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Recent stratospheric negative ion composition measurements
between 45 and 22 km altitude

by

E. ARIJS, D. NEVEJANS, J. INGELS and P. FREDERICK

FOREWORD

This paper is the text of a contribution, which has been presented at the "VII th International Conference on Atmospheric Electricity" which has been held at the State University of New York at Albany (June 3-8, 1984). A slightly modified version of it will be published in the Journal of Geophysical Research.

AVANT-PROPOS

Cet article résume une communication qui a été présentée à la "VIIth International Conference on Atmospheric Electricity" qui s'est tenu au State University of New York à Albany (3 - 8 Juin, 1984). Une version légèrement modifiée sera publié dans le Journal of Geophysical Research.

VOORWOORD

Deze tekst is een samenvatting van een mededeling, die gehouden werd op de "VIIth International Conference on Atmospheric Electricity" die doorging aan de State University of New York te Albany van 3 tot 8 juni 1984. Een lichtjes gewijzigde versie ervan zal gepubliceerd worden in de Journal of Geophysical Research.

VORWORT

Dieser Aufsatz wurde zur "VIIth International Conference on Atmospheric Electricity" in Albany (State University of New York) von 3 zum 8 Juni, vorgestellt. Eine leicht modifizierte Version wird herausgegeben werden in Journal of Geophysical Research.

RECENT STRATOSPHERIC NEGATIVE ION COMPOSITION

MEASUREMENTS BETWEEN 22 AND 45 KM ALTITUDE

by

E. ARIJS, D. NEVEJANS, J. INGELS AND P. FREDERICK

Abstract

Recently new composition measurements of negative ions in the stratosphere have been performed with a balloon borne quadrupole mass spectrometer. The altitude region has been extended by the use of valve controlled balloons, which enable a slow descent of the instrument and by the use of a large volume balloon (1,000,000 m^3).

The data obtained during three flights performed in June 1982; September 1982 and September 1983 are reported. The ion spectra obtained are shown and the results of the data analysis are presented. The lower altitude limit of the measurements is imposed by the decrease of the instrument sensitivity due to ion scattering in the mass spectrometer and the upper limit by present ballooning techniques. At high altitudes the ion spectra may be disturbed by contamination, whereas at low altitudes ion cluster break up is a severe problem.

Nevertheless the relative abundances of the different ion mass peaks, mainly belonging to the $NO_3^-(HNO_3)_n$ and $HSO_4^-(HNO_3)_m(H_2SO_4)_\ell$ cluster families allow the derivation of concentrations of H_2SO_4 in the altitude region mentioned above. 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.

Résumé
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　　　Récemment des nouvelles données sur la composition des ions négatifs dans la stratosphère ont été obtenues avec un spectromètre de masse quadrupolaire porté en ballon. La région d'altitude où les mesures ont été effectuées a été étendue par l'emploi de ballons à clapet, qui permettent une descente lente de l'instrument et par l'emploi d'un grand ballon de 1.000.000 m^3.

　　　Les résultats obtenus pendant trois vols (juin 1982, septembre 1982 et septembre 1983) sont rapportés et analysés. La limite inférieure d'altitude où les mesures sont possibles est imposée par le décroissement de la sensibilité de l'appareil, dû au scattering et l'altitude maximale est limitée par la présente technologie des aérostats.

　　　A haute altitude les spectres de masse peuvent être influencés par la contamination, quant à plus basse altitude la dissociation des agglomérats d'ions devient un problème sérieux.

　　　Néanmoins, les abondances relatives des ions $NO_3^-(HNO_2)_n$ et $HSO_4^-(HNO_3)_m(H_2SO_4)_\ell$ permettent le calcul des concentrations de H_2SO_4 dans le domaine d'altitude entre 45 et 22 km.

　　　A 45 km un rapport de mélange augmenté de SO_2 est déduit des spectres de masse des ions négatifs. Cette augmentation est probablement causée par les activités volcaniques récentes.

　　　Les données sont discutées dans le cadre des mesures précédentes et des modèles. Un intérêt spécial est attribué à la chimie du souffre.

Samenvatting

Onlangs werden nieuwe metingen van het negatieve ionenbestand in de stratosfeer uitgevoerd door middel van ballongedragen quadrupolaire massaspectrometers. Het hoogtegebied werd uitgebreid door gebruik te maken, enerzijds van ventielgecontroleerde ballons, die een langzaam dalen van het instrument toelaten, en anderzijds door het gebruik van een ballon van $1.000.000 \ m^3$.

