

Stratospheric negative ion composition measurements, ion abundances and related trace gas detection

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

Belgian Institute for Space Aeronomy, Ringlaan 3, B-1180 Brussels, Belgium

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Abstract—Negative ion spectra obtained during four flights with a balloon-borne quadrupole mass spectrometer are reported and critically investigated. Ion abundances for NO_3^- and HSO_4^- core ions are reported and concentrations of HNO_3 and H_2SO_4 at altitudes between 32 and 35 km are deduced. The detection of minor mass peaks in negative ion spectra obtained at an altitude of 32 km is discussed. Major mass peaks observed at lower altitudes (from 20 to 28 km) are mainly NO_3^- due to core ions.

1. INTRODUCTION

The first identification of natural stratospheric negative ions obtained by *in situ* mass spectrometry at 36 km altitude was reported by ARNOLD and HENSCHEN (1978). Although due to the low resolution used, some doubt remained about the observed mass numbers, the ions were tentatively identified as ion clusters belonging to the families $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_l(\text{HNO}_3)_m$ and $\text{NO}_3^-(\text{HNO}_3)_n$. Whereas the NO_3^- core ions had been expected on the basis of our knowledge of trace gases in the stratosphere (ACKERMAN, 1979) and of laboratory measurements (FEHSENFELD *et al.*, 1975), the presence of HSO_4^- core ions came as a surprise. It was suggested (ARNOLD and HENSCHEN, 1978) that those ions were originating from ion molecule reactions of sulphuric acid vapour with NO_3^- core ions. The plausibility of such reactions was shown by laboratory measurements (VIGGIANO *et al.*, 1980). In 1980 negative ion composition measurements with higher resolution were performed by ARIJS *et al.* (1981a). In this way an unambiguous determination of the mass numbers was possible and the H_2SO_4 hypothesis was confirmed. Furthermore some minor ions were detected and a more complete reaction scheme for the negative ion formation in the stratosphere was proposed. In the meantime a critical investigation of the ion abundances (ARNOLD *et al.*, 1981a) reinforced their identification as nitrate and sulphate cluster ions. Meanwhile negative ion composition measurements have been extended down to 24 km (VIGGIANO and ARNOLD, 1981a) and the results of these experiments have been used to obtain sulphuric acid vapour concentration profiles (VIGGIANO and ARNOLD, 1981b).

Recently the detection of minor negative ions at 34 km altitude was reported by MCCRUMB and ARNOLD (1981).

In the present paper the abundances of the major

negative ions detected between 32 and 35 km altitudes (typical float altitudes of 100,000 m³ stratospheric balloons) during different flights are compared and analysed. These spectra are also investigated for minor ion peaks and the implications of the data for trace gas detection are critically investigated. Furthermore recent data obtained between 28 and 20 km altitude will be discussed.

2. EXPERIMENTAL

The balloon-borne payload, which consists of a high speed liquid helium cooled cryopump (INGELS *et al.*, 1978) and a quadrupole mass filter, with the associated electronic modules has been described before (ARIJS *et al.*, 1981b). The instrument is equipped with a microprocessor based controller enabling a flexible choice by remote control of many different measurement programs (defined by resolution, mass domain, a.s.o.). The quadrupole power supply is designed in such a way that DC and RF voltages can be controlled independently, allowing a great variety of possible resolutions and thereby extending the mass range of the instrument (ARIJS *et al.*, 1981a). Because the configuration of the instrument is basically the same as for positive ion composition measurements, we will restrict ourselves to instrument descriptions, essential for negative ion measurements. The voltages applied to the ion lens are simply inverted in polarity and the draw-in potential is chosen for maximum signal, either by remote control or by the microprocessor. The sampled negative ions acquire an energy of 7 eV by applying a positive quadrupole bias fixed with respect to the draw-in plate. To avoid high voltage breakdown at the ion detector output (Spiraltron secondary electron multiplier SEM 4219) the input cone is kept at +1.5 kV. Although the acceleration

Table 1. Technical characteristics of balloon flights during which negative ion spectra were obtained at float altitude

Date of flight	Launching Site	Float altitude		Ambient temperature
		ambient pressure in mbar	km ⁽¹⁾	
16 June 1980	Gap 44°27'N	6.8	34.7	239 K (2)
18 September 1980	Aire 43°42'N	5.7	35.0	232 K (2)
14 September 1981	Aire 43°42'N	8.3 (4)	32.5	234 K (3)

- (1) From *U.S. Standard Atmosphere* (pressure conversion to altitude in kilometres).
 (2) From proton hydrate distribution.
 (3) Direct measurement.
 (4) MKS-Baratron measurement.

voltage of the negative ions is therefore considerably smaller than for positive ions, where -3 kV is used, the detection efficiency is still adequate. This is due to the fact that the primary electrons originate from the impacting negative ion itself and not from the dynode surface (GOODINGS *et al.*, 1972).

The supply voltage of the multiplier is maintained at 3 kV to guarantee a pulse height distribution, suitable for pulse counting techniques. The background or spontaneous pulse count rate for negative ion detection is much higher than for positive ions. This is probably due to electrons escaping from a nearby mounted Penning gauge. Typical values as well as the method to determine this background in flight are discussed in Section 4.2.

3. MEASUREMENTS

The data shown and discussed hereafter have been obtained during four stratospheric balloon flights. During three of them all measurements were performed at the float altitude of the balloon. The flight characteristics are summarized in Table 1. The mentioned float altitudes were obtained from the *U.S. Standard Atmosphere* of 1966 by conversion of the measured ambient pressures. In the last flight (September 1981) two pressure sensors were used; one was a high precision Baratron gauge, kept at constant temperature. The deviation between the two sensors was less than 3%, which strengthens the faith in the pressure data of other flights. Temperatures were obtained either through comparison of the measured and corrected (for collisional break-up) proton hydrate abundances with the theoretical distribution (ARIJS *et al.*, 1981b) or from a direct *in situ* measurement. For this purpose a tiny bead thermistor, with a very small thermal mass was mounted at a distance of 2 m from the payload.

During the June 1980 and September 1981 flights the measurements of negative ions were started after sunrise, while in September 1980 all measurements were performed during night-time. However no pronounced difference in the identity of the major negative ions was observed. In the three flights described in Table 1 a sampling hole of 0.2 mm diameter was used. The fourth flight (not mentioned in Table 1) was performed on 12 June 1981 from the CNES launching base at Gap-Tallard (southern France). In this flight a 100,000 m³ valve controllable balloon was used, which allowed a slow descending of the balloon from float altitude down to 20 km at a rate of 1 m s⁻¹. In this way contamination by balloon and gondola was minimized. Positive ion spectra were obtained between the float altitude of 33 and 20 km. These results will be reported elsewhere.

