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Negative ion composition and sulfuric acid vapour in the upper stratosphere

by

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

FOREWORD

The paper "Negative ion composition and sulfuric acid vapour in the upper stratosphere" will be published in Planetary and Space Science.

AVANT-PROPOS

L'article "Negative ion composition and sulfuric acid vapour in the upper stratosphere" sera publié dans Planetary and Space Science.

VOORWOORD

De tekst "Negative ion composition and sulfuric acid vapour in the upper stratosphere" zal verschijnen in Planetary and Space Science.

VORWORT

Die Arbeit : "Negative ion composition and sulfuric acid vapour in the upper stratosphere" wird in Planetary and Space Science" herausgegeben werden.

NEGATIVE ION COMPOSITION AND SULFURIC VAPOUR

IN THE UPPER STRATOSPHERE

by

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

Abstract

The nature of negative ions in the altitude region 42 - 45 km has been investigated by means of a balloon borne mass spectrometer. Apart from the NO_3^- and HSO_4^- clusters, ions with different cores, which can be identified as CO_3^-, HCO_3^-, Cl^- and ClO_3^- were observed. The spectra have been used to estimate the sulfuric acid number density at 45.2 and 42.3 km altitude.

Résumé

L'identité d'ions négatifs dans le domaine d'altitude allant de 42 à 45 km a été examiné à l'aide d'un spectromètre de masse embarqué à bord d'une nacelle stratosphérique. En dehors des groupes de NO_3^- et de HSO_4^-, des ions de différents noyaux, pouvant être identifiés comme CO_3^-, HCO_3^-, Cl^- et ClO_3^-, ont été trouvés. Les spectres ont été utilisés pour évaluer la concentration de l'acide sulfurique à 45,2 et 42,3 km d'altitude.

Samenvatting

Het negatieve ionenbestand in het hoogtegebied van 42 tot 45 km werd onderzocht door middel van een ballongedragen massaspectrometer. Naast de NO_3^- en HSO_4^- aglomeraten werden een reeks andere negatieve ionen waargenomen, die kunnen geidentificeerd worden als aglomeraten opgebouwd rond CO_3^-, HCO_3^-, Cl^- en ClO_3^- kernen. De spectra werden gebruikt om de concentratie van zwavelzuurdamp af te schatten op de hoogtes van 45,2 en 42,3 km.

Zusammenfassung

Der Charakter von negative Ionen im Höhegebiet von 42 zu 45 km wurde mit einer Massenspektrometer, eingebaut in eine stratosphärische Ballonsonde, untersucht. Neben die NO_3^- und HSO_4^- Agglomeraten, wurden andere Ionen mit verschiedenen Kernen beobacht. die man kann identifizieren als CO_3^-, HCO_3^-, Cl^- und ClO_3^-. Die spectra wurden benutzt zur Bestimmung der Konzentration von Schwefelsäure am 45,2 und 42,3 km Höhe.

INTRODUCTION

Mass spectrometric observations with balloon borne instruments (Arnold and Henschen, 1978; Arijs et al., 1981; Arnold et al., 1981a; Viggiano and Arnold, 1981; Arijs et al., 1982; Arnold et al., 1982) have revealed that the major negative ions in the altitude region 20 to 35 km belong to the $NO_3^-(HNO_3)_n$ and $HSO_4^-(HNO_3)_\ell$ $(H_2SO_4)_m$ families.

Subsequent laboratory measurements (Viggiano et al., 1980, 1982) enabled the use of in-situ data for the derivation of H_2SO_4 vapour concentrations in the stratosphere (Arnold and Fabian, 1980; Arijs et al., 1981; Arnold et al., 1981b; Viggiano and Arnold, 1981, 1983; Arnold and Bührke, 1983; Arijs et al., 1983a).

Up to now however no negative ion composition data in the stratospheric region above 35 km have been reported. In this work we present and discuss the first mass analysis of negative ions between 42 and 45 km altitude.

EXPERIMENTAL AND MEASUREMENTS

The data were obtained during a flight with a 1,000,000 m^3 stratospheric balloon, carrying a quadrupole ion mass spectrometer (Ingels et al., 1978; Arijs et al., 1981) and optical equipment for the detection of aerosols (Ackerman et al., 1981) and ozone. The balloon was launched from the CNES base at Aire-sur-l'Adour (44°N) on 23 September 1982 at 12.38 UT and reached a ceiling altitude oscillating between 45 and 46 km. The flight lasted about 7 hours and after sunset the balloon descended to 41.2 km at a rate of 1.3 m s^{-1}.