De gegevens bekomen gedurende drie vluchten (juni 1982; september 1982 en september 1983) worden voorgesteld en geanalyseerd. Het laagste niveau waarop metingen mogelijk zijn, wordt bepaald door de vermindering in gevoeligheid van de massaspectrometer, te wijten aan verstrooiing der ionen in het toestel zelf. De grootste hoogte daarentegen hangt af van de huidige ballontechnologie. Op grote hoogten kunnen de metingen sterk gestoord worden door contaminatie der ionen en op lage hoogten vormt de opbraak een ernstig probleem.

Desondanks kon uit de relatieve intensiteit der massapieken van de $NO_3^-(HNO_3)_n$ en $HSO_4^-(HNO_3)_n(H_2SO_4)_\ell$-ionen de zwavelzuurconcentratie berekend worden tussen 45 en 22 km hoogte. Tevens werd een verhoogde SO_2-mengverhouding op 45 km hoogte afgeleid uit de ionenspectra. Deze verhoging werd toegeschreven aan de recente vulkanische activiteit.

De bekomen gegevens worden verder besproken in het raam van vroegere metingen en modellen. Bijzondere aandacht wordt verleend aan de zwavelchemie.

Zusammenfassung

Kürzlich wurden neue Messungen der negativer stratosphärischer Ionen durchgeführt mit Ballongetragen quadrupolaren Massenspektrometer. Das Höhegebiet wurde ausgebreitet durch einerseits, Ventilkontrolierten Ballonen zu gebrauchen, die eine langsame Senkung der Instrument zulassen, und anderseits, ein Ballon von 1.000.000 m^3 Volumen zu benützen.

Die Daten bekommen während drei Flüge (Juni 1982; September 1982 und September 1983) wurden vorgestellt und analysiert. Das geringste Niveau worauf Messungen möglich sind, wird bestimmt durch die Empfindlichkeitsverringerung dem Massenspektrometer, verursacht durch die Ionenzerstreuung im Apparat selbst. Die gröste Höhe dagegen ist abhängig von der heutige Ballontechnologie. Auf grösse Höhen können die Messungen gestört werden durch Kontamination und auf geringe Höhe ist die Dissoziation der Clusterionen ein grösses Problem.

Dessenungeachtet konnte man von der relative Intensität der Massapiken der $NO_3^-(HO_3)_n$ und $HSO_4^-(HNO_3)_n(H_2SO_4)_\ell$ Ionen die Schwefelsäurekonzentration berechnen zwischen 45 und 22 km Höhe. Auch wird eine erhöhtere SO_2-Mischungsverhältnisse auf 45 km Höhe abgeleitet von den Ionenspektra. Diese Erhöhung kann man zuschreiben an der rezenten vulkanischen Aktivität.

Die bekommen Daten werden weiter besprochen im Rahmen früheren Messungen und Modellen. Die Schwefelchemie wird besondere Aufmerksamkeit geschenkt.

1. INTRODUCTION

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

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 $NO_3^-(HNO_3)_n$ and $HSO_4^-(H_2SO_4)_m$ $(HNO_3)_\ell$. Whereas the $NO_3^-(HNO_3)_n$ cluster ions had been predicted on the basis of earlier laboratory measurements (Fehsenfeld et al., 1975), and modelling efforts, evidence for the formation of HSO_4^- clusters in the stratosphere 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; Mc Crumb and Arnold, 1981; Arijs et al., 1982, 1983a; Viggiano et al., 1983) and the fractional ion abundances have been used 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, 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 experiments. 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 hereafter were performed during three balloon flights over southern France at about 44°N. A detailed description of the quadrupole ion mass spectrometer, used in these flights has already been given before (Arijs et al., 1980; Ingels et al., 1978; Nevejans et al., 1982; Nevejans et al., 1984).

The first flight (J-82), performed on 16 June 1982, with a 100,000 m^3 valve controlled balloon 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 m^3 Wintzen balloon was used. A ceiling altitude of about 45.5 km was reached 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 data of these two flights have already been published before (Arijs et al., 1983a,b,c).

The third flight (S-83) took place on 18 September 1983. Again a 100,000 m^3 valve controlled balloon was used and negative ion mass spectra were recorded between 32 and 22 km.