Negative ion composition measurements were performed between 28 and 20 km altitude. In view of the higher ambient pressures encountered in this flight a sampling hole of 0.1 mm diameter was used this time. The results of these measurements will be discussed and analysed hereafter.

4. RESULTS AND DISCUSSION

4.1. Ion abundances of observed major negative ions and related trace gas detection

The observed major mass numbers, their identification and relative abundances for the three flights of Table 1 are summarized in Table 2. For the sake of comparison some data of the Max Planck Institute of Heidelberg (termed MPI group hereafter, ARNOLD *et al.*, 1981a) are included in this table.

A typical spectrum in the high resolution mode as obtained in flight in September 1981 is shown in Fig. 1(a). To facilitate the interpretation of these spectra a three point smoothing technique (HILDEBRAND, 1956)

Table 2. Mass numbers, identifications and relative abundances (in %) of major negative ions observed at float altitude

Mass	Identification	Abundances in different flights (%)			
		June 80	Sept. 80	Sept. 81	MPI (1)
125	$\text{NO}_3^-\cdot\text{HNO}_3$	5	2	2	2.6
160	$\text{HSO}_4^-\cdot\text{HNO}_3$	9	16	10	5.3
188	$\text{NO}_3^-(\text{HNO}_3)_2$	8	15	14	65.6
195	$\text{HSO}_4^-\cdot\text{H}_2\text{SO}_4$	7	14	14	6.6
206	$\text{HSO}_4^-(\text{HNO}_3)_2\cdot\text{H}_2\text{O}$	-	-	3	-
223	$\text{HSO}_4^-(\text{HNO}_3)_2$	4	5	7	14.2
275	$\text{HSO}_4^-\cdot\text{H}_2\text{SO}_4\cdot\text{HNO}_3\cdot\text{H}_2\text{O}$	-	-	3	-
293	$\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2$	19	14	16	2.6
391	$\text{HSO}_4^-(\text{H}_2\text{SO}_4)_3$	48	34	31	-

(1) For comparison a set of data of the Max Planck Institute group (ARNOLD *et al.*, 1981) is included in the table. Missing percentage in this column is represented by mass 260 ± 3 with an abundance of 3.1%.

has been applied, resulting in the transformation of the spectrum of Fig. 1(a) into that of Fig. 1(b). As will be seen later on, minor mass peaks can be recognized easier in the smoothed spectra.

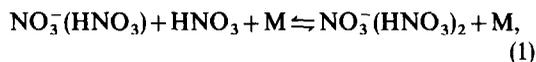
As was described in an earlier paper (ARIJS *et al.*, 1981a) two resolution modes have been used for negative ion composition measurements. Both modes have been employed to derive ion abundances, except for the June 1980 data, where only coarse resolution spectra ($U/V = 0.135$) had been obtained. Therefore these data are susceptible to somewhat larger errors than the other ones. In the coarse resolution mode the ion identification is less precise since peak identification is based on the recognition of edges of mass peaks extending over several a.m.u. However identifications from high resolution spectra are of great help here. Another disadvantage of the low resolution mode is that it is difficult to identify small mass peaks and hence to determine their abundance. Neglecting such minor mass peaks may introduce serious errors in the fractional abundance of other peaks, especially for ions with low abundances such as mass 125 in the September 1980 data. However the ratios of fractional abundances of different peaks are unaffected by neglecting them. A distinct advantage of this mode is that the transmission of the mass filter is practically independent of the ion mass.

It should also be noticed that an additional source of error in the determination of the ion abundances is the natural signal fluctuation. This is clearly illustrated in Fig. 2, representing the first of 19 mass scans, which gave rise to Fig. 1(a). As can be seen an erroneous value for the abundance of mass 195 might be deduced from it, due to incomplete statistics and short-term effects. It is therefore of primary importance that reports on ion

composition data and abundances should be as complete as possible. Integration times as well as total numbers of accumulated counts in each mass peak should be mentioned. In spite of all these possible error sources it is believed that the ion abundances reported here are exact to within 30%.

Laboratory and *in situ* measurements (ARNOLD *et al.*, 1981a), (VIGGIANO and ARNOLD, 1981a) have shown that cluster break-up effects due to sampling are much less pronounced for ambient pressures of a few torr or altitudes above 32 km. Since the data of Table 2 relate to altitudes above 32 km no correction for collisional dissociation has been applied to those.

We will now discuss the $\text{NO}_3^-(\text{HNO}_3)_n$ ions. As can be seen from Table 2 only two major ions belonging to this family were observed, namely mass 125 and 188. Since the time to establish the equilibrium for the reaction:



is much shorter than the lifetime of the ions vs recombination (ARNOLD *et al.*, 1981a) and since the equilibrium constants of this reaction have been measured in the laboratory (DAVIDSON *et al.*, 1977) the ratio of the abundances of mass 125 and 188 can be used to derive a nitric acid vapour concentration in the stratosphere, as was shown by ARNOLD *et al.* (1980). From the measured $\Delta H^\circ = 18.3 \pm 1$ kcal mol⁻¹ and $\Delta S^\circ = 22.1 \pm 2$ e.m.u. (DAVIDSON *et al.*, 1977) and

$$RT \ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (2)$$

the equilibrium constant K has been derived for the three flights and the HNO_3 concentration was

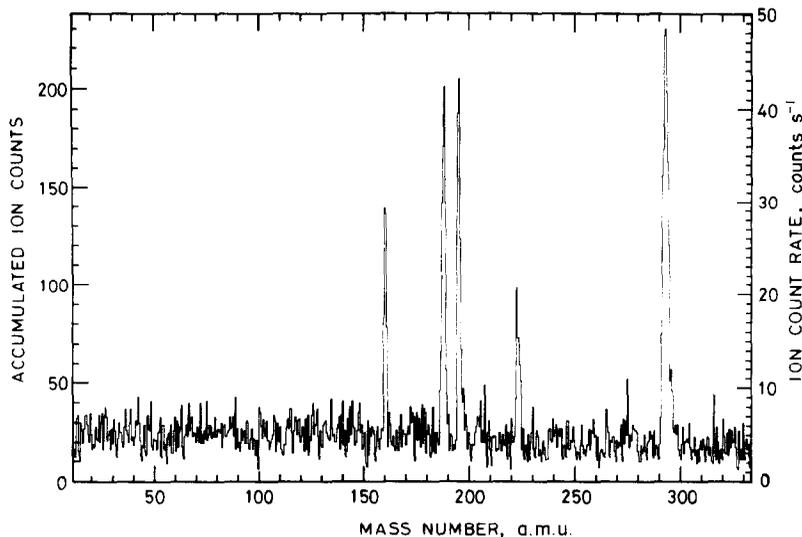


Fig. 1(a). Typical negative ion spectrum obtained at float altitude (32.5 km) after summations of 19 scans. Duration of each scan 160 s for the mass domain 10–330 a.m.u.