Negative ion spectra were recorded mainly during float time and during a fraction of descent (around 42.3 km). The remaining flight time was exploited for positive ion measurements reported elsewhere (Arijs et al., 1983b).

For negative ion detection preprogrammed measuring programs, specifying different resolutions and mass domains were used (Nevejans et al., 1982). At float altitude spectra were recorded at high and moderate resolution as well as in the total ion mode (no DC on the quadrupole rods). During descent only moderate resolution and total ion mode were selected in order to economize integration time.

RESULTS AND DISCUSSION

A spectrum obtained at float altitude with a moderate resolution ($m/\Delta m \cong 17$), is depicted in figure 1A. Peak width analysis shows that for this moderate resolution some adjacent mass peaks overlap. This is further demonstrated by the high resolution spectra of figure 2, recorded in the constant peak width mode ($\Delta m = 0.8$ amu) and covering small mass domains. These spectra for example, show that in figure 1A the mass peak around 60 amu, and the large signal appearing around 100 amu, are composed of 2 (60 and 62 amu) and 3 major peaks (97, 99 and 101 amu) respectively.

Similar high resolution spectra obtained during float in medium sized mass domains (48-88 amu, 86-126 amu and 124-164 amu) revealed unambiguously the nature of the most abundant ions. Minor ions (e.g. the group 112-116 amu) could not be identified un-ambiguously because counting statistics was incomplete within available integration time.
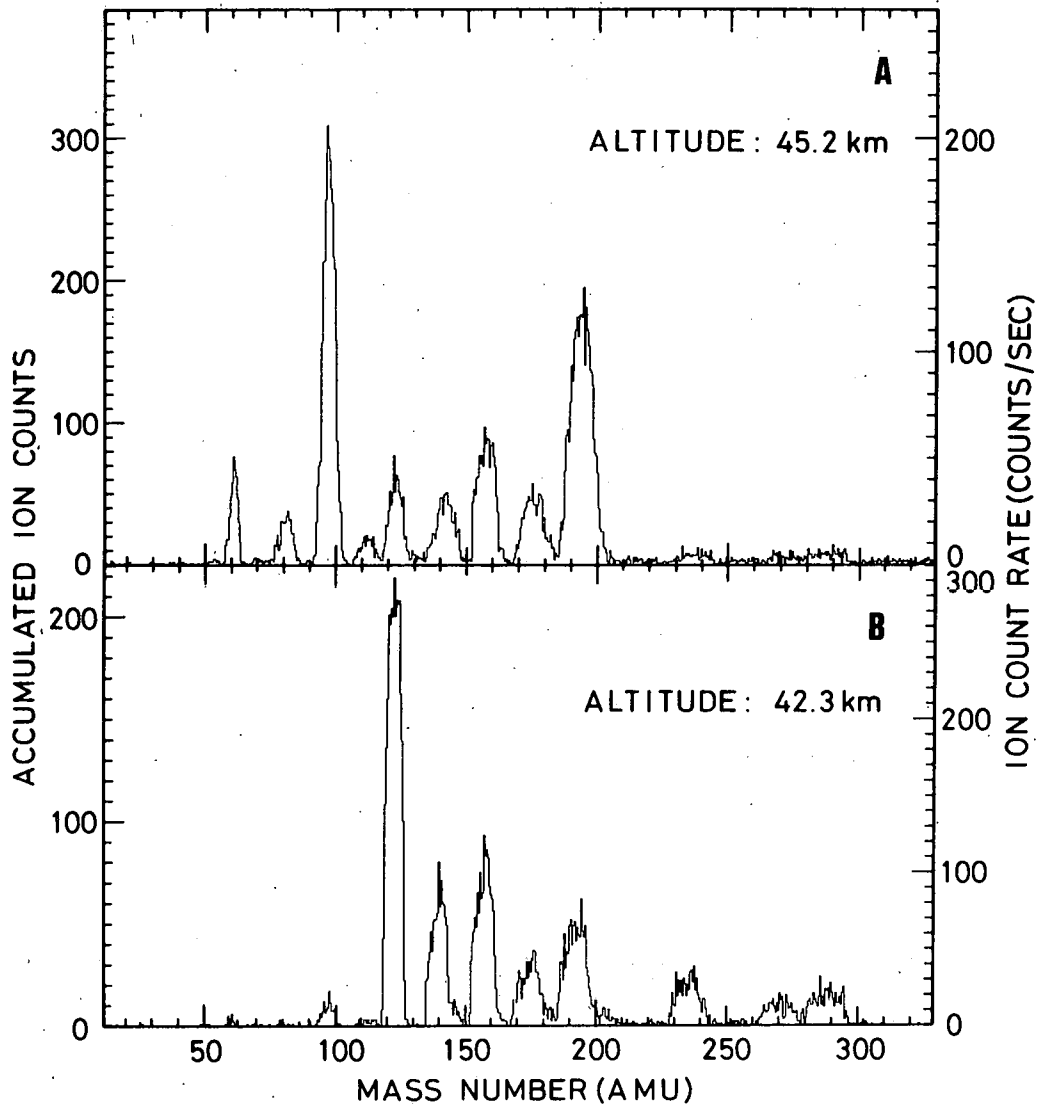
Figure 1: Negative ion spectra obtained in the moderate resolution mode ($m/\Delta m \cong 17$). Spectrum A is the sum of 6 scans of 160 s each, while the instrument floated between 45.1 and 45.3 km. Solar elevation angle was 13°. Spectrum B is the sum of 3 scans recorded during descent between 42.5 and 42.1 km. Solar depression angle was 10°. Both spectra are presented unsmoothed.
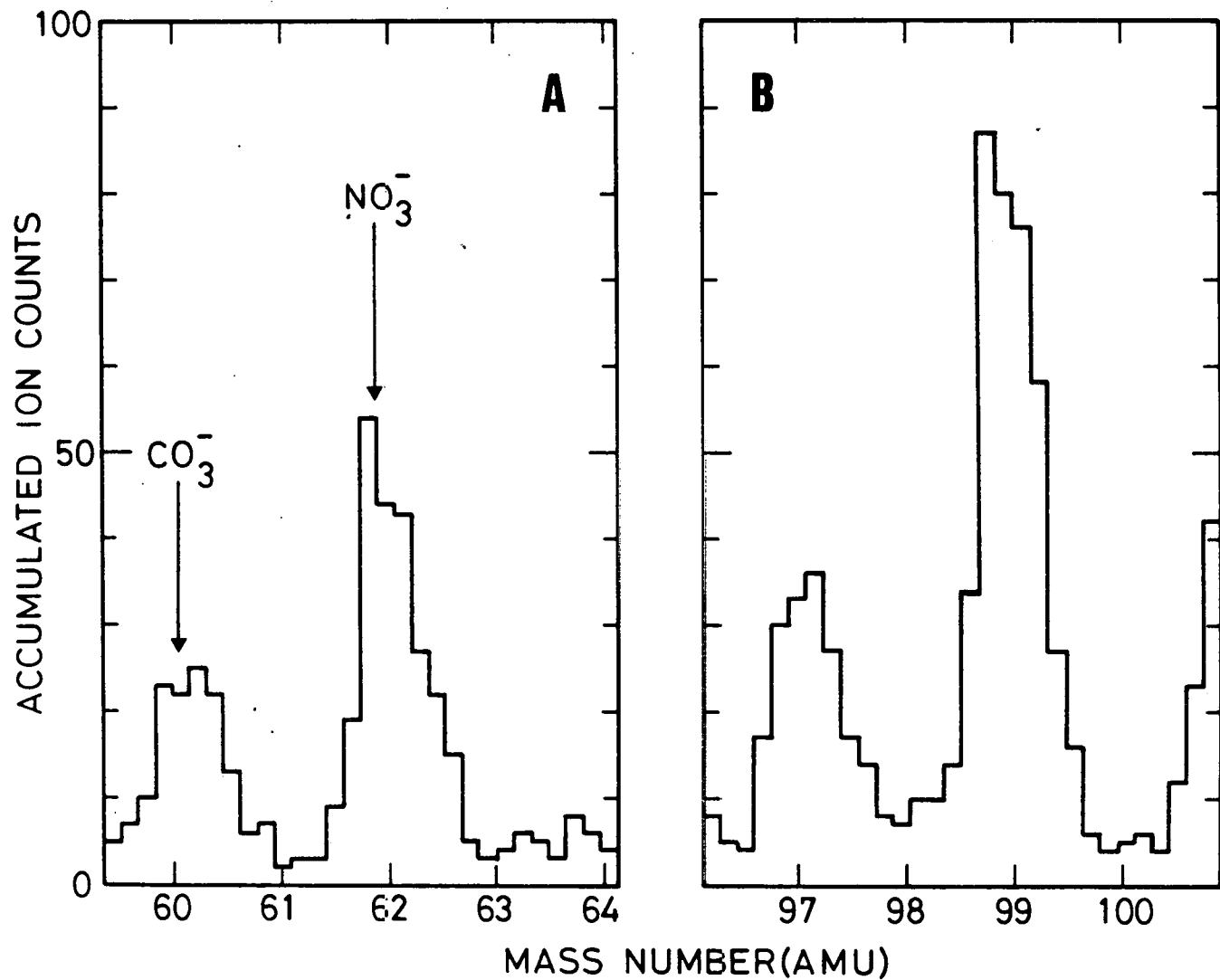
Figure 2: Sample negative ion spectra recorded in small mass domains during float. Spectrum A covers the mass domain 59 to 64 amu and was obtained after summation of 18 scans of 30 s each. Each mass (1 amu) is subdivided into 6 channels (dwell time per channel 1 s). Spectrum B is the sum of 19 similar scans in the mass domain 96 to 101 amu. The spectra were not smoothed.