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

During the last two flights (S-82 and S-83) the gondola also contained an instrument with photographic equipment for the detection of aerosols (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 previously (Arijs et al., 1982. Similar spectra of the J-82 and S-82 flights have been shown in earlier publications (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 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 they 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 al., 1982) the major peaks of figure 1A can be attributed to $NO_3^-(HNO_3)$, $HSO_4^-(HNO_3)$, $NO_3^-(HNO_3)_2$, $HSO_4^-(H_2SO_4)$, $HSO_4^-(HNO_3)_2$ and $HSO_4^-(H_2SO_4)_2$. The minor peaks above mass 125 are probably hydrates of the previous ions, apart from 258 being $HSO_4^-.HNO_3. H_2SO_4$ and 276 which has been interpreted as $HSO_4^-.H_2SO_4.HSO_3$ by Arnold et al. (1982). Although it is the summation of 17 scans, spectrum B only shows two major mass peaks, namely mass 125 ($NO_3^-.HNO_3$)and 188 ($NO_3^-(HNO_3)_2$). This is of course due to a sharp decrease of the sulfuric acid concentration in the lower stratosphere, as will be discussed further on. The mass numbers and the abundance of the minor peaks in this spectrum can only be determined with a consider-
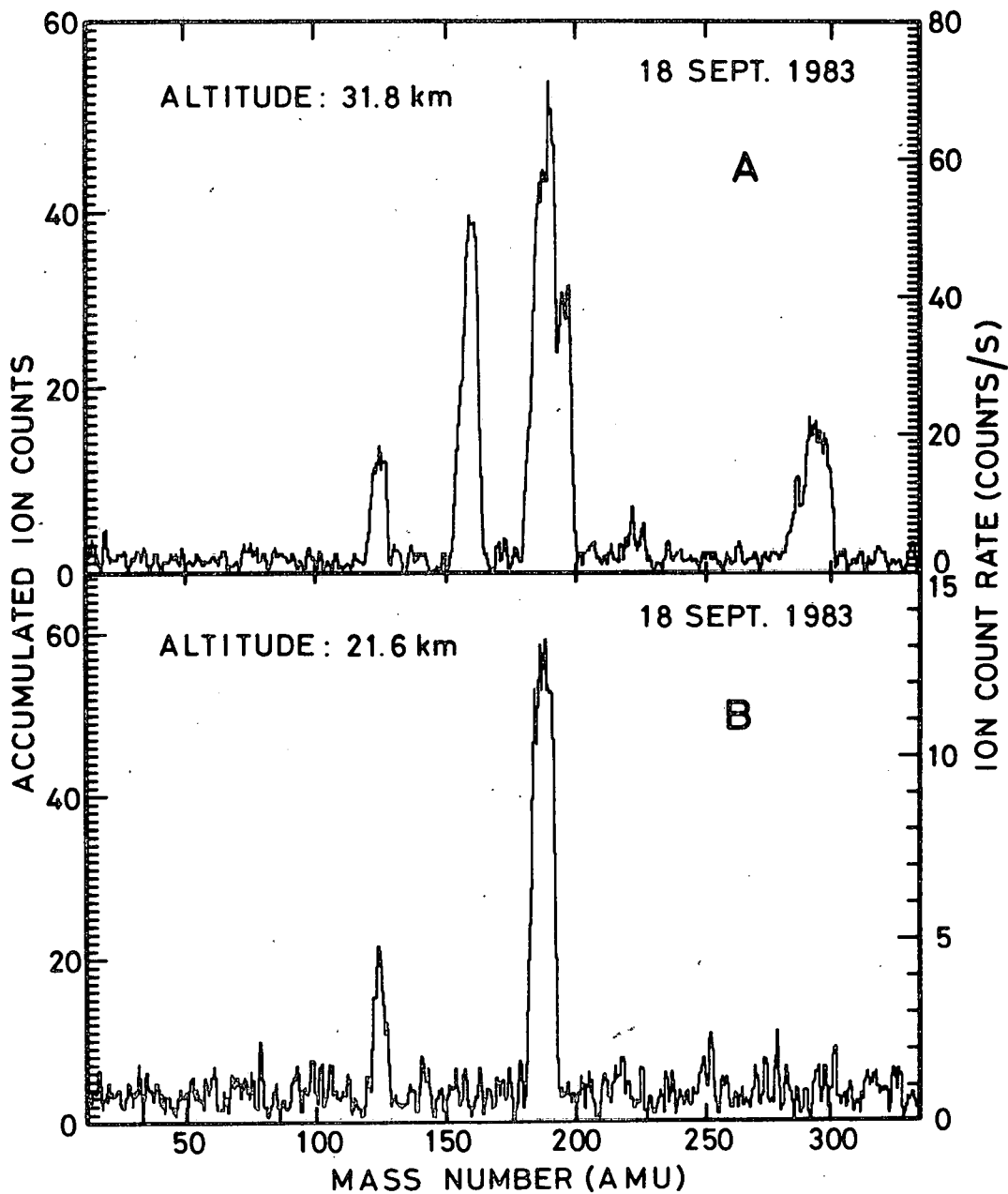
Fig. 1.- Typical negative ion spectra obtained in the moderate resolution mode for the S-83 flight.