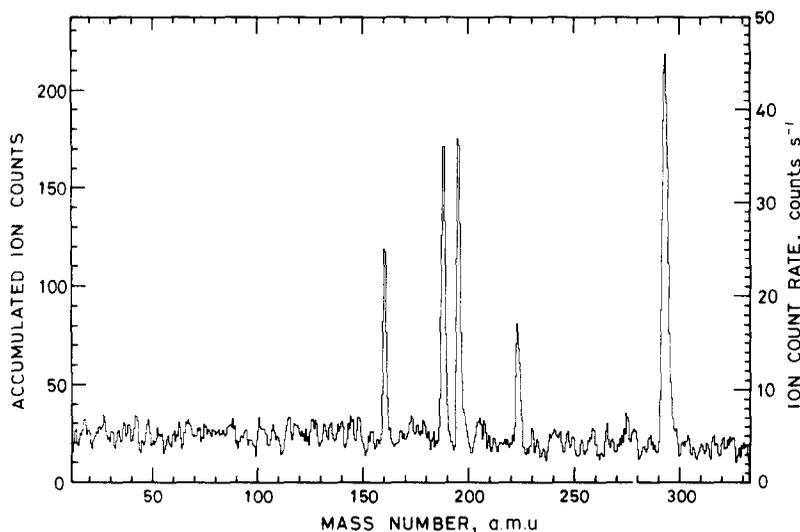


Fig. 1(b). Smoothed version of Fig. 1(a).

calculated from

$$[\text{HNO}_3] = \frac{[188]}{[125]} K^{-1}, \quad (3)$$

where $[188]/[125]$ is the ratio of the relative abundances for $\text{NO}_3^- (\text{HNO}_3)$ and $\text{NO}_3^- (\text{HNO}_3)_2$. The results are given in Table 3 and Fig. 3.

At present there are very few data for HNO_3 volume mixing ratios above 32 km altitude. To the best of our knowledge the only ones which were not obtained from

ion composition data, are those by LAZRUS and GANDRUD (1974) and EVANS *et al.* (1977). Those data have also been included in Fig. 3, as were the measurements of ARNOLD *et al.* (1980). More recently, the nitric acid vapour concentration was inferred from negative ion composition data by a method, which relies on the existence of a kinetic state with respect to the nitric and sulphuric acid cluster ions taken as a whole (VIGGIANO and ARNOLD, 1981a; MCCRUMB and ARNOLD, 1981). The results of this analysis are also

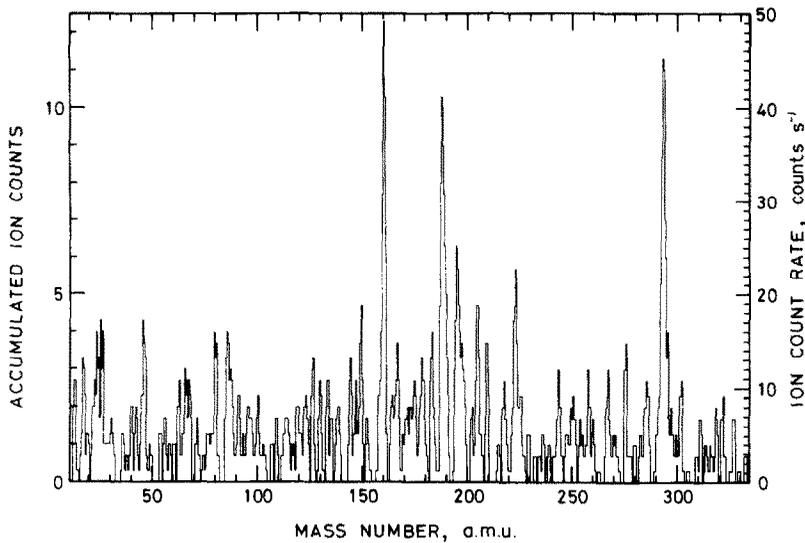


Fig. 2. First of 19 scans which gave rise to Fig. 1(a).

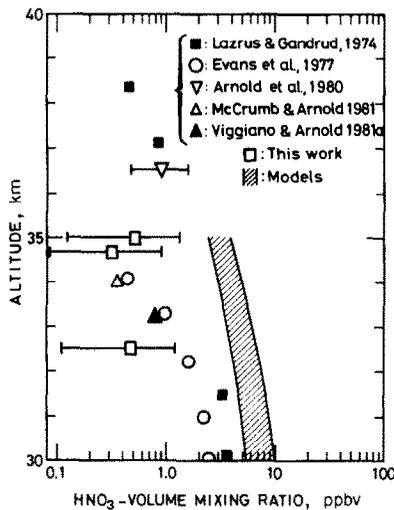


Fig. 3. HNO₃ concentration vs altitude (above 30 km) as measured by different techniques and calculated by current models.

pictured in Fig. 3. The range of the one-dimensional models as available up to 35 km at present (HUDSON and REED, 1979) is also shown. As can be seen on Fig. 3, a reasonable agreement is found between our data and the HNO₃ concentrations found with other techniques. It is also noticed that our HNO₃ mixing ratios are lower than those predicted by current models. As mentioned by HUDSON and REED (1979) this may be due to an incorrect treatment of photolysis in the models and an uncertainty about the effect of transport above 30 km altitude.

The error bars, for our data as shown on Fig. 3 are only taking into account the 30% error on the ion abundances (60% on their ratio) and the possible error of 3 K on the temperature derivation or measurement. We believe that concerning these two errors a rather conservative and safe value was used. We feel that by taking into account the possible errors on the thermochemical data as mentioned in the original paper by DAVIDSON *et al.* (1977), namely 1 kcal mol⁻¹

Table 3. Equilibrium constants for HNO₃ clustering to NO₃⁻.HNO₃ and HNO₃ mixing ratio derived for different flights*

Flight	$[\text{NO}_3^-(\text{HNO}_3)_2] / [\text{NO}_3^-. \text{HNO}_3]$	Equilibrium constant K (atm ⁻¹)	HNO ₃ mixing ratio (ppbv)
June 80	1.6	8.0×10^{11}	0.30
Sept. 80	7.7	2.5×10^{12}	0.53
Sept. 81	7.1	1.8×10^{12}	0.48

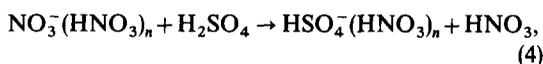
* Square brackets denote number densities.

on ΔH° and 2 e.m.u. on ΔS° , an unreasonable stretching of the error bars is obtained.

