ION MASS SPECTROMETRY RESEARCH AT THE BELGIAN INSTITUTE FOR SPACE AERONOMY

E. Arijs, D. Nevejans, J. Ingels and D. Fussen

Belgisch Instituut voor Ruimte-Aëronomie, Ringlaan 3, B-1180 Brussel, Belgium

Abstract

A progress report of the research work in stratospheric ion mass spectrometry at the Belgian Institute for Space Aeronomy is given. The results obtained from 1977 up to now are summarized.

In-situ measurements with balloon borne quadrupole mass spectrometers, between 20 and 45 km. altitude are reviewed and discussed. The major stratospheric positive ions observed are proton hydrates $H^+(H_2O)_n$ and ions of the form $H^+X_l(H_2O)_m$. The obtained results allowed a derivation of the mixing ratio profile of X (most probably CH_3CN), which is compared with model calculations.

From the negative ion composition data, showing the presence of NO_3^- and HSO_4^- cluster ions, the density of sulphuric acid in the stratosphere is inferred.

Finally some present and future research is briefly described.
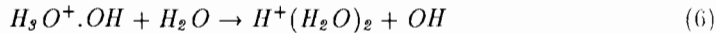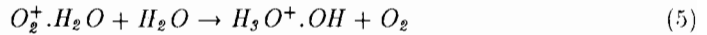
1   Introduction

The main ionization source in the stratosphere is galactic cosmic radiation, yielding mainly N_2^+ and O_2^+ as well as electrons as primary charged particles. The electrons however attach very rapidly to molecular oxygen and as a result the rarefied plasma consists of positive and negative ions. Due to the low ionization rate Q (about 5 ion pairs $cm^{-3}s^{-1}$ at 25 km.)[1] and the value of the ion-ion recombination coefficient α (about $5 \times 10^{-7}cm^3s^{-1}$ at 25 km.) [2], the ion density in the stratosphere is very low. In fact, an application of the simple steady state equation:

$$Q = \alpha n^2 \tag{1}$$

shows that the ion density n at 25 km. is about 3,200 cm^{-3}. Thus very low ion concentrations are expected in the stratosphere. The corresponding lifetime being very long ($\tau = 1/\alpha n$), the ions make many collisions before disappearing through ion-ion recombination.

Some of these inelastic collisions give rise to ion-molecule reactions changing the nature of the ions.

Typical examples of such ion-molecule reactions are:

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2 \tag{2}$$

$$O_2^+ + O_2 + M \rightarrow O_4^+ + M \tag{3}$$

$$O_4^+ + H_2O \rightarrow O_2^+.H_2O + O_2 \tag{4}$$

$$O_2^+.H_2O + H_2O \rightarrow H_3O^+.OH + O_2 \tag{5}$$

$$H_3O^+.OH + H_2O \rightarrow H^+(H_2O)_2 + OH \tag{6}$$

Reactions (2 – 6) are the onset of a rather complicated reaction chain for the positive ions, the description of which is beyond the scope of this report and which is explained in full details in the literature [3, 4]. This reaction chain is completed very fast and converts the primary N_2^+ and O_2^+ ions into the so-called proton hydrates (PH), represented by the formula $H^+(H_2O)_n$, with n ranging from 1 to 4, which were believed to be the terminal positive ions in the stratosphere.

Another reaction chain, involving trace gases such as NO, NO_2 and HNO_3 converts the primary O_2^- ions into $NO_3^-(HNO_3)_m$ clusters.

The information described before was already known before 1977 and had been derived from laboratory work, giving an insight in the possible ion-molecule reactions involved, or from theoretical studies extrapolating the experimental results obtained at higher altitudes (D-region mass spectrometric measurements) [5].

No experimental data for the stratospheric ion composition were available however before 1977. One of the initial objectives of the ION project at our institute therefore was to build a mass spectrometer capable of measuring the ion composition in the stratosphere. This instrument, as well as the results obtained with it, will be briefly described hereafter. It will also be shown that the measurement of the stratospheric ion composition can lead to new detection methods for some trace gases and future possible perspectives will be touched upon.