able 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 abundance of ions with a mass beyond the range of the instrument (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 signal strength at higher altitudes.

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 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 $1m\ s^{-1}$, which permits a longer measuring time at a given altitude level than during ascent.

We will now discuss the abundances of the different ions of the $NO_3^-(HNO_3)_n$ and the $HSO_4^-(H_2SO_4)_m\ (HNO_3)_\ell$ families as measured in the different flights.

3.2 NO_3^- cluster ions

As seen in figure 1, the main ions observed belonging to the $NO_3^-(HNO_3)_n$ family are $NO_3^-(HNO_3)$ at mass 125 and $NO_3^-(HNO_3)_2$ at mass 188. Mass 63 (NO_3^-) and mass 251 ($NO_3^-(HNO_3)_3$) 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 formulae :

$$[NO_3^-(HNO_3)_{n+1}] = K_{n,n+1} \ [NO_3^-(HNO_3)_n] \ [HNO_3] \qquad (1)$$

and

$$- RT \ \ln K_{n,n+1} = \Delta H_o - T\Delta S_o \qquad (2)$$

where square brackets denote number densities.

For n = 1, ΔH_o and ΔS_o are known from laboratory measurements (Davidson et al., 1977). Therefore $[HNO_3]$ can be deduced from the relative abundances of mass 125 and mass 188 if the temperature is known. In order to assess the validity of the method, throughout the altitude range 35 to 20 km we have calculated $[NO_3^-(HNO_3)_2]/$ $[NO_3^-.HNO_3]$ using formulae (1) and (2) and a compilation of nitric acid measurements, recently reported (WMO, 1981). The results are compared with the $[NO_3^-(HNO_3)_2]/$ $[NO_3^-.HNO_3]$ 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 $[NO_3^-(HNO_3)_2]/[NO_3^-.HNO_3]$ 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
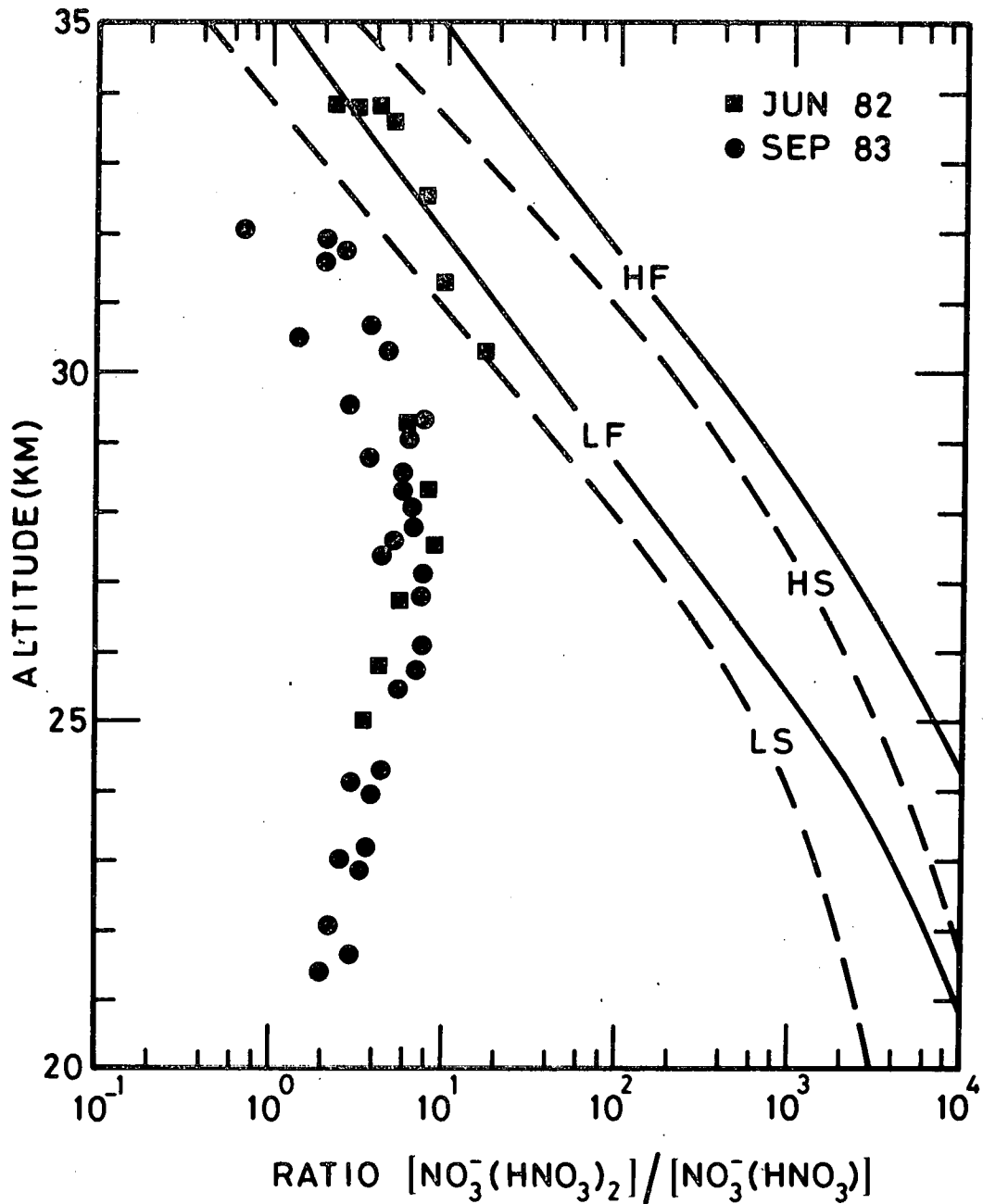
Fig. 2.- Abundance ratio $[NO_3^-(HNO_3)_2]/[NO_3^-\cdot HNO_3]$ as measured in the J-82 and S-83 flight. For comparison theoretically deduced abundance ratios are also shown. LF and HF are calculated for a spring-fall temperature profile and low and high HNO_3 mixing ratio respectively. LS and HS are for summer temperature conditions.