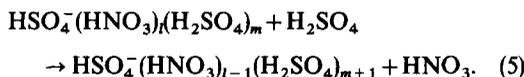
Apart from the data of DAVIDSON *et al.* (1977), another set of thermochemical data for reaction (1) is available in the literature (WLODECK *et al.*, 1980). It was found that by using those data ($\Delta H^\circ = 16.0 \pm 0.8$ kcal mol⁻¹ and $\Delta S^\circ = 23.1 \pm 2.4$ e.m.u.) HNO₃ mixing ratios were deduced which were much too high, according to both the model and the other experimental data. The results of negative ion abundances at float altitude therefore seem to suggest that the thermochemical data of DAVIDSON *et al.* (1977) are closer to the true values of ΔH° and ΔS° than those of WLODECK *et al.* (1980).

On condition that more exact ambient temperatures and ion abundance ratio measurements were combined with HNO₃ concentration derivations by another independent technique, the *in situ* data might have been used to derive thermochemical data. The previous discussion therefore clearly demonstrates another aspect of ion composition measurements, namely the detection of fundamental physico-chemical constants by using the stratosphere as a laboratory.

Our next item of discussion will be the family of the HSO₄⁻ core ions. ARNOLD *et al.* (1981a) proposed and verified that those ions were formed in the stratosphere by the switching reactions:



and



The reaction rate constants for reaction (4) were measured in the laboratory by the NOAA group in Boulder, Colorado (VIGGIANO *et al.*, 1980). It followed that:

$$k_1 = 8.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \text{for } n = 1,$$

and

$$k_2 = 4.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \text{for } n = 2.$$

From a steady state treatment it follows that:

$$[\text{H}_2\text{SO}_4] \{ k_1 [\text{NO}_3^-(\text{HNO}_3)] + k_2 [\text{NO}_3^-(\text{HNO}_3)_2] \} = \alpha [n_s] [n], \quad (6)$$

where the square brackets denote number densities, $[n]$ the total number density of positive (or negative) ions and $[n_s]$ the total number density of the HSO₄⁻ core ions.

The recombination coefficient to be used in equation (6) is composed of two components: the binary recombination coefficient α_b and the effective ternary combination coefficient α_t . The binary recombination coefficient α_b has been measured recently by SMITH *et al.* (1981) and was found to be practically independent of the nature of the ions. A value of $6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, in good agreement with most of the data of the previous authors, will be used for further calculations. However much less information is available on the ternary component of the recombination coefficient. This α_t is strongly dependent on the gas number density. A value of $6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ will be assigned to it for the altitude 34.7 and 35 km (June 1980 and September 1980 flights) and for 32.5 km α_t will be taken as $9 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. These values were obtained by interpolation between the numbers given by SMITH and CHURCH (1977) for 30 and 40 km. The total ion number density $[n]$ was not measured in flight. Therefore the value is calculated from $(Q/\alpha)^{1/2}$, where Q is the production rate taken from WEBBER (1962). For the altitude ranges under consideration Q is about 2 ions cm⁻³ s⁻¹. These values have been used to allow a comparison with the most recent data from VIGGIANO and ARNOLD (1981b) who have used the same source for $[n]$.

The results of our H₂SO₄ vapour number density determinations are given in Table 4 for the different flights discussed here. In view of the uncertainties on the different data used to derive those numbers, an error of a factor of three is adopted here. No correction has been applied for missing ions in our case, since a mass scanning without DC on the quadrupole rods showed that the fraction of ions having a mass higher than 391 a.m.u. was negligible for the present purpose. This technique to obtain H₂SO₄ number densities is at present the only experimental one available. It was used for the first time by ARNOLD and FABIAN (1980) and it was exploited later on to determine H₂SO₄ concentration profiles (ARNOLD *et al.*, 1981b; VIGGIANO and ARNOLD, 1981a). The most recent data of the MPI group have also been added to Table 4. As can be seen our data are in reasonable agreement with those of the MPI group, especially in view of the uncertainties on the values of α , $[n]$, k_1 and k_2 , and the signal fluctuations of about 30%.

According to ARNOLD *et al.* (1981a) the sulphate ions were grouped into different subfamilies, namely A: (HSO₄⁻)_i(HNO₃)_i, B: HSO₄⁻(H₂SO₄)_j(HNO₃)_j and C: HSO₄⁻(H₂SO₄)₂(HNO₃)_k. More generally we can define a family F_m as consisting of all the ions of the form HSO₄⁻(H₂SO₄)_m(HNO₃)_i, for $m \geq 0$. F_{-1} will be defined as the family of the NO₃⁻(HNO₃)_n ions. From an oversimplified steady state treatment, which assumes the same reaction rate constant k for all the reactions of

Table 4. Values of H₂SO₄ number densities, equilibrium constants and thermochemical constants for H₂SO₄ clustering for different flights

	June 80	Sept. 80	Sept. 81
[H ₂ SO ₄] (cm ⁻³) (1)	5.6 × 10 ⁶ (1.5 × 10 ⁷)	5.1 × 10 ⁶ (1.5 × 10 ⁷)	6.2 × 10 ⁶ (6 × 10 ⁶)
K _{1,2} (atm ⁻¹)	1.5 × 10 ¹³	6.2 × 10 ¹²	5.8 × 10 ¹²
ΔG _{1,2} ^o (kcal.mole ⁻¹)	14.4	13.6	13.7
ΔH _{1,2} ^o (2) (kcal.mole ⁻¹)	21.6	20.5	20.7
K _{2,3} (atm ⁻¹)	1.4 × 10 ¹³	1.5 × 10 ¹³	9.8 × 10 ¹²
ΔG _{2,3} ^o (kcal.mole ⁻¹)	14.4	14.0	13.9
ΔH _{2,3} ^o (2) (kcal.mole ⁻¹)	21.5	21.0	21.0

(1) Numbers in parentheses are data of MPI group for the same altitude (VIGGIANO and ARNOLD, 1981b).

(2) ΔH^o is derived assuming ΔS^o to be 30 e.m.u. Indexes *l, l+1* relate to reaction:



type (4) and (5) it then follows that:

$$R_l = \left(\sum_{i=1} [F_i] \right) / [F_{l-1}] = k[\text{H}_2\text{SO}_4] / \alpha[n]. \quad (7)$$

In practice the summation of equation (7) has only to be expanded to *i* = 3 for the altitudes under consideration. The *R_l* values, as well as the abundances of the subfamilies *F_m* have been summarized in Table 5. According to equation (7) all *R_l* should have the same value, independent of *l*. As can be seen the measured *R_l* values are all of the same order of magnitude for the different flights, although large variations occur within the uncertainty limits (± 60%). It was suggested by ARNOLD *et al.* (1981a) from the somewhat lower value of *R₂* in their data that an ion with mass 391 a.m.u. should exist though it was not present in their spectra. This conclusion was confirmed by recent measurements of our group (ARIJS *et al.*, 1981).

