

## NEGATIVE ION COMPOSITION AND SULFURIC ACID VAPOUR IN THE UPPER STRATOSPHERE

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**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  $\text{NO}_3^-$  and  $\text{HSO}_4^-$  clusters, ions with different cores, which can be identified as  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{ClO}_3^-$  were observed. The spectra have been used to estimate the sulfuric acid number density at 45.2 and 42.3 km altitude.

### 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 20–35 km belong to the  $\text{NO}_3^-$  ( $\text{HNO}_3$ )<sub>n</sub> and  $\text{HSO}_4^-$  ( $\text{HNO}_3$ )<sub>i</sub> ( $\text{H}_2\text{SO}_4$ )<sub>m</sub> families.

Subsequent laboratory measurements (Viggiano *et al.*, 1980, 1982) enabled the use of *in situ* data for the derivation of  $\text{H}_2\text{SO}_4$  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<sup>3</sup> 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 U.T. and reached a ceiling altitude oscillating between 45 and 46 km. The flight lasted about 7 h and after sunset the balloon descended to 41.2 km at a rate of 1.3 m s<sup>-1</sup>.

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 measur-

ing 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 Fig. 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 Fig. 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 Fig. 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 unambiguously because counting statistics was incomplete within available integration time.

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

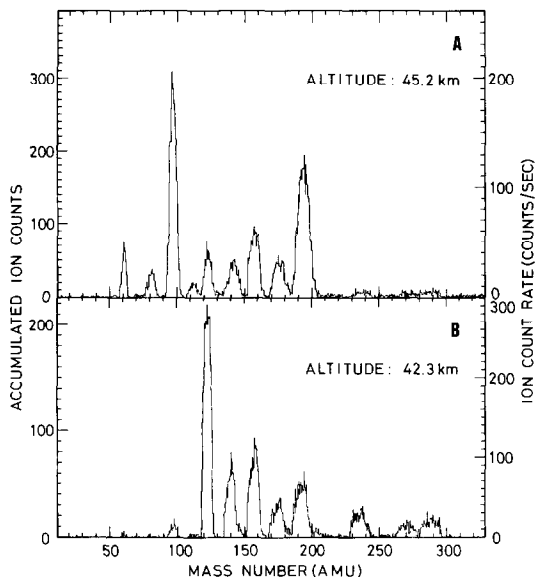


FIG. 1. NEGATIVE ION SPECTRA OBTAINED IN THE MODERATE RESOLUTION MODE ( $m/\Delta m \cong 17$ ).

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  $13^\circ$ . Spectrum B is the sum of 3 scans recorded during descent between 42.5 and 42.1 km. Solar depression angle was  $10^\circ$ . Both spectra are presented unsmoothed.

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 Fig. 1B are considerably narrower than those of 1A, although this

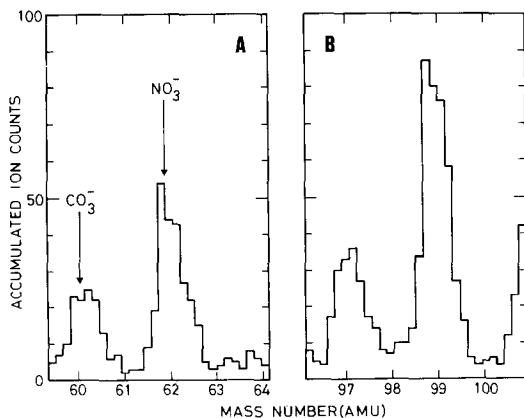


FIG. 2. SAMPLE NEGATIVE ION SPECTRA RECORDED IN SMALL MASS DOMAINS DURING FLOAT.

Spectrum A covers the mass domain 59–64 amu and was obtained after summation of 18 scans of 30 s each. Each mass (1 amu) is subdivided into six channels (dwell time per channel 1 s). Spectrum B is the sum of 19 similar scans in the mass domain 96–101 amu. The spectra were not smoothed.

is scarcely visible on the reduced spectra of Fig. 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; McCrumb and Arnold, 1981). Even some of the low mass minor ions were reported previously (McCrumb 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:  $\text{OH}^-$ ,  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{O}_4^-$ ,  $\text{CO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{HSO}_4^-$ ,  $\text{HSO}_3^-$  or  $\text{ClO}_3^-$ . Apart from the last two, all of these have been predicted before (Ferguson *et al.*, 1979) and all of the ligands of Table 1, except  $\text{SO}_2$ , were introduced earlier (McCrumb and Arnold, 1981; Arijs *et al.*, 1982).