fact a marked increase of this cluster break up effect is noticed as a function of altitude and the fraction of $NO_3^-(HNO_3)_2$ converted into $NO_3^-\cdot HNO_3$ is roughly varying from 1/8 to 1/2 between 30 and 20 km.
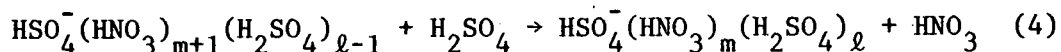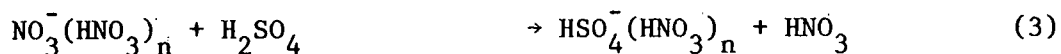
It should be emphasized that cluster break up strongly depends on the sampling orifice diameter and on the instrumental arrangement. Therefore the altitude above which fragmentation can be neglected varies from flight to flight. The value of 32 km stated here is typical for the S-83 experiment where a sampling aperture of about 0.2 mm was used.

The derivation of HNO_3 number densities from 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 $NO_3^-(HNO_3)_3$ ion is also strongly affected by cluster break up.

It is evident that in order to use the relative abundances of the $NO_3^-(HNO_3)_n$ ions to derive HNO_3 number densities the cluster break up 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. $\underline{HSO_4^-}$ $\underline{\text{cluster ions and sulfur chemistry}}$

Apart from the NO_3^- cluster ions a second family of major ions, represented by $HSO_4^-(HNO_3)_m(H_2SO_4)_\ell$, is detected in the stratosphere. They result from a set of ion molecule reactions, such as

$$NO_3^-(HNO_3)_n + H_2SO_4 \rightarrow HSO_4^-(HNO_3)_n + HNO_3 \qquad (3)$$

$$HSO_4^-(HNO_3)_{m+1}(H_2SO_4)_{\ell-1} + H_2SO_4 \rightarrow HSO_4^-(HNO_3)_m(H_2SO_4)_\ell + HNO_3 \qquad (4)$$

and

$$HSO_4^-(H_2SO_4)_{\ell-1} + H_2SO_4 + M \rightarrow HSO_4^-(H_2SO_4)_\ell + M \qquad (5)$$