Table 5. Abundances of subfamilies *F_l* and *R_l* values for different flights*

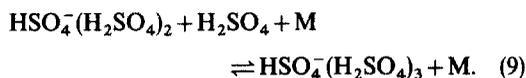
	June 80	Sept. 80	Sept. 81
[F ₀]	13	21	12
[F ₁]	7	14	17
[F ₂]	19	14	16
[F ₃]	48	34	31
[F ₋₁]	13	17	16
R ₀	6.69	4.88	4.75
R ₁	5.69	2.95	5.33
R ₂	9.57	3.43	2.76
R ₃	2.53	2.43	1.94

* For definition of *F_l* and *R_l* see text.

However strong fluctuations of *R_l* do occur, most probably due to signal fluctuations and therefore care should be taken in the interpretation of equation (7). One of the basic assumptions in putting all *R_l* equal was that the main loss process for the ions is recombination. If for instance thermal dissociation of HSO₄⁻(H₂SO₄)₃ ions is faster than ion-ion recombination the ratio *R₃* will be given by:

$$R_3 = K[\text{H}_2\text{SO}_4], \quad (8)$$

where *K* is the equilibrium constant of the reaction:



On the other hand using equation (8) to derive thermochemical data such as ΔG^o and ΔH^o, will allow us to find a lower limit for these values. Indeed the non-validity of equation (8) would mean that the dissociation rate constant is smaller than assumed and therefore *K* would be larger. Consequently ΔG^o values derived with the aid of equation (2) would be larger.

To derive *K* values the H₂SO₄ concentrations found by equation (6) have been used. It is very unlikely that equation (6) is wrong, since reconversion from HSO₄⁻ to NO₃⁻ core ions is not plausible. Therefore, the H₂SO₄ mixing ratios can be trusted within the uncertainty limits mentioned. The *K* values calculated with the aid of equation (8) are then 1.38 × 10¹³, 1.50 × 10¹³ and 9.81 × 10¹² atm⁻¹ for the June 1980, September 1980 and September 1981 flights, respectively. Then an average ΔG^o value of 14 kcal mol⁻¹ results for the three flights; the deviation on each flight being less than 0.3 kcal mol⁻¹.

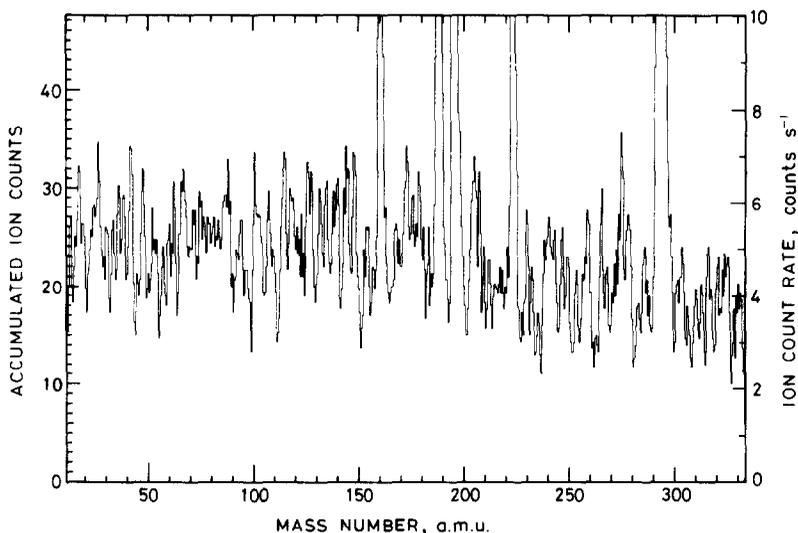


Fig. 4. Expanded version of the spectrum of Fig. 1(b).

It is known that the bond dissociation energies of 'small' clusters is larger than the bulk phase vaporization energy ΔH_v° of the solvent molecules and approaches this value for larger cluster size (CASTLEMAN, 1979; KEESEE *et al.*, 1980). For sulphuric acid ΔH_v° is 18 kcal mol⁻¹ (SCHLESSINGER, 1971). Therefore ΔH° for reaction (9) is expected to be larger than this value. In order to check whether our lower limit of ΔG° satisfies this condition, the entropy change ΔS° for reaction (9) has to be known. Since no laboratory data are available on sulphuric acid clustering, this entropy change is unknown. By taking a reasonable average of 30 e.m.u., (KEESEE *et al.*, 1981) a lower limit of ΔH° of 21 kcal mol⁻¹ is found, larger than the heats of vaporization, reported in literature. Similar derivations may be performed for the conversion of HSO_4^- (H_2SO_4) into HSO_4^- (H_2SO_4)₂ clusters. A lower limit of ΔH° of 20.9 kcal mol⁻¹ is then found using an average of our data on the three flights. This is in good agreement with the value of 21.4 kcal mol⁻¹ found by ARNOLD *et al.* (1981a).

From the previous considerations, it turns out that H_2SO_4 is much more strongly bound to the HSO_4^- core than HNO_3 is to the NO_3^- core. It is therefore expected that the sulphate ions will be less susceptible to field induced cluster break-up than the nitrate ions.

4.2. Minor mass peaks

So far only major ions have been considered throughout the discussion. In order to reveal the existence of minor mass peaks the spectrum shown in Fig. 1(b) has been expanded as shown in Fig. 4.

It can be seen that many additional mass peaks are appearing. However care must be taken not to confuse spontaneous counts with real mass peaks. Since in the negative ion mode the background pulse counting rate is about 50 times higher than in the positive ion mode, it is difficult to distinguish between real signal and background. In order to exclude peaks due to background pulses, we have adopted the following procedure. At the beginning of a series of measurements the draw-in potential is optimized by the microprocessor based controller. To do so the DC and RF on the quadrupole rods are arranged so as to obtain maximum negative ion signal at the most positive draw-in potential (+5 V). Subsequently draw-in potential ramps in the range -5 to +5 V are produced while DC and RF remain fixed. The ion signal of successive ramps is accumulated and finally the draw-in potential associated with the maximum count rate is chosen by the microprocessor and used for further sampling. Optimization of the draw-in potential can be called for by remote control whenever judged necessary during the flight such as during altitude variation, sunrise, a.s.o. A typical result of such a 'draw-in ramping' is shown in Fig. 5. The negative ion signal starts only to be appreciable at draw-in potentials larger than -0.68 V. The count rate observed for more negative draw-in potentials is considered as background. The mean value μ of this background count rate is 2.59 counts s⁻¹ with a dispersion σ of 1.85 counts s⁻¹.

We now define the confidence level as being the mean value plus two root mean square deviations ($\mu + 2\sigma$).

