

RECENT STRATOSPHERIC NEGATIVE ION COMPOSITION MEASUREMENTS BETWEEN 22 AND 45 KM

E. Arijs, D. Nevejans, J. Ingels and P. Frederick
 Belgian Institute for Space Aeronomy
 Ringlaan, 3, B-1180 Brussels, Belgium

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 before 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. (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; Mc Crumb and Arnold, 1981; Arijs et al., 1982, 1983a) 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, 1983b; Viggiano and Arnold, 1981b, 1981c; 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 Chichón (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 hereafter were performed during three balloon flights over southern France at about 44°N. The first flight (J-82), performed with a 100,000 m³ valve controlled balloon on 16 June 1982, allowed to take negative ion mass spectra between 34 and 25 km. In the second one (S-82), realized on 25 September 1982, a 1,000,000 m³ Wintzen balloon was used. A ceiling altitude of about 45.5 km was reached at about 16.00 U.T. and after sunset the balloon descended to 41.2 km at a rate of 1.3 m/s. 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 18 September 1983. Again a 100,000 m³ valve controlled balloon was used and negative ion mass spectra were recorded between 32 and 22 km.

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., 1983).

For the negative ion measurements, discussed hereafter, a moderate resolution mode ($m/\Delta m \approx 17$) 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. Similar spectra of the J-82 and S-82 flights have been shown previously (Arijs et al. 1983a, b). The spectra as depicted here were smoothed with a technique described previously (Arijs et al., 1982).

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 3 scans of 160 s each, contains much 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 appear, 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 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 might be due to $\text{HSO}_4^-\cdot\text{H}_2\text{SO}_4$ HSO_3 (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 the sharp decrease of sulfuric acid concentration in the lower stratosphere, as will be discussed further on. 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 limited 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

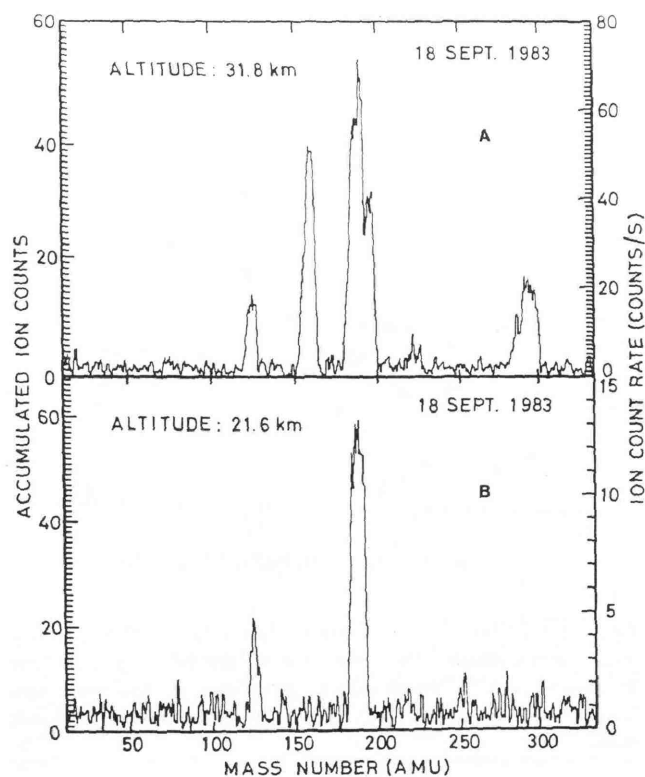


Figure 1 : Typical negative ion spectra obtained in the moderate resolution mode for the S-83 flight.

estimation of the heavy ion abundance (Arijs et al., 1983d).

As can be seen in figure 1B both the signal to background ratio and the 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 pressure in the instrument is proportional to the ambient pressure. In fact it is this phenomenon which 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 to 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 we will only discuss those within the framework of the sulfur chemistry treatment later on in this paper. 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 the possible contaminating influences, valve controlled balloons also offer the advantage of allowing a controlled descent at about 1 m/s, 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 $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m$ (HNO_3)₂ 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