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 :

$$k[n_N^-] \; [H_2SO_4 + HSO_y] = \alpha[n^+] \; [n_s^-] \qquad (6)$$

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 $NO_3^-(HNO_3)_2$ a value of 1×10^{-9} cm^3 s^{-1} was found by Viggiano et al. (1982). Since the most
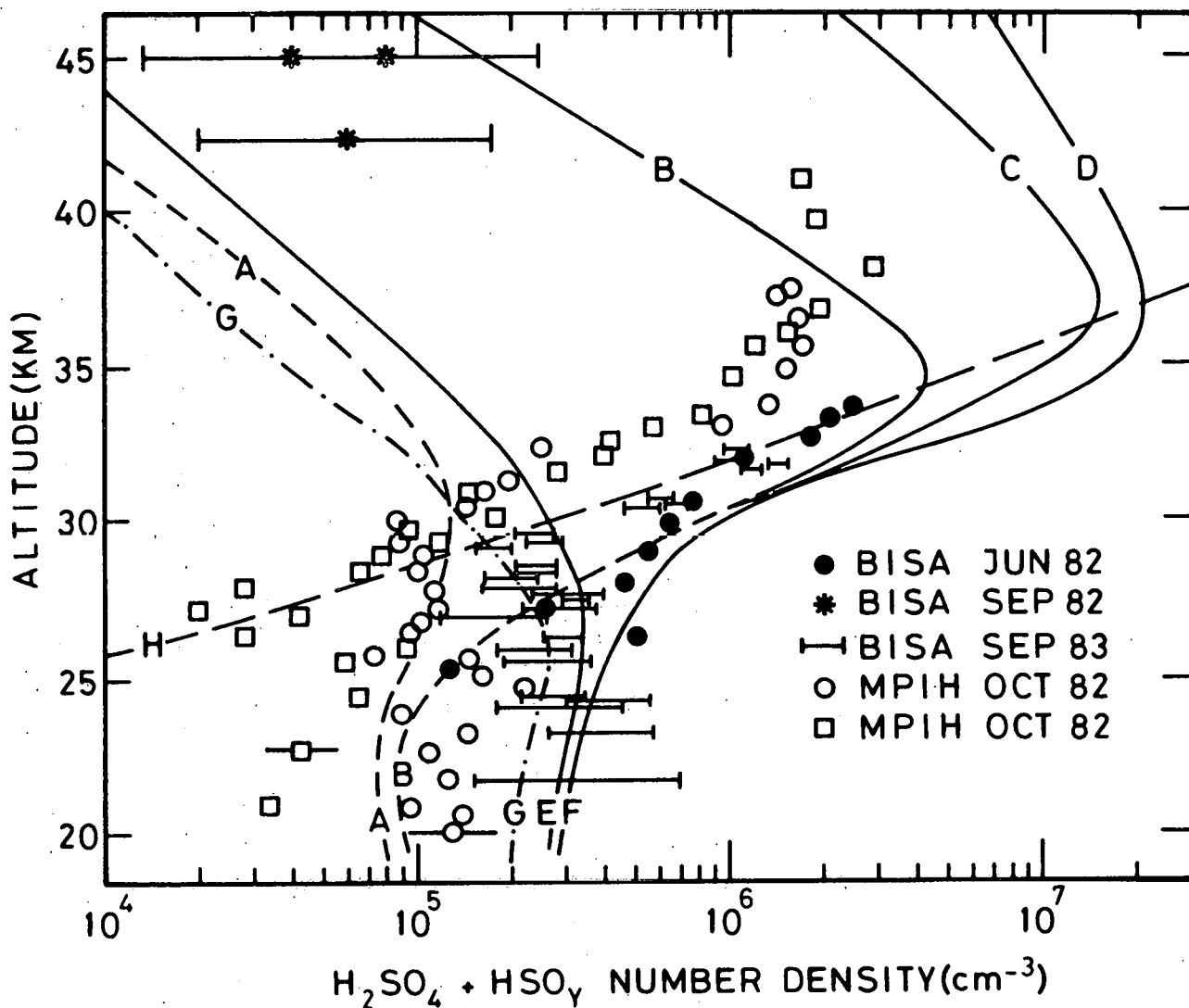
Fig. 3.- $[H_2SO_4 + HSO_y]$ concentrations as obtained for different in-situ measurements. Data labeled MPIH are those reported by Qiu and Arnold (1984) and obtained by the group of the Max Planck Institute of Heidelberg during balloon flights on 4 (circles) and 17 (squares) October 1982. Measurements 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.