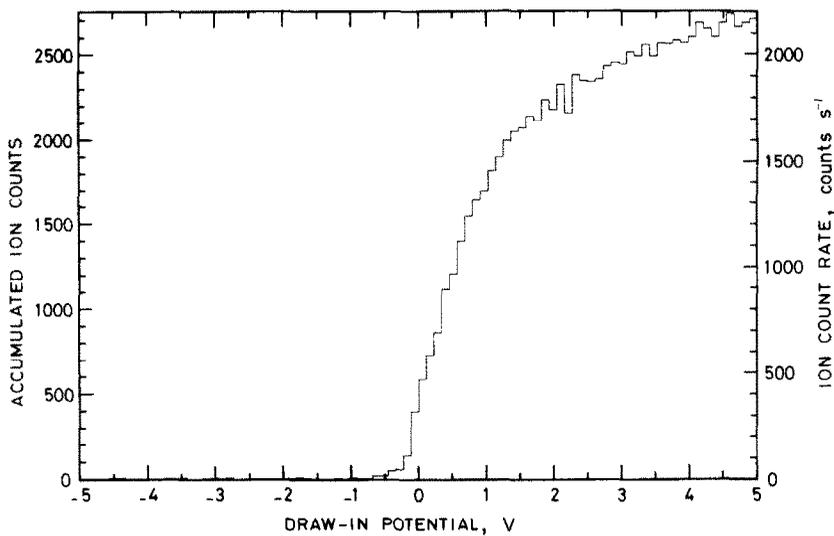


Fig. 5(a). Negative ion signal vs draw-in potential.

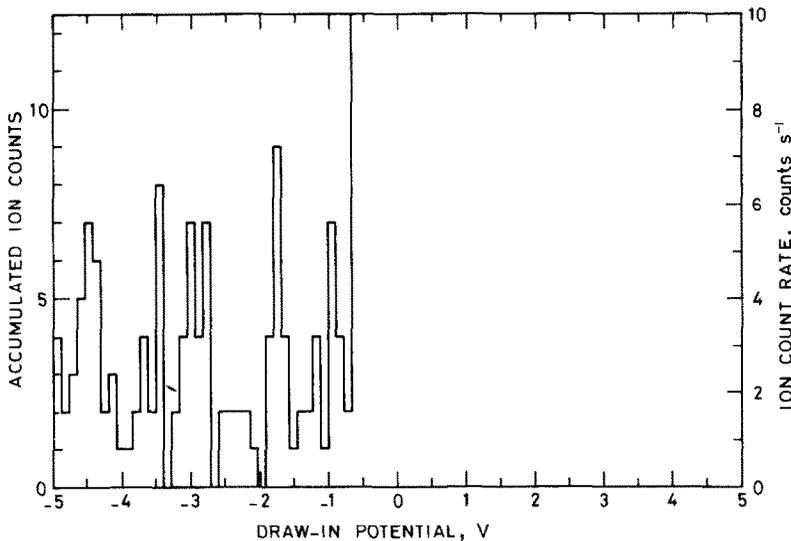


Fig. 5(b). Expanded version of Fig. 5(a).

With the previous value of μ and σ , this gives $6.29 \text{ counts s}^{-1}$ or about 30 accumulated counts on Fig. 4. By considering masses lying above this confidence level a number of mass peaks are distinguished which are most likely real. The mass numbers derived in this way and their tentative identifications are summarized in Table 6 under the heading 'Group A'. Due to poor counting statistics and associated poor peak shape, an error of ± 2 a.m.u. is accepted for mass numbers below 200 a.m.u. and ± 3 a.m.u. for higher ones.

We feel that the above procedure to distinguish real

counts from background is rather conservative and safe. It has indeed been found in the laboratory, that even for draw-in potentials below -1 V, several ions were leaking into the mass spectrometer at pressures of 8 mb (same pressure as in the last flight, from which Fig. 4 was obtained). This penetration of ions through the applied electric field is caused by the gas flow, dragging the ions into the sampling hole (PARKES, 1971; KEARLE *et al.*, 1966). Therefore the estimation of the spontaneous pulse count rate of $6.29 \text{ counts s}^{-1}$ is probably a safe upper limit.

Table 6. Mass numbers and tentative identifications of minor mass peaks observed in the September 1981 flight*

Group A		Group B	
Mass (± 2 amu)	Tentative identification	Mass (± 2 amu)	Tentative identification
17	OH ⁻	36	Cl ⁻ (Cl = 35)
26	CN ⁻	38	Cl ⁻ (Cl = 37)
42	CN ⁻ .H ₂ O	52	ClO ⁻ , CN ⁻ .HCN
47	NO ₂ ⁻	81	NO ₃ ⁻ .H ₂ O, CO ₃ ⁻ .H ₂ O
62	NO ₃ ⁻ , CO ₃ ⁻	94	NO ₂ ⁻ .HNO ₂
67	NO ₂ ⁻ .H ₂ O	107	NO ₃ ⁻ .HNO ₂ , CO ₃ ⁻ .HNO ₂
87	NO ₃ ⁻ .HCN	118	NO ₂ ⁻ (HCl) ₂
101	NO ₂ ⁻ .HOCl, NO ₃ ⁻ .HCl	133	NO ₃ ⁻ .HOCl.H ₂ O, HSO ₄ ⁻ .HCl
115	NO ₃ ⁻ .HOCl	140	Cl ⁻ (HOCl) ₂ , NO ₂ ⁻ (HNO ₂) ₂
125	NO ₃ ⁻ .HNO ₃	154	ClO ⁻ (HOCl) ₂
144	NO ₃ ⁻ .HNO ₃ .H ₂ O	168	NO ₃ ⁻ (HOCl) ₂
148	HSO ₄ ⁻ .HOCl	175	NO ₃ ⁻ .HNO ₃ .HOCl
173	NO ₃ ⁻ .HNO ₃ .HNO ₂	230	HSO ₄ ⁻ .H ₂ SO ₄ .HCl
179	NO ₃ ⁻ .HNO ₃ .HOCl, HSO ₄ ⁻ .HNO ₃ .H ₂ O	240	NO ₃ ⁻ (HNO ₃) ₂ .HOCl, HSO ₄ ⁻ (HNO ₃) ₂ .H ₂ O
205	NO ₂ ⁻ (HNO ₃) ₂ .H ₂ O	247	HSO ₄ ⁻ .H ₂ SO ₄ .HOCl
275	HSO ₄ ⁻ .H ₂ SO ₄ .HNO ₃ .H ₂ O	258	HSO ₄ ⁻ .H ₂ SO ₄ .HNO ₃
		265	HSO ₄ ⁻ .HNO ₃ (HOCl) ₂
		278	HSO ₄ ⁻ .H ₂ SO ₄ .HNO ₃ .H ₂ O

* Group A was obtained accepting a confidence level of 6 counts s⁻¹ as background. For Group B a level of 5 counts s⁻¹ was accepted. Note that ion identification is tentative and sometimes speculative.