Nevertheless a careful study of rising and trailing mass peak edges (Arijs et al., 1981) enabled the mass determination of most of the observed ions within certain limits. The results of such an investigation are summarized in table 1 for spectrum 1A obtained at float altitude.

Spectrum 1B was obtained during the slow balloon descent after sunset. Due to the limited residence time of the balloon in a defined altitude region, integration time was insufficient for high resolution measurements. We must therefore again rely upon the technique of rising and trailing peak edges for mass determination. It turns out that the mass peaks of figure 1B are considerably narrower than those of 1A, although this is scarcely visible on the reduced spectra of figure 1. Application of this technique then results in table 2.

We will now discuss the possible identifications reported in both tables.

Inspection of table 1 learns that the major ions having a mass number higher than 125 amu have already been observed at lower altitudes (Arnold et al., 1978, 1981a; Arijs et al., 1981, 1982; Mc Crumb and Arnold, 1981). Even some of the low mass minor ions were reported previously (Mc Crumb and Arnold, 1981; Arijs et al., 1982).

Furthermore it can be seen from the list of possible ion identifications that all ions have as core : OH^-, CO_3^-, HCO_3^-, NO_2^-, NO_3^-, O_4^-, CO_4^-, Cl^-, HSO_4^-, HSO_3^- or ClO_3^-. Apart from the last two ones, all of these have been predicted before (Ferguson et al., 1979) and all of the ligands of table 1, except SO_2, were introduced earlier (Mc Crumb and Arnold, 1981; Arijs et al., 1982).

The most unexpected core ions found are HSO_3^- and ClO_3^-. It is proposed here that HSO_3^- core ions would be formed by :

TABLE 1 : Mass numbers, possible identifications and fractional ion count rates of negative ions at 45.2 km. The ions are subdivided into 2 groups depending upon count rates. The mass numbers of column 1 (MASS) are derived from rising and trailing peak edges of figure 1A. The numbers of column 3 (MOST ABUNDANT MASS NUMBERS) are derived from high resolution spectra except for mass 178 and 198 which follow from peak edge analysis of figure 1A. For details about possible peak identifications see text.
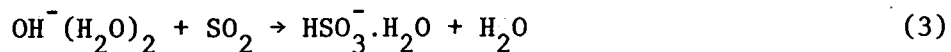
MASS	POSSIBLE IDENTIFICATION	MOST ABUNDANT MASS NUMBERS	FRACTIONAL ION COUNT RATE (%)
	GROUP I		
60-62	CO_3^- (33%) NO_3^- (66%)		8
81-87	HSO_3^-, $NO_2^-(H_2O)_2$, $NO_2^-\cdot HCl$, $O_4^-\cdot H_2O$ ClO_3^-, $Cl^-\cdot HOCl$	83	4
96-103	$CO_3^-(H_2O)_2$, $CO_3^-\cdot HCl$, $HCO_3^-(H_2O)_2$, $HCO_3^-\cdot HCl$ HSO_4^-, $NO_3^-\cdot HCl$, $NO_3^-(H_2O)_2$, $HSO_3^-\cdot H_2O$ Cl^-SO_2, $NO_2^-(H_2O)_3$, $NO_2^-\cdot HCl\cdot H_2O$, $ClO_3^-\cdot H_2O$	97, 99, 101	34
112-116	$CO_3^-\cdot HOCl$, $CO_4^-(H_2O)_2$, $CO_4^-\cdot HCl$ $HCO_3^-\cdot HOCl$, $NO_3^-\cdot HOCl$		2
124-126	$HCO_3^-\cdot HNO_3$, $NO_3^-\cdot HNO_3$, $HCO_3^-\cdot HNO_2\cdot H_2O$	124, 125	7
142-146	$HCO_3^-\cdot HNO_3\cdot H_2O$, $NO_3^-\cdot HNO_3\cdot H_2O$, $ClO_3^-\cdot HNO_3$	143, 146	6
160-162	$HSO_4^-\cdot HNO_3$, $HCO_3^-\cdot HNO_3\cdot HCl$	160	10
177-182	$NO_3^-HNO_3\cdot HOCl$, $HSO_4^-\cdot HNO_3\cdot H_2O$, $ClO_3^-\cdot HNO_3\cdot HCl$	178	5
195-202	$HSO_4^-\cdot H_2SO_4$	195	20