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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 $NO_3^-(HNO_3)$ and thus k was put equal to 2×10^{-9} cm^3 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 shown on figure 3. Furthermore different modelling results are indicated. Curves A, B, C and D are taken from a model by Turco et al. (1981), wherein $[H_2SO_4]$ 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 cm^{-2} 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 $[HSO_3]$ by Turco et al. (1979).
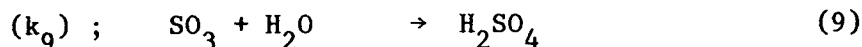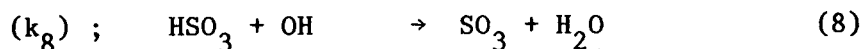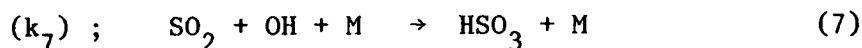
Curve E (full line) represents $[H_2SO_4 + HSO_3]$ as given by A + G. Curves FB, FC and FD represent $[H_2SO_4 + HSO_3]$ as given by G+B, G+C and G+D respectively. Again these 3 curves merge into one (curve F) below 30 km.

The dashed line (H) on figure 3 is a vapour pressure calculation of H_2SO_4 using a temperature profile as measured in flight S-83 and a computation method explained in detail before (Arijs et al., 1983a).

In comparing the derivations of $[H_2SO_4 + HSO_y]$ 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 $[H_2SO_4 + HSO_y]$ 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 $[HSO_3]$ with a method described by Arnold and Bührke (1983) indicates that in this altitude region H_2SO_4 is the major sulfur component of $[H_2SO_4 + HSO_y]$. 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 $[H_2SO_4 + HSO_y]$ 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 bearing gases, which are injected into the stratosphere (Turco et al., 1979). The major production paths leading to H_2SO_4 and HSO_3 formation k are assumed to be

$$(k_7) \; ; \quad SO_2 + OH + M \quad \rightarrow \quad HSO_3 + M \qquad (7)$$

$$(k_8) \; ; \quad HSO_3 + OH \quad \rightarrow \quad SO_3 + H_2O \qquad (8)$$

$$(k_9) \; ; \quad SO_3 + H_2O \quad \rightarrow \quad H_2SO_4 \qquad (9)$$

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

In comparing the $[H_2SO_4 + HSO_y]$ 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 the data points below 28 km. The S-83 results however show a more pronounced behavior. Between 25 and 30 km altitude the values of $[H_2SO_4 + HSO_y]$ 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 (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 (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 $[H_2SO_4 + HSO_y]$ consists of HSO_3 in this altitude region.

Although this seems to be an experimental support for the model of Turco (1979, 1981) care should be taken with this interpretation for different reasons. First of all the error bars on the S-83 $[H_2SO_4 + HSO_y]$ data below 25 km are rather large, due to possible incomplete counting statistics for the HSO_4^--ion signals, which are rather low in this altitude region. These errors can partially explain the difference between the results of Qiu and Arnold (1984) and ours. Secondly 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 three (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_5) not taken into account in Turco's model. In fact, if the conversion of HSO_3 to H_2SO_4 would proceed according to :

$$(k_{10}) \; ; \quad HSO_3 + O_2 \rightarrow SO_3 + HO_2 \qquad \qquad (10)$$
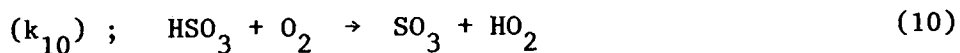
followed by reaction (9), as suggested by Stockwell and Calvert (1983), the existence of HSO_3 in any detectable amounts in the stratosphere becomes very questionable as well as the recent HSO_3 derivation of Qiu and Arnold (1984). More information on the atmospheric sulfur chemistry is therefore needed before the data can be fully exploited.

Above 35 km two data points for $[H_2SO_4 + HSO_y]$ were obtained in the S-82 flight. At 45.1 km a number density between 4×10^4 cm^{-3} and 8×10^4 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 cm^{-3} is derived for $[H_2SO_4 + HSO_y]$. 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 2×10^{-9} cm^3 s^{-1} was used for the reaction rate coefficient k between n_N^- type and n_S^- ions, because $NO_3^-.HNO_3$ (mass 125) was the dominant n_N^- ion observed in the S-82 flight, whereas Qiu and Arnold put k = 1×10^{-9} cm^3 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 $\times$ 10^{-9} should be applied. Consequently the data of Qiu and Arnold corresponding to 40 km altitude as plotted on 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 (Arnold, private communications).