It should also be pointed out that all masses, listed in Table 6 under group A were also found by inspecting separately the 19 spectra from which Fig. 4 was built by summation. In some of those (from which Fig. 2 is the first one) minor peaks can be distinguished more clearly than in the final spectrum because of counting statistics. This is obvious from Fig. 2 where the masses 26, 47, 67, 81, 87, 125, 144, 206 and 275 can be seen very clearly (they are larger than 10 counts s⁻¹, which is certainly too high to be due to spontaneous pulses).

Inspection of Fig. 4 gives the impression that there is a very high background signal. An investigation however of the 19 separate spectra told us that this 'background' is composed of spontaneous pulses plus signal from many small mass peaks (probably even more than those listed in Table 6) which are close to each other, and which cannot be identified due to poor counting statistics and peak crowding.

Most of the minor ions summarized in Table 6 (group A) have a NO₃⁻ or HSO₄⁻ core as may be expected. Unexpected however are the OH⁻, CN⁻ and NO₂⁻ core ions. The OH⁻ core ions are most probably formed by the reaction of H₂O with the primary O⁻ ions (FERGUSON *et al.*, 1979). The CN⁻ core was also observed by McCrumb and Arnold (1981) in a recent high sensitivity mass spectrum. It was proposed by

these authors that the CN⁻ ions were originating from the reaction of HCN with O₂⁻, O₃⁻ or CO₃⁻ ions. It should be noted that the presence of HCN in the stratosphere was already deduced from positive ion spectra (HENSCHEN and ARNOLD, 1981; ARIJS *et al.*, 1981b) and that HCN was recently observed from infrared spectra by Coffey *et al.* (1981). From the abundances of the CN⁻ core ions a HCN concentration of the same order of magnitude as the HNO₃ concentration was derived by McCrumb and Arnold (1981), which was in agreement with the data of Coffey *et al.* (1981). At 32.5 km altitude however NO₂ has a higher number density (ACKERMAN, 1979) than HNO₃ and therefore we expect NO₂⁻ core ions to be present among the minor ions. Moreover NO₂⁻ ions are assumed to be the precursors of the NO₃⁻ ions. It should be noted that ions may be sampled before they have completed their full chemical lifetime and therefore non-final ions may appear in the spectrum as minor peaks. HCl being equally abundant as HNO₃ (ACKERMAN, 1979) the presence of Cl⁻ ions may also be expected.

By lowering the confidence level of minor ions from 6.29 to 5 counts s⁻¹, which is still above $\mu + \sigma$, the ions of group B in Table 6 can be distinguished. It is seen that in this case also Cl⁻ ions are present.

Although the use of group B of Table 6 is highly speculative, it is instructive for the identification of the ions of group A since the presence of some members of expected ion families may be deduced.

All minor ions recently reported by MCCRUMB and ARNOLD (1981) are present in Table 5 (group A and B) as well as some others not detected by these authors. From the ion hydration equilibria for CN^- and NO_2^- a ΔG° value can be derived for our data. Values of 8 ± 2 kcal mol^{-1} for CN^- and 8.5 ± 2 kcal mol^{-1} for NO_2^- are found. Both data are in reasonable agreement with those reported in the literature (PAYZANT *et al.*, 1971; LEE *et al.*, 1980). The poor counting statistics for minor mass peaks, the associated uncertainties on the ion abundances, and the possible errors on the temperature and water number density at 32.5 km altitude make these agreements most certainly fortuitous. It is therefore clear that further *in situ* measurements are needed to obtain higher accuracy and better ion identifications. A lowering of the background pulse counting rate and a longer integration time (or higher sensitivity) would certainly improve the results and open new perspectives for the *in situ* measurements. Efforts in this direction are planned in the near future.

4.3. Measurements at lower altitudes

So far very few data are available on the ion composition of the stratosphere at altitudes below 23 km. The first height measurements of the negative ion composition in the altitude range from 23.8 to 38.9 km have recently been reported by VIGGIANO and ARNOLD (1981a,b). In order to obtain further information on the ion identities in the stratosphere at lower altitudes a flight with a valve controlled balloon was released on 12 June 1981 from the CNES launching base at Gap-Tallard (France). In this flight positive ion spectra were obtained from 33 km down to 20 km altitude. These spectra as well as their discussion will be reported elsewhere. Negative ion spectra have been taken in the

altitude range from 28 km down to 20 km. In view of the high ambient pressure encountered (about 55 mb or 41 torr at 20 km) a sampling hole of 0.1 mm diameter was used in order to maintain the pressure inside the mass spectrometer below the scattering limit (10^{-4} torr). As a result of this small aperture a very low ion counting rate was observed. Therefore spectra were built up in the coarse resolution mode, where ion identification is based on the recognition of the edges of very broad mass peaks. This procedure has been explained to full extent in an earlier publication (ARJUS *et al.*, 1981). During the measurements the balloon was descending with a speed of 1 m s^{-1} . A typical sequence of spectra consisted of: two scans without DC voltage on the quadrupole rods and four scans with moderate resolution in the positive ion mode followed by similar scans in the negative ion mode. Each scan consisted of 640 steps 0.25 s long. As a result spectra (sum of four scans) with moderate resolution were obtained about every 2 km, with an altitude resolution of about 640 m.

A typical spectrum obtained at 28 km is shown in Fig. 6. It is obvious that from this kind of spectra only major mass peaks can be deduced. Moreover it is very difficult to distinguish masses which are close to each other, such as mass 188 and 195. An additional factor hampering the derivation of ion abundances is the natural signal fluctuation, which seems to be much more pronounced during the descending phase of the balloon flight. Therefore the errors on the abundances deduced from this kind of spectra are very large. The estimated abundances for the major mass peaks at six altitude levels are summarized in Table 7 as well as the H_2SO_4 number densities, calculated from these data with the aid of formula (6). Again α was derived by interpolation between the numbers of SMITH and CHURCH (1979) and Q was borrowed from REID (1979). Their values at different altitudes are also shown in Table 7. As can be seen the H_2SO_4 concentrations are about a factor of ten higher than those obtained by the

Table 7. Relative ion abundances, H_2SO_4 number densities, ion production rate and recombination rate coefficient at different altitudes*

Altitude	Relative abundances %				Q $\text{cm}^{-3} \text{ s}^{-1}$	α $\text{cm}^3 \text{ s}^{-1}$	$[\text{H}_2\text{SO}_4]$ cm^{-3}
	mass 125	160	188	195			
27.3	10	16	67	7	5	2.8×10^{-7}	7.6×10^5
27.0	41	8	51	-	5	3.0×10^{-7}	1.7×10^5
25.1	45	11	44	-	7	3.9×10^{-7}	3.2×10^5
23.5	54	9	37	-	9	5.0×10^{-7}	3.1×10^5
21.7	51	12	37	-	12	6.6×10^{-7}	5.7×10^5
20.2	59	6	35	-	15	8.3×10^{-7}	3.3×10^5

* It should be stressed that the relative abundances mentioned are rough estimates and may be subject to large uncertainties (see text). Mass numbers are determined within 3 a.m.u.

