s⁻¹ and $J_{14} \cong 8 \times 10^{-4}$ s⁻¹ around 45 km. It should be kept in mind, however, that the derivations of the previous values for the photodissociation frequencies might suffer from large errors.

The SO₂ number density, which was derived from the abundance ratio of Cl⁻ · SO₂ and Cl⁻ · H₂O [Arijs *et al.*, 1983b], can be overestimated. Cl⁻ · H₂O being only a minor ion peak, the error on [SO₂] can be considerable as a result of incomplete counting statistics as well as contamination effects.

Further, the values of the reaction rate coefficients are highly uncertain. As far as we know, no laboratory measurement is available for k_8 , and the applied value is only an assumed upper limit [Turco *et al.*, 1979]. Finally, the steady state considerations as used in (15) and (16) may be oversimplified, due to the incomplete knowledge of the sulfur chemistry and the neglect of vertical transport phenomena.

It should also be emphasized that the previous derivations of the photodissociation frequencies are only valid if (8) is the major loss mechanism for HSO₃. If, however, (10) represents the main sink for HSO₃, the HSO₃ concentrations will most probably be much lower than the values deduced above. It then becomes very doubtful to assign HSO₄⁻ · H₂SO₄ · HSO₃ to mass 276, and mass 276 might well be a hydrated form of mass 258. Unfortunately, not enough thermochemical data are available on negative ion molecule reactions, such as those represented by (11), and an unambiguous identification of mass 276 is so far impossible. The present results therefore do not preclude (10).

A continuation of in situ negative ion mass spectrometry, combined with an effort to measure thermochemical and kinetic quantities of the appropriate ion-molecule reaction, may shed some new light on this problem, which is very important for our understanding of the atmospheric sulfur cycle and the behavior of the OH balance during volcanically active periods [McKeen *et al.*, 1984].

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