TABLE 1 : (continued)

MASS	POSSIBLE IDENTIFICATION	MOST ABUNDANT MASS NUMBERS	FRACTIONAL ION COUNT RATE (%)
		GROUP II	
53-55	$OH^-(H_2O)_2$; Cl^-H_2O		< 0.5
71-80	$OH^-(H_2O)_3$; $Cl^-(H_2O)_2$, $Cl^-.HCl$, CO_4^-		< 0.5
223 ± 3	$HSO_4^-(HNO_3)_2$		< 1
241 ± 3	$HSO_4^-(HNO_3)_2.H_2O$		1
258 ± 3	$HSO_4^-.H_2SO_4.HNO_3$		< 0.5
276 ± 3	$HSO_4^-.H_2SO_4.HNO_3:H_2O$		< 1
293 ± 3	$HSO_4^-(H_2SO_4)_2$		1

TABLE 2 : Mass numbers, possible ion identifications and fractional
ion count rates of negative ions at 42.3 km.

MASS (AMU)	POSSIBLE IDENTIFICATION	FRACTIONAL ION COUNT RATE (%)
62 ± 1	NO_3^-	1
81-83	$NO_3^-.H_2O$; ClO_3^-	0.6
98-100	$NO_3^-.HCl$	2.3
114-116	$NO_3^-.HOCl$	0.6
125 ± 1	$NO_3^-.HNO_3$	39
143 ± 1	$NO_3^-.HNO_3.H_2O$	13
146 ± 1	$ClO_3^-.HNO_3$	2
160-165	$HSO_4^-.HNO_3$ (most abundant) $ClO_3^-.HNO_3.H_2O$ (minor)	16
178 ± 1	$HSO_4^-.HNO_3.H_2O$	6
195 ± 1	$HSO_4^-.H_2SO_4$	8
200-210	$ClO_3^-.HNO_3.HCl.H_2O$ $ClO_3^-(HNO_3)_2$	1.4
241 ± 2	$HSO_4^-(HNO_3)_2.H_2O$	3.8
258 ± 2	$HSO_4^-\ H_2SO_4.HNO_3$	0.4
276 ± 2	$HSO_4^-\ H_2SO_4\ HNO_3.H_2O$	2.6
293 ± 2	$HSO_4^-(H_2SO_4)_2$	3.1

$$OH^- + SO_2 + M \rightarrow HSO_3^- + M \tag{1}$$

$$HSO_3^- + H_2O + M \rightarrow HSO_3^-.H_2O + M \tag{2}$$

$$OH^-(H_2O)_2 + SO_2 \rightarrow HSO_3^-.H_2O + H_2O \tag{3}$$

Reactions (1) and (3) have been measured in the laboratory and were found to be fast (Fehsenfeld and Ferguson, 1974).

The presence of the mass peak at 83 amu can be explained by accepting the existence of ClO_3^-. This ion might be formed through a reaction of the form :

$$O_2^- + ClO + M \rightarrow ClO_3^- + M \tag{4}$$

although laboratory data are not available. It should be noted however that André et al. (1982) introduced this core ion ClO_3^- to explain recent high resolution negative ion mass spectra obtained in the D-region.