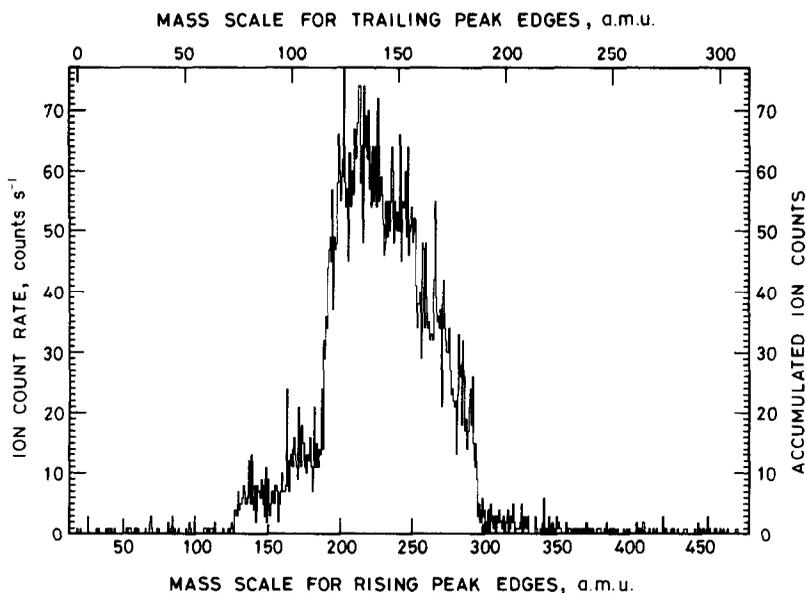


Fig. 6. Sample negative ion spectrum obtained in the coarse resolution mode at 28 km altitude, after summation of four scans. Each scan consists of 640 steps of 0.25 s long.

MPI group (VIGGIANO and ARNOLD, 1981a,b). It should be stressed however that apart from the error of a factor of three, introduced through the calculations and the uncertainties on k_1 , k_2 , α and Q , another important error is added here: the relative abundance error, which in view of the low signal and poor resolution may be as high as a factor of two or larger. This is especially true for the abundance of mass 160 which in our case is sometimes smaller than one-third of the signal of mass 125, fluctuating itself over about 30%. The abundance of mass 160 being derived from a signal superimposed on mass 125 (in the rising edge mode) a great uncertainty results for this value. The same reasoning holds in the trailing peak edge detection mode since mass 160 has to be deduced here from a reduction of the signal of mass 160 + mass 188. The existence of a rising as well as a trailing edge however helps in distinguishing real mass peaks from signal fluctuations.

In view of the above problems the inferred sulphuric acid concentrations of Table 7 are highly uncertain, as well as some of the estimated relative abundances. The numbers in Table 7 should therefore not be interpreted as detailed and exact information, but are merely given to show general tendencies, such as the increase of the relative abundance of mass 125 with decreasing altitude and the decrease of H_2SO_4 number density at lower altitudes.

The absence of peaks larger than 188 a.m.u., suggests the strong influence of cluster break-up. Especially for NO_3^- core ions we expect to find higher order clusters at

lower altitudes because of the higher HNO_3 mixing ratios. The effect of cluster break-up is even more clearly illustrated at the lowest altitude (20 km) where $NO_3^-HNO_3$ becomes the most dominant detected ion, contrary to what one would expect from the theoretical distribution of $NO_3^-(HNO_3)_n$ cluster ions. This means that as expected field induced collisional ion dissociation becomes more efficient at lower altitudes, because of the higher ambient pressure. Similar cluster break-up effects were reported by VIGGIANO and ARNOLD (1981a,b).

Such break-up effects however should not affect the determination of the H_2SO_4 number density since the sum of all sulphate ions is used in equation (6). The decrease in the abundances of HSO_4^- core ions at lower altitudes therefore indicates a decrease in H_2SO_4 concentration at lower altitudes as expected by recent models (TURCO *et al.*, 1981) and measurements (VIGGIANO and ARNOLD, 1981a,b).

It is clear however that the influence of field induced collisional dissociation should be minimized for the detection of trace gases. In our case cluster break-up is very pronounced at low altitudes because of the rather high lens voltages used immediately behind the inlet aperture. In the future the ion lens will be modified so that lower voltage can be used while the sensitivity is maintained or improved. From the good agreement however between the HNO_3 concentrations derived from our data and other experimental and model values above 32 km, it is felt that the $NO_3^-HNO_3$ and

$\text{NO}_3^-(\text{HNO}_3)_2$ signals were not heavily disturbed by cluster break-up above this altitude.

5. SUMMARY AND CONCLUSIONS

The nature and abundance of the major negative ions observed during three recent balloon flights at 32.5, 34.7 and 35 km altitude were shown and discussed.

From the $\text{NO}_3^-(\text{HNO}_3)_n$ ion family abundances a concentration for nitric acid of the order of 0.5 ppb was derived for three altitudes, in good agreement with other experimental data and models. The possibility of using in the future the stratosphere as a laboratory for the determination of basic thermochemical data was demonstrated.

The $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$ ion abundances, measured at float altitudes, were together with these of the NO_3^- core ions to calculate an H_2SO_4 number density of about $5 \times 10^6 \text{ cm}^{-3}$ in the altitude range of 32.5–35 km. A lower limit for the bond dissociation energy of 21.4 and 21 kcal mol⁻¹ was derived for $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_2$ and $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_3$ clusters respectively, indicating a much stronger bonding for sulphate cluster ions than for nitrate cluster ions. The minor mass peaks observed at float altitude show the possibility of detecting other trace gases such as HCl

and HOCl from stratospheric negative ion composition measurements.

Previously hypochlorous acid has been tentatively identified as a ligand of stratospheric negative ions (MCCRUMB and ARNOLD, 1981; VIGGIANO and ARNOLD, 1981a). It should be noted that the detection of HOCl may be relevant for the understanding of the catalytic destruction of stratospheric ozone (GLASGOW *et al.*, 1979).

Preliminary data obtained at lower altitudes $\text{NO}_3^-(\text{HNO}_3)_n$ clusters are the most abundant ions but the measurements are heavily disturbed by cluster break-up. Present experimental data however lack sensitivity to deduce exact H_2SO_4 profiles.

The results clearly illustrate the potential possibilities of ion composition measurements for trace gas detection and the extent of our knowledge of basic ion thermochemistry. Further *in situ* as well as laboratory measurements are needed to elucidate the remaining problems.

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