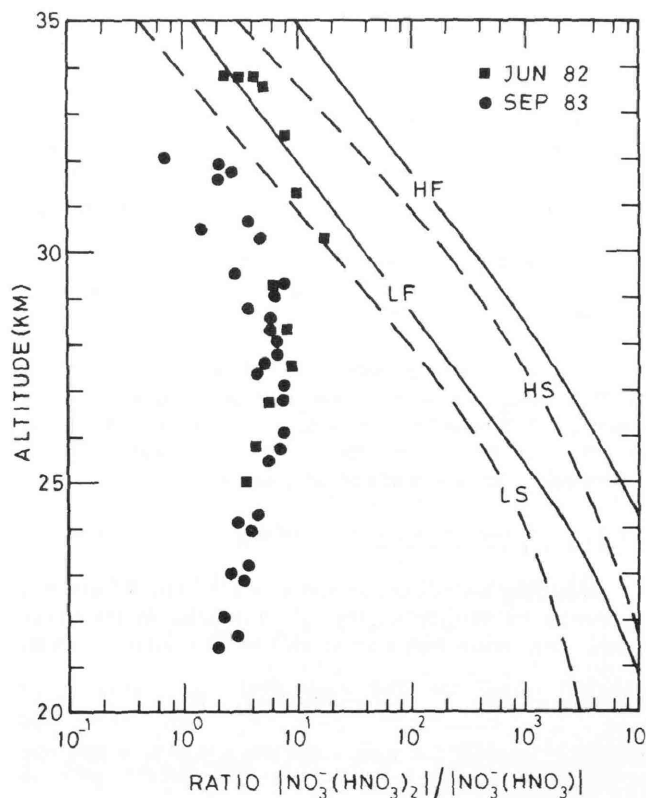


Figure 2 : Abundance ratio of $[\text{NO}_3^-(\text{HNO}_3)_2]/[\text{NO}_3^-\cdot\text{HNO}_3]$ as measured in the J-82 and S-83 flight. For comparison theoretically deduced abundance ratios are also shown. LF and HF are calculated for a Spring-Fall temperature profile and low and high HNO_3 mixing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

relative abundances of these ions (Arnold et al., 1980). This method is based on the formulae :

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

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 to 20 km we have calculated $[\text{NO}_3^-(\text{HNO}_3)_2]/[\text{NO}_3^-\cdot\text{HNO}_3]$ using formulae (1) and (2) and a compilation of nitric acid measurements, recently reported (WMO, 1983). The results are compared with the $[\text{NO}_3^-(\text{HNO}_3)_2]/[\text{NO}_3^-\cdot\text{HNO}_3]$ values, as measured in the J-82 and S-83 flights, in figure 2. The 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 break up of mass 188. This cluster break up 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 break up 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.

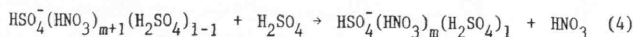
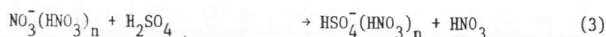
It should be emphasized that cluster break-up strongly depends on the sampling orifice diameter and on the instrumental arrangement. Therefore the altitude above which fragmentation can be neglected may vary from flight to flight. The value of 32 km stated here is typical for the S-83 experiment where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

The derivations of HNO_3 number densities from equations (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 altitudes, indicating that the $\text{NO}_3^-(\text{HNO}_3)_3$ ion is also strongly affected by cluster break-up.

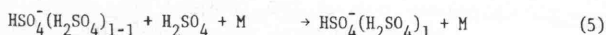
It is evident that in order to use the relative abundances of the $\text{NO}_3^-(\text{HNO}_3)_n$ ions to derive HNO_3 number densities the cluster break up effects must be either avoided or be known very well so that they can be corrected for. Therefore modifications of our present instrument as well 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 $\text{HSO}_4^-(\text{HNO}_3)_m(\text{H}_2\text{SO}_4)_l$ 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, 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 :

$$k[n_{\text{N}}^-][\text{H}_2\text{SO}_4 + \text{HSO}_y] = \alpha[n^+][n_{\text{S}}^-] \quad (6)$$

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^- ion number density is denoted by $[n_{\text{S}}^-]$, $[n^+]$ 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 the same for all ion-molecule and all ion-ion reactions.

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) mass 188 being the most abundant peak among n_{N}^- type ions in the J-82 and S-83 flight 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).

