

NEGATIVE ION COMPOSITION MEASUREMENTS IN THE STRATOSPHERE

E. Arijs, D. Nevejans, P. Frederick and J. Ingels

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

Abstract. Composition measurements of negative ions in the stratosphere were performed at altitudes near 35 km by means of a balloon borne quadrupole mass spectrometer during two balloon flights. Some typical ion spectra are shown and discussed. The observed ions were identified as $\text{NO}_3 \cdot \text{nHNO}_3$ and $\text{HSO}_4 \cdot \text{mHNO}_3 \cdot \text{pH}_2\text{SO}_4$ clusters. Hydrated clusters of both ion families have also been detected. A reaction scheme is proposed to explain the data. The relative abundances of the ion mass peaks, as well as the measurement of minor constituents with large gas-phase acidities, such as HNO_3 and H_2SO_4 are briefly discussed.

Introduction

Considerable progress has been made during the last few years in the technology of ion detection in the stratosphere. Positive ions have been measured by balloon borne mass spectrometers [Arijs et al., 1978, Arnold et al., 1978] and the mass numbers of the major positive ions have been unambiguously determined very recently [Arijs et al., 1980] at an altitude near 34 km. The only negative ion composition measurements in the stratosphere reported so far are those of Arnold and Henschen [1978]. These measurements, conducted with a balloon borne mass spectrometer at altitudes between 34 and 37 km, revealed the existence of two cluster ion sequences. The first one was identified as being $\text{NO}_3 \cdot \text{nHNO}_3$ and resulted from the reaction of nitric acid, present as a trace gas in the stratosphere, and the hydrated NO_3^- ions. This ion family was expected, since it has been pointed out that NO_3^- is the terminal core ion in the atmosphere below 40 km altitude and that HNO_3 will displace H_2O from $\text{NO}_3^- \cdot \text{H}_2\text{O}$ [Fehsenfeld et al., 1975].

The second ion sequence could be identified as $\text{R}^- \cdot \text{mHR} \cdot \text{nHNO}_3$. It was suggested by Arnold and Henschen [1978] that HR most likely was H_2SO_4 in the gas-phase. Support for this suggestion was given by laboratory measurements, conducted by the NOAA group in Boulder, which showed a rapid reaction between $\text{NO}_3^- \cdot \text{HNO}_3$ and $\text{NO}_3^- \cdot 2\text{HNO}_3$ with sulfuric acid vapour [Viggiano et al., 1980].

Recently the relative abundances of the negative ions observed in the stratosphere have been used to determine the mixing ratio of nitric and sulfuric acid in the vapour phase in the altitude range 34-37 km [Arnold and Fabian, 1980, Arnold et al., 1980]. Unfortunately the mass spectra of Arnold and Henschen [1978] lack resolution (peak widths of the order of 15 amu were reported) and an unambiguous mass identification of the negative ions was not possible.

In this paper we report a set of mass spectra of negative ions in the stratosphere, obtained during two recent balloon flights, with better resolution thus permitting a higher degree of certainty in the identification of the ions. The

relative abundances of the mass peaks and their implication on the detection of trace gases such as HNO_3 and H_2SO_4 will be briefly discussed.

Experimental and Measurements

The balloon borne payload basically consists of a quadrupole mass filter with a high speed liquid helium cryopump and the appropriate electronic modules.

Stratospheric ions and neutral constituents are sampled through a small hole of 0.2 mm diameter which is drilled through a stainless steel flange of 0.1 mm thickness. Draw-in potentials between -5 and +5V can be applied to this flange. The neutral gas is pumped by the cryopump, while the ions are focussed by an electrostatic lens into the quadrupole mass filter. Next they reach a high gain electron multiplier working in the pulse counting mode. Treatment of the ion count rates is done by a microprocessor, which also takes care of the mass setting and other control functions [Nevejans et al., 1981]. The instrument can operate in different modes, such as positive and negative ion sampling, and the neutral mode. In the neutral mode, a small electron impact ion source incorporated into the ion lens is switched on while an argon, krypton and xenon mixture is injected into the cryopump. Thus, an in flight calibration of the mass scale of the quadrupole can be performed.