Most surprising however is the high signal at mass 99. According to figures 1A and 2B, it represents about 17% of the total ion signal at 45.2 km. A likely candidate for mass 99 would be Cl^-SO_2, as suggested by the existence of mass 101 (caused by the chlorine isotope at 37 amu). For the formation of this ion one could imagine the reactions :

$$Cl^- + H_2O + M \rightleftharpoons Cl^-.H_2O + M \tag{5}$$

$$Cl^-.H_2O + SO_2 \rightleftharpoons Cl^-SO_2 + H_2O \tag{6}$$
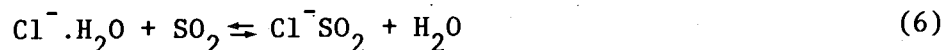
with a forward rate coefficient for reaction (6) of 1.6×10^{-9} cm^3 s^{-1} at 296 K (Fehsenfeld and Ferguson, 1974). The SO_2 number density at 45 km can be calculated from the thermochemical data about the equilibrium between $Cl^- H_2O$ and $Cl^- SO_2$, as reported by Keesee et al. (1980), and the observed fractional abundance of these ions. Assuming a water mixing ratio of 3 ppm and an ambient temperature of 270 K (measured in situ) leads us to a SO_2 mixing ratio of about 3 ppb. This value is about 100 times larger than the one deduced from model calculations by Turco et al. (1979, 1981b). In fact a study of the hydration equilibrium of Cl^- (equation 5) using the thermochemical data of Keesee et al. (1980) and spectrum 1A, as well as the proton hydrate distribution, measured in this flight at the same altitude, suggests an increased H_2O mixing ratio and therefore an even higher SO_2 mixing ratio. The high SO_2 mixing rato as deduced in this work, can partly be explained by an underestimation of H_2SO_4 photodissociation in the model calculations (Turco et al, 1979, 1981b). The fact that mass 99 ($Cl^- SO_2$) virtually disappears in spectrum 1B, recorded at 42.3 km during descent after sunset, seems to plead for this interpretation. In this context however we should not exclude possible contamination effects by degassing of the gondola at float altitude. Laboratory studies at our Institute have shown that the main contaminant which could disturb the negative ion chemistry is chlorine, released by solar heating of the black painted parts of the optical equipment. This chlorine excess can explain some of the observed ions of table 1 and triggers the formation of $Cl^- SO_2$ through reactions (5) and (6). During descent (spectrum 1B) the effects of contamination are less important, which results in a much lower chlorine concentrations and a smaller $Cl^- SO_2$ formation.

At present however it remains questionnable to explain mass 99 by $Cl^- SO_2$.

The mass peaks as reported in table 2 look more familiar and the major peaks all belong to the NO_3^- or HSO_4^- cluster ion families.

Since spectrum 1B was recorded during descent, minimizing possible contamination, it is believed to be representative for the ambient ion composition.

It is also remarkable that the $NO_3^-(HNO_3)_2$ ion, which produces a very pronounced mass peak at altitudes below 35 km (Arijs et al., 1980, 1982) is not observed very clearly in the altitude range covered in this flight. If it is existing it is buried in the signal between mass 178 and 195 amu. Therefore only upper limits for the HNO_3 concentration can be derived here from the ion spectra and the thermochemical equilibrium data (Davidson et al., 1977) for the reaction

$$NO_3^- \cdot HNO_3 + HNO_3 + M \rightleftarrows NO_3^-(HNO_3)_2 + M \qquad (7)$$
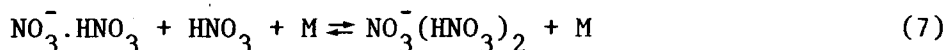
For 42.3 km (spectrum 1B) e.g. an upper limit of 0.3 ppb for the HNO_3 mixing ratio is derived, whereas for 45.2 km (spectrum 1A) a value of 20 ppb is found. In view of the large differences of these values, we believe that these derivations are only very approximate, due to the difficulties to separate mass 188 from the adjacent mass peaks.

As was pointed out before (Arnold et al., 1982) negative ion mass spectra can also be used to derive a sulfuric acid number density through the continuity equation :

$$k[n_N^-]([H_2SO_4] + [HSO_y]) = \alpha[n^+][n_S^-] \qquad (8)$$

where $[n^+]$ is the total positive ion number density, α the ion-ion recombination coefficient and k the reaction rate coefficient for switching reactions between NO_3^- cluster ions and $(H_2SO_4 + HSO_y)$. The total number density of all NO_3^- clusters and of all HSO_4^- clusters are represented by $[n_N^-]$ and $[n_S^-]$ respectively. The values of k and α are assumed to be the same for all ion-molecule and all ion-ion reactions considered. Sulfur compounds other than H_2SO_4 reacting with HNO_3^- cluster ions to form HSO_4^- cluster ions are represented by HSO_y. We believe however that above 35 km sulfuric acid represents the main part of $(H_2SO_4 + HSO_y)$ as is suggested by recent measurements and calculations of Arnold and Bührke (1983).