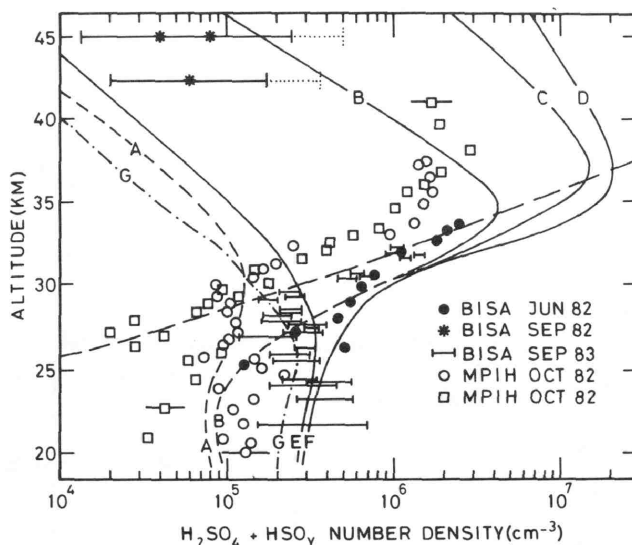


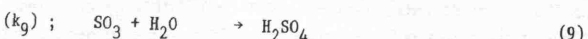
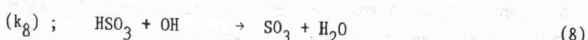
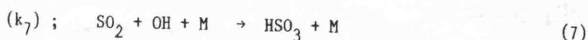
Figure 3 : $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ concentrations as obtained for different in-situ measurements. The error bars for the S-83 flights are due to uncertainties in ion abundance measurements. The error bars indicated for the S-82 flights result from uncertainties in kinetic data.

For the sake of comparison some recent derivations of Qiu and Arnold (1984), reduced with the same α and $[n^+]$ values as used here have also been indicated on figure 3. Furthermore different modelling results are shown. Curves A, B, C and D (full lines above 30 km and dashed lines below 30 km) are taken from a model of Turco et al. (1982) where $[\text{H}_2\text{SO}_4]$ is calculated for different cases. The dot and dash line G is a model result for $[\text{HSO}_3]$ by Turco et al. (1979). The dashed line (no label) on figure 3 is a vapour 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 $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ 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 $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ measurements of the S-83 flight in this altitude region are in good agreement with the calculated H_2SO_4 vapour 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 $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$. It is concluded that in the altitude region 28 to 33 km the H_2SO_4 vapour is mainly controlled by the evaporation equilibrium between aerosol droplets and the vapour phase.

Below 28 km however the $[\text{H}_2\text{SO}_4 + \text{HSO}_y]$ values are much larger than those derived from vapour pressure calculations. In this region H_2SO_4 and HSO_3 are formed by photochemical conversion of SO_2 , COS and other sulfur 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. Curves A and B (which splits into B, C and D above 30 km) are calculations of H_2SO_4 number densities of Turco et al (1981) taking into account these processes. By adding $[\text{H}_2\text{SO}_4]$, represented by curve A and B to $[\text{HSO}_3^-]$ as shown by curve G we get curves E and F respectively. Curve E seems to be a rather unrealistic case, because it assumes a zero H_2SO_4 vapour pressure. Therefore we expect $[\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$ number density to behave according to curve F.

In comparing the $[\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$ data of the J-82 and S-83 flights with this curve it seems difficult to draw conclusions for the J-82 experiment because of the large scattering of the data points below 28 km. The S-83 results however show a more pronounced behavior. Below 25 km the agreement between curve F and the data seems to be acceptable. Between 25 and 28 km however $[\text{HSO}_4^- + \text{HSO}_3^-]$ seems to be lower than model predictions, although it should be kept in mind that a systematic error of about a factor of 3 in the $[\text{HSO}_4^- + \text{HSO}_3^-]$ derivations is possible in view of the uncertainty in α , k and the total ion density $[n^+]$.

However a minimum seems to exist around 28 km, probably caused by a larger loss rate of H_2SO_4 at this altitude. We believe that this is due to an increase in aerosol density above the natural background. Probably this increase still is a result of the El Chichon eruption of 1982. In situ aerosol measurements performed during the same balloon flight (S-83) indicate that a pronounced aerosol layer starts at about 28 km (Ackerman, private communication). A more detailed analysis of these aerosol measurements however is required, before definite correlations can be affirmed.

The present data seem to indicate that $[\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$ as derived from ion composition data below 28 km for the S-83 flight, mainly consists of HSO_3^- , most of the H_2SO_4 being destroyed by an excess of aerosol particles.