2 Experimental

The experimental problem, we were faced with at the beginning of this research, was to sample thermalized ions from a gas at rather high pressures (the pressure in the stratosphere is of the order of a few millibars) and to bring them into a *balloon borne* mass spectrometer, which is functioning at high vacuum. This problem, which can be solved rather easily in the laboratory by differential pumping, is far from easy considering that the instrument has to be limited in weight and power consumption, because it has to be brought into the atmosphere with a balloon. Fortunately, stratospheric ballooning techniques allow to carry weights as high as several hundreds of kilograms (at the start of the project in the early seventies, this weight was limited to 350 kg. in Europe). Nevertheless

it should be taken into account that the instrument must be powered by batteries and that it should contain adequate electronics. Furthermore appropriate provisions should be made to recover the instrument undamaged after the balloon flight, meaning that it has to be mounted in a special mechanical support structure capable of withstanding the landing shock. All this means extra, but necessary weight. Through a series of extensive laboratory tests and three technological balloon flights, a solution for all these problems has evolved, which has been described in detail in the literature [6, 7, 8]. We will therefore limit the description to the heart of the instrument as shown in figure 1, which represents the high vacuum part of a typical payload as developed at our institute.
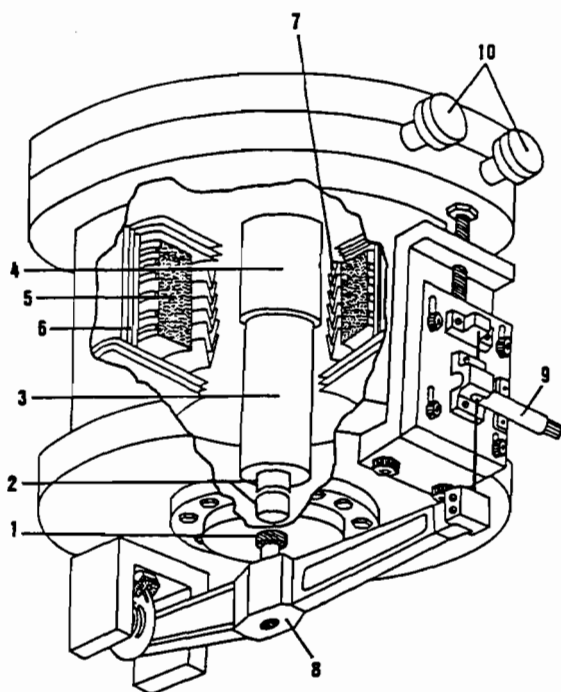

FIG. 1: Sketch of the high vacuum part of the balloon borne mass spectrometer.

1. – Sampling orifice; 2. – Electrostatic ion lens; 3. – Quadrupole mass filter; 4. – Electron multiplier (Spiraltron type 4219); 5. – Liquid helium reservoir; 6. – Aluminized glass fiber superinsulation; 7. – Chevron baffles or thermal shields; 8. – Opening device; 9. – Pyrotechnical cable cutter; 10. – Liquid helium inlet and gaseous helium outlet.

It consists of a high speed cryopump, a sampling hole, a remote opening device and a quadrupole mass filter with an ion focussing device and an ion detector.

On the downward looking large flange of the cryopump, a smaller flange is mounted, electrically insulated from the pump body. This *sampling* flange can by remote control be put on different voltages (*draw-in potentials*) to attract ions. A small hole with a diameter of the order of 0.2 mm is drilled in its central part, which is locally thinned to about 0.1 mm. Prior to the balloon launching, the sampling aperture is covered with a polyimide plunger. When the balloon reaches the desired altitude (between 25 an 45 km.), an opening device activated by telecommand removes this plunger, thus allowing the atmospheric air to flow into the instrument dragging with it the ions. Whereas the neutral gas molecules are pumped by adsorption on the cold walls of the liquid helium container, the ions are

focussed by an electrostatic lens into the quadrupole, where they are filtered according to their mass to charge ratio. Each ion hitting the electron multiplier gives rise to a signal count, which is treated by a pulse discriminator and counter and routed to an on-board microprocessor, which builds up the ion spectra sent to the ground station by telemetry. With an outside pressure of several millibars, the cryopump maintains a vacuum better then 10^{-4} millibar, required to allow proper functioning of the quadrupole and to avoid voltage breakdown in the electron multiplier. The liquid helium cryopump has a standing time of about 10 hours, thus allowing long balloon flights.