The most unexpected core ions found are  $\text{HSO}_3^-$  and  $\text{ClO}_3^-$ . It is proposed here that  $\text{HSO}_3^-$  core ions would be formed by:



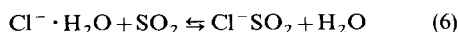
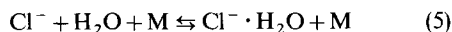
Reactions (1) and (3) have been measured in the laboratory and were found to be fast (Fehsenfeld and Ferguson, 1974).

The presence of the mass peak at 83 amu can be explained by accepting the existence of  $\text{ClO}_3^-$ . This ion might be formed through a reaction of the form:



although laboratory data are not available. It should be noted however that André *et al.* (1982) introduced this core ion  $\text{ClO}_3^-$  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 Figs. 1A and 2B, it represents about 17% of the total ion signal at 45.2 km. A likely candidate for mass 99 would be  $\text{Cl}^- \cdot \text{SO}_2$ , 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:



with a forward rate coefficient for reaction (6) of  $1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 296 K (Fehsenfeld and Ferguson, 1974). The  $\text{SO}_2$  number density at 45 km can be calculated from the thermochemical data about the

TABLE 1. MASS NUMBERS, POSSIBLE IDENTIFICATIONS AND FRACTIONAL ION COUNT RATES OF NEGATIVE IONS AT 45.2 km. The ions are subdivided into two groups depending upon count rates. The mass numbers of column 1 (Mass) are derived from rising and trailing peak edges of Fig. 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 Fig. 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 <sub>3</sub> <sup>-</sup> (33%) NO <sub>3</sub> <sup>-</sup> (66%)		8
81–87	HSO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> , NO <sub>2</sub> <sup>-</sup> ·HCl, O <sub>4</sub> <sup>-</sup> ·H <sub>2</sub> O	83	4
	ClO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> ·HOCl		
96–103	CO <sub>3</sub> <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> , CO <sub>3</sub> <sup>-</sup> ·HCl, HCO <sub>3</sub> <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> , HCO <sub>3</sub> <sup>-</sup> ·HCl		
	HSO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> ·HCl, NO <sub>3</sub> <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> , HSO <sub>3</sub> <sup>-</sup> ·H <sub>2</sub> O	97, 99, 101	34
	Cl <sup>-</sup> SO <sub>2</sub> , NO <sub>2</sub> <sup>-</sup> (H <sub>2</sub> O) <sub>3</sub> , NO <sub>2</sub> <sup>-</sup> ·HCl·H <sub>2</sub> O, ClO <sub>3</sub> <sup>-</sup> ·H <sub>2</sub> O		
112–116	CO <sub>3</sub> <sup>-</sup> ·HOCl, CO <sub>4</sub> <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> , CO <sub>4</sub> <sup>-</sup> ·HCl		2
	HCO <sub>3</sub> <sup>-</sup> ·HOCl, NO <sub>3</sub> <sup>-</sup> ·HOCl		
124–126	HCO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> , NO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> , HCO <sub>3</sub> <sup>-</sup> ·HNO <sub>2</sub> ·H <sub>2</sub> O	124, 127	7
142–146	HCO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> ·H <sub>2</sub> O, NO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> ·H <sub>2</sub> O,	143, 146	6
	ClO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub>		
160–162	HSO <sub>4</sub> <sup>-</sup> ·HNO <sub>3</sub> , HCO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> ·HCl	160	10
177–182	NO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> ·HOCl, HSO <sub>4</sub> <sup>-</sup> ·HNO <sub>3</sub> ·H <sub>2</sub> O,	178	5
	ClO <sub>3</sub> <sup>-</sup> ·HNO <sub>3</sub> ·HCl		
195–202	HSO <sub>4</sub> <sup>-</sup> ·H <sub>2</sub> SO <sub>4</sub>	195	20
Group II			
53–55	OH <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> ; Cl <sup>-</sup> ·H <sub>2</sub> O		<0.5
71–80	OH <sup>-</sup> (H <sub>2</sub> O) <sub>3</sub> ; Cl <sup>-</sup> (H <sub>2</sub> O) <sub>2</sub> , Cl <sup>-</sup> ·HCl, CO <sub>4</sub> <sup>-</sup>		<0.5
223±3	HSO <sub>4</sub> <sup>-</sup> (HNO <sub>3</sub> ) <sub>2</sub>		<1
241±3	HSO <sub>4</sub> <sup>-</sup> (HNO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O		1
258±3	HSO <sub>4</sub> <sup>-</sup> ·H <sub>2</sub> SO <sub>4</sub> ·HNO <sub>3</sub>		<0.5
276±3	HSO <sub>4</sub> <sup>-</sup> ·H <sub>2</sub> SO <sub>4</sub> ·HNO <sub>3</sub> ·H <sub>2</sub> O		<1
293±3	HSO <sub>4</sub> <sup>-</sup> (H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub>		1