Taking into account the previous remarks, the apparent discrepancies become less dramatic. In fact, the data then suggest an $[H_2SO_4 + HSO_y]$ profile similar to the model curve B of Turco et al. (1981). This curve was obtained assuming an additional loss process for H_2SO_4, consisting of reactions with "smoke" particles, caused by a downward metal flux of 1×10^6 cm^2 s^{-1} from meteoric debris.

It would be premature however to conclude that the model therefore represents a good representation of reality. Instead of assuming a loss of $[H_2SO_4 + HSO_3]$ through reaction with smoke particles, a similar

fitting can be obtained by introducing a larger photodissociation frequency for H_2SO_4, as is demonstrated by the following considerations.

From the relative abundances of the Cl^-SO_2 and Cl^-H_2O 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 (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 a high SO_2 concentration , probably due to volcanic activities (El Chichon) 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 $HSO_4^-.HNO_3.H_2SO_4.H_2O$ (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 attractive to attribute mass 276 to $HSO_4^-.H_2SO_4.HSO_3$ as suggested by Arnold et al. (1982). Accepting that mass 276 is formed through

$$(k_{11}) \; ; \; HSO_4^-.H_2SO_4 + HSO_3 + M \rightarrow HSO_4^-.H_2SO_4.HSO_3 + M \quad (11)$$
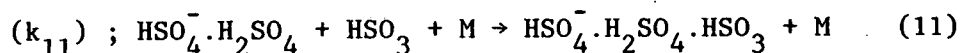
and assuming that product ions are lost by recombination, the HSO_3 number density can be calculated with the steady state equation

$$k_{11}[HSO_3][HSO_4^-.H_2SO_4] = \alpha[HSO_4^-.H_2SO_4.HSO_3][n^+] \quad (12)$$

Taking the same k_{11} value as for the association of H_2SO_4 to $HSO_4^-.H_2SO_4$, $[HSO_3]/[H_2SO_4]$ 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 H_2SO_4 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 :

$$(J_{13}) \; ; \; H_2SO_4 + h\nu \rightarrow HSO_3 + OH \tag{13}$$

$$(J_{14}) \; ; \; HSO_3 + h\nu \rightarrow SO_2 + OH \tag{14}$$
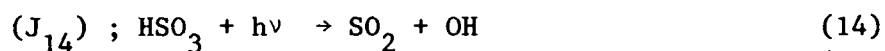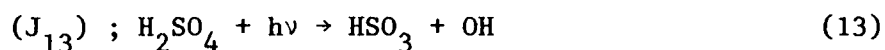
Steady state considerations about HSO_3 and H_2SO_4, combining equations (7), (8), (9), (13) and (14) lead to :

$$J_{13}[H_2SO_4] = k_8[HSO_3][OH] \tag{15}$$

and

$$J_{14}[HSO_3] = k_7[SO_2][OH][M] \tag{16}$$

Accepting an upper limit for k_8 of 10^{-11} cm^3 s^{-1} as proposed by Turco et al. (1979) and taking for k_7, $3 \times 10^{-31}(300/T)^{2.9}$ cm^6 s^{-1} as reported by De More et al. (1982), the values of $[SO_2]$, $[HSO_3]$ and $[H_2SO_4]$ derived from ion composition measurements lead to : $J_{13} \cong$ 1.6×10^{-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 SO_2 number density, which was derived from the abundance ratio of $Cl^-.SO_2$ and $Cl^-.H_2O$ (Arijs et al., 1983b), may be overestimated. Cl^-H_2O being only a minor ion peak, the error on $[SO_2]$ can be considerable as a result of uncomplete 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 equations (15) and (16) may be oversimplified, due to the incomplete knowledge of the sulfur chemistry and the neglection of vertical transport phenomena.

It should also be emphasized that the previous derivations of the photodissociation frequencies are only valid if reaction (8) is the major loss mechanism for HSO_3. If however reaction (10) represents the main sink for HSO_3, the HSO_3 concentrations will most probably be much lower than the values deduced above. It then becomes very doubtful to asign $HSO_4^-\cdot H_2SO_4\cdot HSO_3$ 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 equation (11) and an unambiguous identification of mass 276 is so far impossible. The present results do therefore not preclude reaction (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 reactions in the laboratory 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 and Liu, 1984).

ACKNOWLEDGEMENTS

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