The cryopump is suspended on a large aluminium flange of about 80 cm diameter, on which is bolted an hermetically sealed container. This pressurized vessel houses the different electronic modules, such as: the ion lens power supply, the high voltage power supply for the electron multiplier, the power supply for a Penning gauge, the quadrupole drive unit and a microprocessor (*INTEL 8080*) based control and data management system. The quadrupole drive unit generates the DC and RF voltages for the mass filter and is designed such that DC and RF can be controlled independently, thus enabling a great variety of operating modes. With a quadrupole of 6.3 mm diameter rods, the present unit can cover a mass range from 10 to 330 amu at high resolution, using 1500 V peak-to-peak RF excitation at 2 MHz.

The microprocessor based control unit allows, by the combination of a set of simple telecommand signals, the choice of different measurement programs, such as: selection of positive or negative ion mode, selection of mass range and resolution, and choice of pre-programmed measurement tasks.

The electronic modules assembly is connected to an independent telecommand-telemetry system (*SITTEL TM-TC*), which is delivered by the balloon launching organisation (*CNES, Centre National d'Etudes Spatiales, Divisions Ballons, France*).

The complete set up (cryopump, electronics modules and TM-TC) is mounted in a special all metal structure, which protects the instrument during the landing by parachute in the recovery after flight.

3 Results

Since 1977 several balloon flights have been performed with ion mass spectrometers to determine the natural ion composition in the stratosphere. All of these flights were realized in Europe, at the launching base of the *Centre National d' Etudes Spatiales – CNES* in Aire sur l'Adour or Gap-Tallard in Southern France. Only two groups have been successfully active in this field; our group of the *Belgian Institute for Space Aeronomy*, further on abbreviated as *BISA*, and the one of the *Max Planck Institut für Kernphysik* in Heidelberg (FRG), abbreviated hereafter as *MPIH*.

Progress in ballooning techniques (valve controlled balloons, allowing slow descent of the balloon from ceiling altitude, and high volume carriers up to 1,000,000 m^3) have allowed the probing of an atmospheric layer from roughly 20 to 45 km altitude.

The results of most of the measurements have been described extensively in the literature (see review papers by Arnold [9] and Arijs [4, 10]). Therefore we will only give a concise description of it here and focus on the implications for trace gas detection.

3.1 Positive ions

A typical result for positive ions obtained at 35 km altitude is shown in figure 2., which represents the very first spectrum obtained with a balloon borne instrument in the stratosphere [11].This spectrum, taken at moderate resolution, clearly shows the major positive ions present in the stratosphere [11].
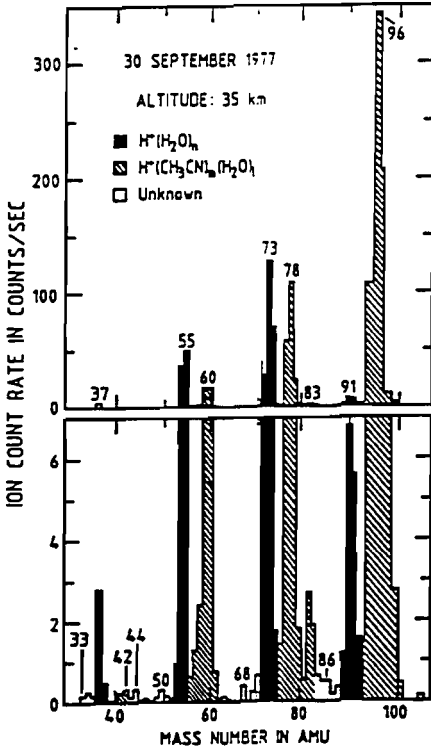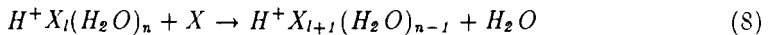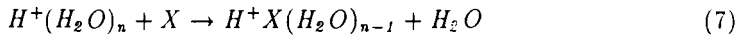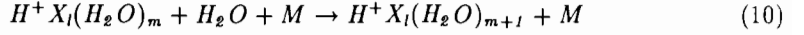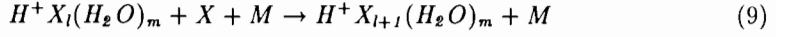

FIG. 2: Positive ion spectrum

First mass spectrum obtained in the stratosphere with a balloon borne instrument on 30 September 1977 at an altitude of 35 km. The spectrum was recorded during nighttime and the mass range was limited to 110 amu.