Mass range and sensitivity of the mass filter are both dependent upon the resolution, which is determined by the ratio of DC to RF (U/V) applied to the quadrupole rods. Choosing a high resolution (U/V = 0.167) means working with a weak signal in the minimum mass range, the extent of which is determined by the dimensions of the quadrupole, the RF frequency and the maximum attainable RF voltage V. Scanning under the same conditions but with a low resolution (U/V < 0.167), results in larger signals and mass peak broadening so that the rising edges of peaks shift to lower RF voltages. Thus the mass range of the instrument can be considerably extended without increasing V, and high mass ions, falling beyond the upper mass limit at high resolution, become detectable if their peak edges are well defined.

In our instrument, resolution can be programmed by the on-board microprocessor in a very flexible way so that very coarse and very fine resolutions can be achieved in the same flight. Even scans with constant peak width all over the mass range are feasible. In the high resolution mode, the mass domain covered by the quadrupole ranges from 0 to 330 amu. In low resolution modes, well defined edges are obtained with values of U/V as low as 0.123 and reasonable mass identification should be possible up to 460 amu.

The data which are shown and discussed in this letter have been obtained during two balloon flights. The first one was performed from Gap-Tallard in Southern France (44°27'N) on 16 June 1980. Measurements of negative ions were started

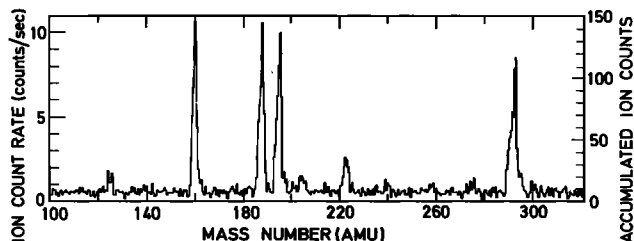


Fig. 1. Typical nighttime spectrum for negative ions obtained near 35 km altitude. The recording was obtained after 55 scans with a resolution $m/\Delta m = 100$. Each mass unit is divided in 2 channels, dwell time per channel is 0.25 sec in each scan. Draw in potential was + 5V.

after sunrise on 17 June at the ceiling altitude of 34 km. The second flight took place at Aire sur l'Adour in South-Western France ($43^{\circ}42'N$) on 18 September 1980. During this flight all measurements were performed during nighttime at an altitude of 35 km (5.9 mbar).

Results and Discussion

A typical negative ion spectrum obtained near 35 km altitude during nighttime is shown in figure 1. The resolution used here is given by $m/\Delta m = 100$, where Δm is defined as the full peak width measured at half maximum. With this kind of "high" resolution spectra, the highest observable mass is 330 amu. For the detection of ions with masses larger than 330 amu, a low DC to RF ratio was used. A typical "spectrum" obtained in this way is shown in figure 2. Although U/V was chosen 0.135 for this recording, the shifted rising edges of the major masses were still distinguishable and a mass peak, not seen at high resolution, appeared around 400 amu. By linear extrapolation of the rising edge positions of the negative ions already identified at high resolution, the highest mass observed in figure 2 was found to be 391 ± 2 amu. In principle, masses larger than 391 amu can be observed by making U/V even lower. In fact a scan has been performed in flight with U/V = 0.05. With such a low U/V value, the mass range extends to 1150 amu if we still rely on rising edge detection. However, the edges of the mass peaks become less pronounced resulting in an inaccurate mass number identification. Moreover, natural signal fluctuations hinder the detection of less abundant ions. Therefore, ions with mass numbers larger than 391, if at all present, were not observed. From spectra such as those shown in figures 1 and 2, a set of masses has been determined as well as their fractional abundances. These results are summarized in table 1. Mass uncertainties have been determined as follows. For major ions below 200 amu, the peak shape allowed an unambiguous identification by the in flight calibration and linear extrapolation of the mass scale. Beyond mass 200, the higher peak width introduced an error of ± 1 amu for major peaks up to 293 amu. The determination of mass 391 from rising edges implies an error of ± 2 amu. The mass uncertainties for minor peaks are mostly due to lack of signal and, thus, to poor statistics.

It should be noted that the fractional abundances are only tabulated if they are larger than 2%, and because of signal variation in flight the

error on these values is at least 20%.

For the derivation of the ion abundances, only the September flight has been used. As far as the identity of the major ion mass peaks is concerned, however, no marked differences are observed between the June and September flight.

When comparing our results with those of Arnold and Henschen [1978], some agreements as well as some striking differences are noticed. Our data agree with those of Arnold and Henschen [1978] in the observation of the masses 125, 160, 188, 195, 223, 258 and 293 which were termed by the previous authors as 125 ± 2 , 161 ± 2 , 188 ± 2 , 197 ± 3 , 224 ± 3 , 260 ± 3 and 295 ± 3 . We do not observe masses 253 ± 3 nor 289 ± 3 which were reported by the Heidelberg group (MPIH) in their original publication [Arnold and Henschen, 1978].