Since for spectrum 1B the major mass peaks belong to the NO_3^- and HSO_4^- cluster families, application of formula (8) will result in a valuable estimation of the H_2SO_4 concentration. The main NO_3^- cluster ion which appears in this spectrum is $NO_3^-.HNO_3$ (mass 125 amu) and therefore we have used a value of $k = 2 \times 10^{-9}$ cm^3 s^{-1} as reported by Viggiano et al. (1982). The total positive ion number density $[n^+]$ was calculated with the formula of Heaps (1978) and for the ion-ion re-combination coefficient α a value of 7×10^{-8} cm^3 s^{-1} was adopted. This is in good agreement with the two-body recombination coefficient as measured by Smith et al. (1981) and with a parametrization used before (Arijs et al., 1983a). Using the ion abundances of spectrum 1B (table 2) and formula (8) now results in a H_2SO_4 number density of 6×10^4 cm^{-3} at 42.3 km altitude. Within the uncertainties on the parameters $[n^+]$, α and k the error on this number is estimated to be a factor of 3.

The same procedure can now be applied to spectrum 1A, assuming that all ions with mass larger than or equal to 160 amu are HSO_4^- clusters. In a first calculation it was accepted that all ions below 160 amu eventually lead to HSO_4^- cluster ions and therefore can be considered as source ions n_N^-. This leads to a lower limit for $[H_2SO_4]$

of 4×10^4 cm^{-3}. Identifying mass 97 as HSO$_4^-$ gives an upper limit of 8×10^4 cm^{-3}. Again these numbers can be in error by a factor of 3.

The error on the derived H$_2$SO$_4$ concentrations, induced by neglecting ions beyond the mass range of the instrument (330 amu), is estimated to be smaller than 10% from an inspection of the spectra obtained in the total ion mode.

The results of the previous deviations are plotted in figure 3, together with a compilation of data previously obtained at lower altitudes. When comparing the set of data with recent model calculations of [H$_2$SO$_4$] by Turco et al. (1981a) we see that the limits of the present data fall between a H$_2$SO$_4$ vapour profile calculated assuming a metal flux (from meteoric debris) of 5×10^6 cm^{-2} s^{-1} and one assuming zero H$_2$SO$_4$ vapour pressure and no metal flux (curve C and D).

In fact the most recent data suggest a profile similar to curve E, arbitrarily drawn by us. To explain the present data, additional loss processes should be introduced in the model calculations. These might be an even larger metal flux or a larger photodissociation rate for H$_2$SO$_4$. The latter could also explain the high SO$_2$ concentrations derived at 45 km, since one of the major products of sulfuric acid photodissociation is believed to be SO$_2$ (Turco et al., 1979).