equilibrium between Cl<sup>-</sup>·H<sub>2</sub>O and Cl<sup>-</sup>SO<sub>2</sub>, as reported by Keese *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<sub>2</sub> 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<sup>-</sup> (equation (5)) using the thermochemical data of Keese *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<sub>2</sub>O mixing ratio and therefore an even higher SO<sub>2</sub> mixing ratio. The high SO<sub>2</sub> mixing ratio as deduced in this work, can partly be explained by an underestimation of H<sub>2</sub>SO<sub>4</sub> photodissociation in the model calculations (Turco *et al.*, 1979, 1981b). The fact that mass 99 (Cl<sup>-</sup>SO<sub>2</sub>) 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<sup>-</sup>SO<sub>2</sub> through reactions (5) and (6). During descent (spectrum 1B) the effects of contamination are less important, which results in a much lower chlorine concentration and a smaller Cl<sup>-</sup>SO<sub>2</sub> formation.

At present however it remains questionable to explain mass 99 by Cl<sup>-</sup>SO<sub>2</sub>.

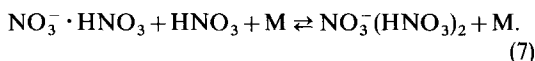
The mass peaks as reported in Table 2 look more familiar and the major peaks all belong to the NO<sub>3</sub><sup>-</sup> or HSO<sub>4</sub><sup>-</sup> cluster ion families. Since spectrum 1B was recorded during descent, minimizing possible contamination, it is believed to be representative for the ambient ion composition.

It is also remarkable that the NO<sub>3</sub><sup>-</sup>(HNO<sub>3</sub>)<sub>2</sub> 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<sub>3</sub> concentration can be derived here from the ion spectra and the thermochemical

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 <sub>3</sub> <sup>-</sup>	1
81–83	NO <sub>3</sub> <sup>-</sup> · H <sub>2</sub> O; ClO <sub>3</sub> <sup>-</sup>	0.6
98–100	NO <sub>3</sub> <sup>-</sup> · HCl	2.3
114–116	NO <sub>3</sub> <sup>-</sup> · HOCl	0.6
125 ± 1	NO <sub>3</sub> <sup>-</sup> · HNO <sub>3</sub>	39
143 ± 1	NO <sub>3</sub> <sup>-</sup> · HNO <sub>3</sub> · H <sub>2</sub> O	13
146 ± 1	ClO <sub>3</sub> <sup>-</sup> · HNO <sub>3</sub>	2
160–165	HSO <sub>4</sub> <sup>-</sup> · HNO <sub>3</sub> (most abundant)	16
	ClO <sub>3</sub> <sup>-</sup> · HNO <sub>3</sub> · H <sub>2</sub> O (minor)	
178 ± 1	HSO <sub>4</sub> <sup>-</sup> · HNO <sub>3</sub> · H <sub>2</sub> O	6
195 ± 1	HSO <sub>4</sub> <sup>-</sup> · H <sub>2</sub> SO <sub>4</sub>	8
200–210	ClO <sub>3</sub> <sup>-</sup> · HNO <sub>3</sub> · HCl · H <sub>2</sub> O	1.4
	ClO <sub>3</sub> <sup>-</sup> (HNO <sub>3</sub> ) <sub>2</sub>	
241 ± 2	HSO <sub>4</sub> <sup>-</sup> (HNO <sub>3</sub> ) <sub>2</sub> · H <sub>2</sub> O	3.8
258 ± 2	HSO <sub>4</sub> <sup>-</sup> · H <sub>2</sub> SO <sub>4</sub> · HNO <sub>3</sub>	0.4
276 ± 2	HSO <sub>4</sub> <sup>-</sup> · H <sub>2</sub> SO <sub>4</sub> · HNO <sub>3</sub> · H <sub>2</sub> O	2.6
293 ± 2	HSO <sub>4</sub> <sup>-</sup> (H <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub>	3.1

equilibrium data (Davidson *et al.*, 1977) for the reaction



For 42.3 km (spectrum 1B) e.g. an upper limit of 0.3 ppb for the HNO<sub>3</sub> 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:

$$k[n_{\text{N}^-}]([\text{H}_2\text{SO}_4] + [\text{HSO}_y^-]) = \alpha[n^+][n_{\text{S}^-}] \quad (8)$$