On the other hand, some supplementary ions are seen to exist in our spectra: namely, 178, 206, 213, 241, and 276. Although these ion peaks are minor peaks, they could be observed after long integration times in smaller mass domains, and their abundance is at least of the order of that of mass 258 ($\text{HSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3$). These ions can be identified as hydrated clusters of the members of either one of the two ion sequences $\text{NO}_3 \cdot \text{nHNO}_3$ and $\text{HSO}_4 \cdot \text{nHNO}_3 \cdot \text{mH}_2\text{SO}_4$. Such hydrated ions may be expected on the basis of pre-nucleation processes [Chan and Mohnen 1980].

Another striking difference between our data and those of the MPIH group is the presence of mass 391 in our spectra. From figure 2, it can be seen that this mass is actually the most abundant one (about 1/3 of the total ion signal). It can be easily calculated that, with the resolution of $m/\Delta m = 22$ originally reported by the MPIH group [Arnold and Henschen, 1978] and by assuming that the extent of their mass range is 330 amu at high resolution, the maximum mass which can be identified through its rising flank is 345 amu. It is, therefore, likely that the absence of mass 391 in the MPIH spectra is due to instrumental factors. As we shall see later on, the presence of this peak plays an important role in the determination of the H_2SO_4 number density in the stratosphere.

Furthermore, a marked difference is observed

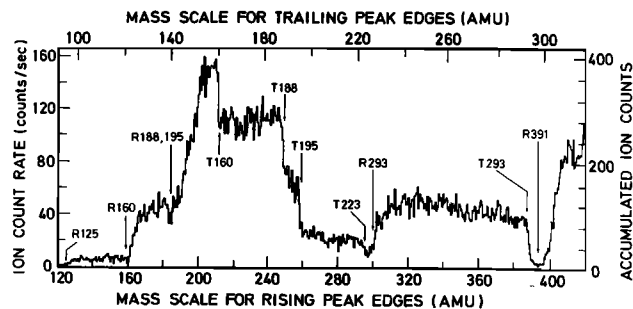
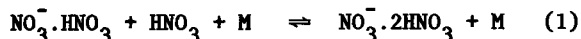


Fig. 2. Low resolution spectrum for negative ions near 35 km altitude, with U/V = 0.135. Rising and trailing edges of the broadened mass peaks are indicated by an arrow. R 125, R 160, R 293 and R 391 are the rising edges of masses 125, 160, 293 and 391 respectively; T 160, T 188, T 195, T 223 and T 293 are trailing edges of masses 160, 180, 195, 223 and 293. The rising edges of masses 188 and 195 are merged in one edge R 188, 195 due to the small difference in masses.

between our ion abundances and those of the MPIH group [Arnold and Fabian, 1980]. These differences may be partly due to temperature effects or cluster break up.

From the observations summarized in table 1, the reaction scheme represented in figure 3 is proposed to explain the different negative ions. In fact this scheme is an extended version of the one proposed by the MPIH group [Arnold and Fabian, 1980]. It should be noted that in this reaction scheme only three reactions have been studied extensively so far: namely, reactions (I), (II) and (III). The reaction



has been studied with M being He [Davidson et al., 1977]. The heat of formation ΔH° and the entropy ΔS° were found to be, respectively, 18.3 ± 1.0 kcal/mole and 22.1 ± 2 cal/mole.deg. These thermochemical data can be used to calculate the equilibrium constant at the appropriate temperature. As has been shown by Arnold et al. [1980], this value can be used together with the relative abundances of the $\text{NO}_3^- \cdot \text{HNO}_3$ and $\text{NO}_3^- \cdot 2\text{HNO}_3$ ions to derive the mixing ratio of nitric acid in the stratosphere assuming that reaction (1) is in equilibrium.

Accepting a temperature of 236 K at 35 km (Spring/Fall values applicable between 30° and 60° N - US. Standard Atmosphere 1966, Supplements p 121), an equilibrium constant K_1 for reaction (1) of $1.3 \times 10^{12} \text{ atm}^{-1}$ is found.¹ The measured abundance ratio $\text{NO}_3^- \cdot 2\text{HNO}_3 / \text{NO}_3^- \cdot \text{HNO}_3$ being 7.5, a volume mixing ratio of 1 ppb for HNO_3 evolves, which is in good agreement with most observed values [Hudson and Reed, 1979].