Although the previous remarks are merely speculative, the present findings represent the first estimation of sulfuric acid concentrations above 42 km and clearly show a decrease of [H$_2$SO$_4$] at higher altitudes. At present however our knowledge on the chemistry of sulfur compounds above 40 km has not made enough progress to explain the results. Future research in this area is therefore urgently needed.
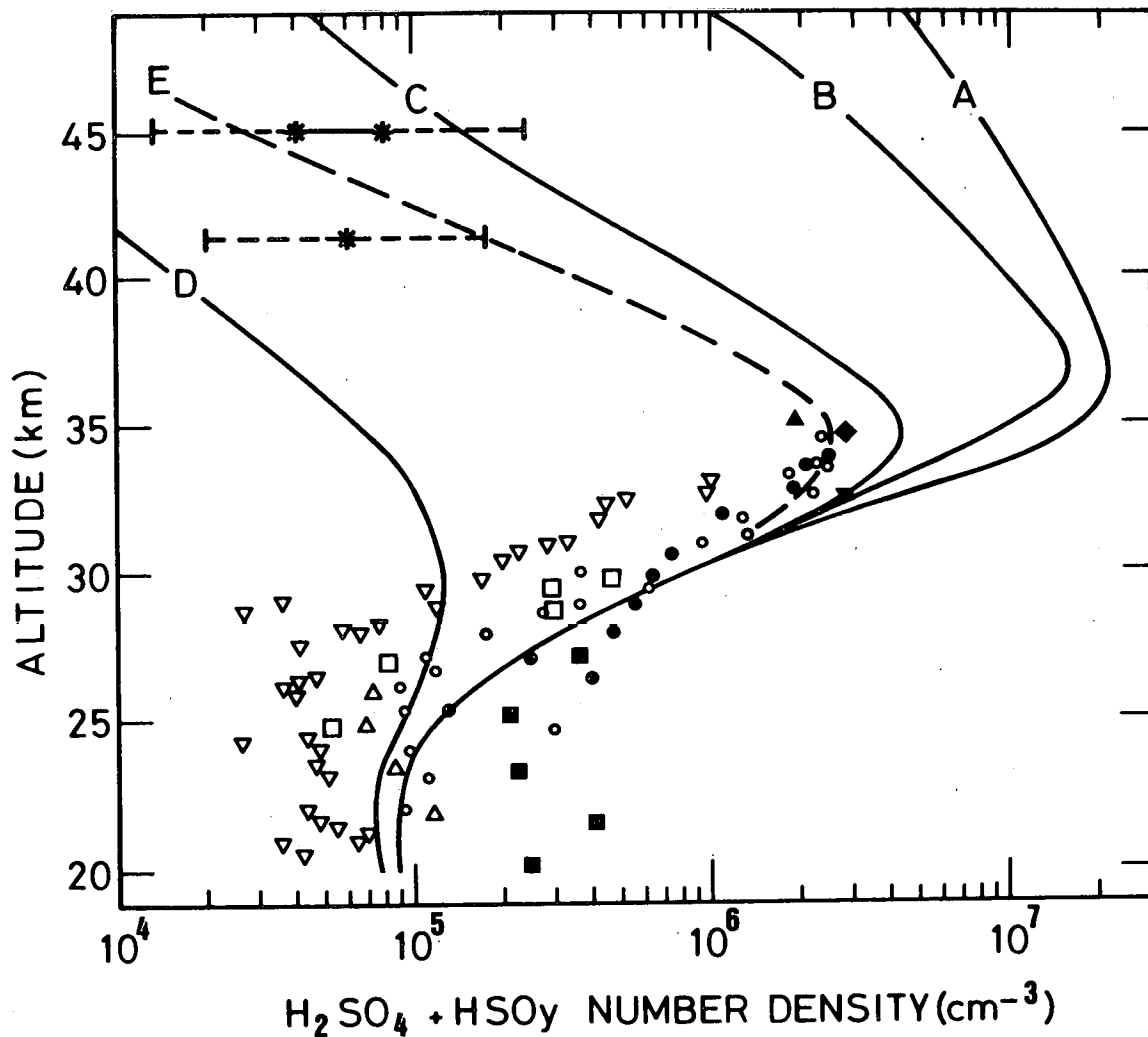
Figure 3: [H_2SO_4 + HSO_y] obtained by different in-situ experiments compared to model calculations of Turco (1981). The open symbols refer to experiments of the Heidelberg group (MPIH) (Viggiano and Arnold, 1983; Arnold and Bührke, 1983), the full symbols represent data of our group (BISA) (Arijs et al. 1983) and the asteriks are the results of this work. Dotted error bars are due to factor of 3 uncertainty resulting from errors on α, k and [n^+]. Full error bar is due to mass 97 uncertainty at 45.2 km. Curves A, B and C are calculations by Turco et al (1981) assuming metal fluxes of zero, 10^6 and 5×10^6 cm^{-2} s^{-1} respectively. Curve D assumes zero H_2SO_4 vapour pressure above aerosols. Curve E is arbitrarily drawn by us.

CONCLUSIVE REMARKS

The reported measurements, which represent the first mass analysis of negative ions in the altitude region 42-45 km, reveal the existence of HNO_3^- and HSO_4^- cluster ions in the upper stratosphere. The ion abundances have been used to estimate the H_2SO_4 number density at those altitudes. Such an estimation clearly shows a decrease of sulfuric acid concentrations with increasing altitude.

Chlorine compounds also seem to play an important role in the upper stratospheric negative ion chemistry. If appropriate laboratory data would be available the spectra could be used to derive the total chlorine concentration in the upper atmosphere. In view of possible contamination effects and the lack of kinetic and thermodynamic laboratory studies about the relevant ions, it seems premature however to perform such calculations. More in-situ and laboratory measurements are needed to elucidate this problem.

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