Above 35 km two data points for $[\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$ 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, the uncertainty is caused by a difficulty in ion identification as explained before (Arijs et al. 1983a). At 42.3 km a value of $6 \times 10^4 \text{ cm}^{-3}$ is derived for $[\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$. 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. First of all it should be noticed that 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 most abundant n_{N}^- ion observed, in the S-82 flight whereas Qiu and Arnold put $k = 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. With the latter value our data points would shift towards curve B (dotted lines in figure 3). In addition it seems that the upper altitudes in the Qiu and Arnold data of October 1982 were overestimated by about 1.5 km (Arnold, private communication).

Taking into account the previous remarks, the discrepancies become less dramatic. In fact, the data then suggest an $[\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$ profile similar to the model curve B of Turco et al (1981), where an additional loss for H_2SO_4 is assumed to be reactions with "smoke" particles, caused by a downward metal flux of $1 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ from meteoric debris. At this point however, it is instructive to recall the following facts.

From the relative abundances of the $\text{Cl}^- \text{SO}_2$ and $\text{Cl}^- \text{H}_2\text{O}$ ions, detected as contaminant ions in our S-82 flight a SO_2 mixing ratio of about 3 ppb was deduced at about 45 km. 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 a high SO_2 concentrations, probably due to volcanic activities (El Chichón) would imply a rather high H_2SO_4 concentration, through reactions (7), (8) and (9). In a previous report on the S-82, flight we have identified mass 276 as $\text{HSO}_4^- \cdot \text{HNO}_3 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Arijs et al., 1983a). In view of the low signal at mass 258, being the non hydrated precursor of mass 276, and considering the high number of ligands which occur in the previous tentative identification, it might be more likely to attribute

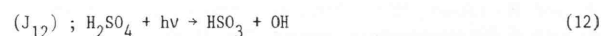
mass 276 to $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HSO}_3^-$ as suggested by Arnold et al. (1982). Accepting that mass 276 is formed through



and assuming that product ions are lost by recombination, the HSO_3^- number density can be calculated with the steady state equation

$$k_{10} [\text{HSO}_3^-] [\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4] = \alpha [\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HSO}_3^-] [n^+] \quad (11)$$

Taking the same k_{10} value as for the association of H_2SO_4 to $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4$, $[\text{HSO}_3^-] / [\text{H}_2\text{SO}_4 + \text{HSO}_3^-]$ 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 HSO_3^- represents about 80% of the $(\text{H}_2\text{SO}_4 + \text{HSO}_3^-)$ content. These high HSO_3^- concentrations and the high SO_2 mixing ratio indicate a much larger photodissociation of H_2SO_4 than used in previous model calculations. Assuming that photolysis occurs according to :



Steady state considerations about HSO_3^- and H_2SO_4 , combining equations (7), (8), (9), (12) and (13) lead to :

$$J_{12} [\text{H}_2\text{SO}_4] = k_8 [\text{HSO}_3^-] [\text{OH}] \quad (14)$$

and

$$J_{13} [\text{HSO}_3^-] + k_8 [\text{HSO}_3^-] [\text{OH}] = k_7 [\text{SO}_2] [\text{OH}] [\text{M}] \quad (15)$$

Accepting an upper limit for k_8 of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ as proposed by Turco et al. (1979) and taking for k_7 , $3 \times 10^{-31} (300/T)^{2.9}$ as reported by De More et al. (1982), the values of $[\text{SO}_2]$, $[\text{HSO}_3^-]$ and $[\text{H}_2\text{SO}_4]$ derived from ion composition measurements lead to : $J_{12} \cong J_{13} \cong 8 \times 10^{-4} \text{ s}^{-1}$ around 45 km. These are extremely high photodissociation frequencies, found only for compounds such as HOCl. It should be kept in mind however that in deriving these values, highly uncertain data (such as k_8 and $[\text{SO}_2]$) were used. Furthermore our knowledge of the sulfur chemistry is still incomplete and the conversion mechanism of HSO_3^- to H_2SO_4 is still not well established (McKeen et al., 1984). It is clear however that the photodissociation frequency of H_2SO_4 is much higher than believed so far and that laboratory data concerning this problem are urgently needed.

Acknowledgements. We thank Dr. M. Ackerman for useful discussions and for supplying us with unpublished aerosol measurements. We also express our gratitude to the technical staff of the Belgian Institute for Space Aeronomy and of the CNES balloon launching base for their cooperation, which made the experiments possible. Part of this work was financed by the NFWO (Belgian National Science Foundation).

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