From the relative abundances of the ions with a

Table 1. Observed negative ions at 35 km, identifications and fractional abundances. For mass uncertainties, see text. The abundances are averaged values obtained from different spectra. Typical error on these values is 20%.

Mass number (amu)	Identification	Abundance in %
125	$\text{NO}_3^- \cdot \text{HNO}_3$	2
160	$\text{HSO}_4^- \cdot \text{HNO}_3$	16
178 ± 2	$\text{HSO}_4^- \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$	-
188	$\text{NO}_3^- \cdot 2\text{HNO}_3$	15
195	$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4$	14
206 ± 2	$\text{NO}_3^- \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$	-
213 ± 2	$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	-
223 ± 1	$\text{HSO}_4^- \cdot 2\text{HNO}_3$	5
241 ± 2	$\text{HSO}_4^- \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$	-
258 ± 2	$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3$	-
276 ± 2	$\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$	-
293 ± 1	$\text{HSO}_4^- \cdot 2\text{H}_2\text{SO}_4$	14
391 ± 2	$\text{HSO}_4^- \cdot 3\text{H}_2\text{SO}_4$	34

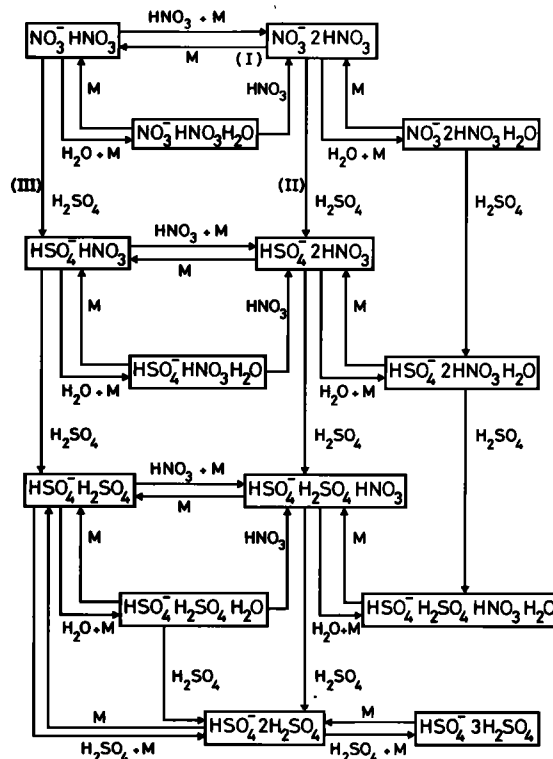


Fig. 3. Proposed reaction scheme, including the observed negative ions. Neutral reaction partners are indicated along the arrows, M means a collision partner.

HSO_4^- core, a number density of H_2SO_4 in the stratosphere can also be derived. To do so, an equation of the form

$$k_2 [\text{NO}_3^- \cdot 2\text{HNO}_3] [\text{H}_2\text{SO}_4] = \alpha n_s \cdot n_+ \quad (2)$$

is used [Arnold and Fabian, 1980]. The reaction rate constant k_2 for the reaction (II), measured in the laboratory [Viggiano et al., 1980] is $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The recombination coefficient α is about $10^{-7} \text{ cm}^3/\text{s}$ in the altitude region of interest [Smith and Church, 1977] and n_+ is about 2000 cm^{-3} . According to Arnold, n_s should be taken as the sum of the product ions $\text{HSO}_4^- \cdot 2\text{HNO}_3$, $\text{HSO}_4^- \cdot \text{H}_2\text{SO}_4 \cdot \text{HNO}_3$ and $\text{HSO}_4^- \cdot 2\text{H}_2\text{SO}_4$. In our case, however, we should add to these, the product ion $\text{HSO}_4^- \cdot 3\text{H}_2\text{SO}_4$, which according to the data is the largest contributor. The hydrated ions with mass 206, 241 and 276 can be neglected. If we then apply equation (2) to our measured relative abundances, a number density of $1.9 \times 10^6 \text{ cm}^{-3}$ is obtained for H_2SO_4 . This corresponds to a mixing ratio of about 10 ppt, with a 300% error. This value is about 6 times larger than the value found by Arnold et al. [1980], which is mainly due to the contribution of mass 391 in the negative ion spectrum. Although closer to the theoretical value of Turco et al. [1979] it still is a factor 10 below it. It should be noted, however, that the measurements of fractional abundances may suffer from break-up of weaker bound clusters and that in this way an erroneous value of the H_2SO_4 mixing ratio may be derived.