where  $[n^+]$  is the total positive ion number density,  $\alpha$  the ion-ion recombination coefficient and  $k$  the reaction rate coefficient for switching reactions between NO<sub>3</sub><sup>-</sup> cluster ions and (H<sub>2</sub>SO<sub>4</sub> + HSO<sub>y</sub><sup>-</sup>). The total number density of all NO<sub>3</sub><sup>-</sup> clusters and of all HSO<sub>4</sub><sup>-</sup> clusters are represented by  $[n_{\text{N}^-}]$  and  $[n_{\text{S}^-}]$  respectively. The values of  $k$  and  $\alpha$  are assumed to be the same for all ion-molecule and all ion-ion reactions considered. Sulfur compounds other than H<sub>2</sub>SO<sub>4</sub> reacting with NO<sub>3</sub><sup>-</sup> cluster ions to form HSO<sub>4</sub><sup>-</sup> cluster ions are represented by HSO<sub>y</sub><sup>-</sup>. We believe however that above 35 km sulfuric acid represents the main part of (H<sub>2</sub>SO<sub>4</sub> + HSO<sub>y</sub><sup>-</sup>) 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<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> cluster families, application of formula (8) will result in a valuable estimation of the H<sub>2</sub>SO<sub>4</sub> concentration. The main NO<sub>3</sub><sup>-</sup> cluster ion which appears in this spectrum is NO<sub>3</sub><sup>-</sup> · HNO<sub>3</sub> (mass 125 amu) and therefore we have used a value of  $k = 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  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 recombination coefficient  $\alpha$  a value of  $7 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  was adopted. This is in good agreement with the two-body recombination coefficient as measured by Smith *et al.* (1981) and with a parameterization used before (Arijs *et al.*, 1983a). Using the ion abundances of spectrum 1B (Table 2) and formula (8) now results in a H<sub>2</sub>SO<sub>4</sub> number density of  $6 \times 10^4 \text{ cm}^{-3}$  at 42.3 km altitude. Within the uncertainties on the parameters  $[n^+]$ ,  $\alpha$  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<sub>4</sub><sup>-</sup> clusters. In a first calculation it was accepted that all ions below 160 amu eventually lead to HSO<sub>4</sub><sup>-</sup> cluster ions and therefore can be considered as source ions  $n_{\text{N}^-}$ . This leads to a lower limit for  $[\text{H}_2\text{SO}_4]$  of  $4 \times 10^4 \text{ cm}^{-3}$ . Identifying mass 97 as HSO<sub>4</sub><sup>-</sup> gives an upper limit of  $8 \times 10^4 \text{ cm}^{-3}$ . Again these numbers can be in error by a factor of 3.

The error on the derived H<sub>2</sub>SO<sub>4</sub> 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 derivations are plotted in Fig. 3, together with a compilation of data previously obtained at lower altitudes. When comparing the set of data with recent model calculations of  $[\text{H}_2\text{SO}_4]$  by Turco *et al.* (1981a) we see that the limits of the present data fall between a H<sub>2</sub>SO<sub>4</sub> vapour profile calculated assuming a metal flux (from meteoric debris) of  $5 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$  and one assuming zero H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub>. The latter could also explain the high SO<sub>2</sub> concentrations derived at 45 km, since one of the major products of sulfuric acid photodissociation is believed to be SO<sub>2</sub> (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  $[\text{H}_2\text{SO}_4]$  at higher altitudes. At

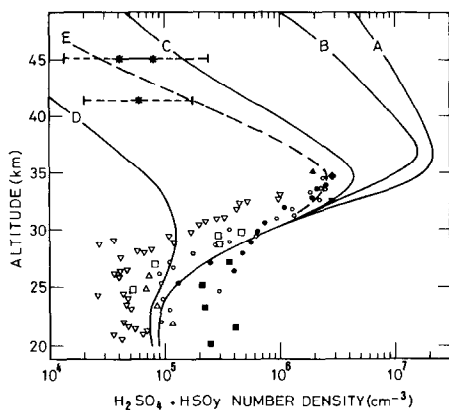


FIG. 3. [H<sub>2</sub>SO<sub>4</sub> + HSO<sub>3</sub>] OBTAINED BY DIFFERENT *in situ* EXPERIMENTS COMPARED TO MODEL CALCULATIONS OF TURCO (1981).

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 asterisks are the results of this work. Dotted error bars are due to factor of 3 uncertainty resulting from errors on  $\alpha$ ,  $k$  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  $5 \times 10^6$  cm<sup>-2</sup>s<sup>-1</sup> respectively. Curve D assumes zero H<sub>2</sub>SO<sub>4</sub> vapour pressure above aerosols. Curve E is arbitrarily drawn by us.

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.

#### 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 NO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> cluster ions in the upper stratosphere. The ion abundances have been used to estimate the H<sub>2</sub>SO<sub>4</sub> 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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