As was pointed out by Arnold and Fabian [1980], temperature dependent nucleation may play an

important role in the number density of gaseous H_2SO_4 in the stratosphere. Since the temperature which we assumed in the last flight (236K) is higher than the one adopted by Arnold (227 K), this may explain some of the observed differences in the ion abundances and consequently in the different deduced values of the H_2SO_4 concentration. The fact however that no ions with a mass larger than 293 amu are reported by the MPIH group makes it difficult to compare the results and, therefore, the role of nucleation cannot be evaluated at present.

Summary and Conclusions

The present measurements confirm the identification of the most abundant negative ions in the stratosphere, around 35 km altitude, as proposed by the MPIH group [Arnold, 1980]. The data of this group are extended through the observation of an ion with mass number 391 ± 2 amu and the detection of hydrated ions of the form $\text{NO}_3^- \cdot n\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{HSO}_4^- \cdot m\text{H}_2\text{SO}_4 \cdot n\text{HNO}_3 \cdot \text{H}_2\text{O}$.

The number densities of gaseous HNO_3 and H_2SO_4 were derived from the relative abundances of the ion peaks. The HNO_3 data are in good agreement with previous measurements, performed by IR spectroscopy and filter sampling techniques.

The derived number density of H_2SO_4 , which is very approximate due to several uncertainties, such as lack of laboratory data, is about 6 times larger than the value derived by the MPIH group. At present time, however, it is difficult to judge whether temperature differences or instrumental factors are responsible for the observed disparities. It is obvious that more in situ and laboratory measurements should be performed to elucidate the problem of negative ion composition in the stratosphere.

References

- Arijs, E., J. Ingels and D. Nevejans, Mass spectrometric measurement of the positive ion composition in the stratosphere, *Nature* **271**, 642-644, 1978.
- Arijs, E., D. Nevejans and J. Ingels, Unambiguous mass determination of the major stratospheric positive ions, *Nature*, **288**, 684-686.

- Arnold, F., H. Böhringer and G. Henschen, Composition measurements of Stratospheric positive ions, *Geophys. Res. Lett.*, **5**, 653-656, 1978.
- Arnold, F. and R. Fabian, First measurements of gas phase sulphuric acid in the stratosphere, *Nature*, **283**, 55-57, 1980.
- Arnold, F., R. Fabian, G. Henschen, and W. Joos, Stratospheric trace gas analysis from ions, H_2O and HNO_3 , *Planet. Space Sci.*, **28**, 681-685, 1980.
- Arnold, F. and G. Henschen, First mass analysis of stratospheric negative ions, *Nature*, **275**, 521-522, 1978.
- Chan, L.Y. and V.A. Mohnen, The formation of ultrafine ion $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ aerosol particles through ion-induced nucleation process in the stratosphere, *J. Aerosol Sci.*, **11**, 35-45, 1980.
- Davidson, J.A., F.C. Fehsenfeld, C.J. Howard, The Heat of Formation of NO_3^- and NO_3^- Association Complexes with HNO_3 and HBr , *Int. J. Chem. Kinetics*, **9**, 17-29, 1977.
- Fehsenfeld, F.C., C.J. Howard and A.L. Schmeltekopf, Gas phase ion chemistry of HNO_3 , *J. Chem. Phys.*, **63**, 2835-2841, 1975.
- Hudson, R.D. and E.I. Reed, The Stratosphere: Present and Future, *NASA reference publication 1049*, 1979.
- Nevejans, D., P. Frederick and E. Arijs, Micro-processor based data acquisition and control system for a balloon borne quadrupole mass filter, to be published.
- Smith D. and M. Church, Ion-recombination rates in the atmosphere, *Planet. Space Sci.*, **25**, 433-439, 1977.
- Turco, R.P., P. Hamill, O.B. Toon, R.C. Whitten and C.S. Kiang, A One-dimensional Model Describing Aerosol Formation and Evolution in the Stratosphere I. Physical Processes and Mathematical Analogs, *J. Atm. Sciences*, **36**, 699-717, 1979.
- Viggiano, A.A., R.A. Perry, D.L. Albritton, E.E. Ferguson and F.C. Fehsenfeld, The Role of H_2SO_4 in stratospheric negative ion chemistry, *J. Geophys. Res.*, **85**, 4551-4555, 1980.

(Received November 18, 1980;
accepted December 8, 1980.)