Apart from the minor mass peaks, indicated as unknown in figure 2, the major positive ions belong to two main groups, which can be represented by $H^+(H_2O)_n$ and $H^+X_l(H_2O)_m$, where X has mass 41. The mass determinations have been confirmed later on by high resolution data of our group [12] and results of the *MPIH* group [13, 14]. As expected from previous modelling work, one major ion family consists of the proton hydrates (*PH*), but apart from this, another group is found, which has been called the non proton hydrates (*NPH*).
The presence of the latter group can be explained by ion-molecule reactions of the type:

$$H^+(H_2O)_n + X \rightarrow H^+X(H_2O)_{n-1} + H_2O \tag{7}$$

$$H^+X_l(H_2O)_n + X \rightarrow H^+X_{l+1}(H_2O)_{n-1} + H_2O \tag{8}$$

$$H^+ X_l (H_2 O)_m + X + M \rightarrow H^+ X_{l+1} (H_2 O)_m + M \qquad (9)$$

$$H^+ X_l (H_2 O)_m + H_2 O + M \rightarrow H^+ X_l (H_2 O)_{m+1} + M \qquad (10)$$

where M is a third body reaction partner (typically oxygen or nitrogen), which does not participate in the reaction, but carries the energy excess. In order to make the switching reactions (7) and (8) possible, the molecule X should have a proton affinity larger than that of water. According to laboratory work [15, 16] and in-situ experiments [17, 18], $CH_3 CN$ or acetonitrile seems to be the most likely candidate for X.

If we accept the formation mechanism of the NPH as proposed in reactions (7) to (10) and assume that the NPH disappear by ion-ion recombination, we can write the steady state equation:

$$k[X][PH] = \alpha[NPH][n^-] \qquad (11)$$

where square brackets denote number densities.

In equation (11) k is the reaction rate coefficient for switching reactions of type (7) and (8), α is the ion-ion recombination coefficient and n^- represent the total negative ion number density, which according to the charge neutrality condition equals the total positive ion number density.

The reaction rate coefficient k and the recombination coefficient α have been measured in the laboratory [15] and n^- can be estimated from previous parametrization studies based on in-situ measurements of total ion densities [19]. Therefore, the number density and consequently the mixing ratio of acetonitrile can be deduced from the observed ratio [NPH]/[PH] in a mass spectrum, if we assume that the peak heights in the spectra are representative for the ion densities.

Figure 3 represents the mixing ratio profile of $CH_3 CN$ as derived with formula (11) for the different balloon flights performed by our group and the MPIH group. The ratio [NPH]/[PH] was derived directly from the spectra.

The ion-ion recombination coefficient was calculated with the expression

$$\alpha = 6 \times 10^{-8} \times (300/T)^{1/2} + 1.25 \times 10^{-25} \times [M] \times (300/T)^4 \qquad (12)$$

where [M] is the total density of the neutral molecules and T the temperature. Expression (12) results in values of α which are in reasonable agreement [20] with laboratory data [15], theoretical values [21] and recent in-situ measurements [22].

The total negative ion density was derived from

$$[n^+] = [n^-] = (Q/\alpha)^{1/2} \qquad (13)$$

where Q was taken from a parametrization of Heaps [23].

The mixing ratio profile of $CH_3 CN$ as shown in figure 3 suggests that we are dealing with a gas which is released at the Earth's surface, diffuses into the atmosphere and is destroyed on its way up. Additional evidence for this was given by the measurements of Snider and Dawson [17], who detected acetonitrile at ground level by an independent method. The results of these authors are also included in figure 3.
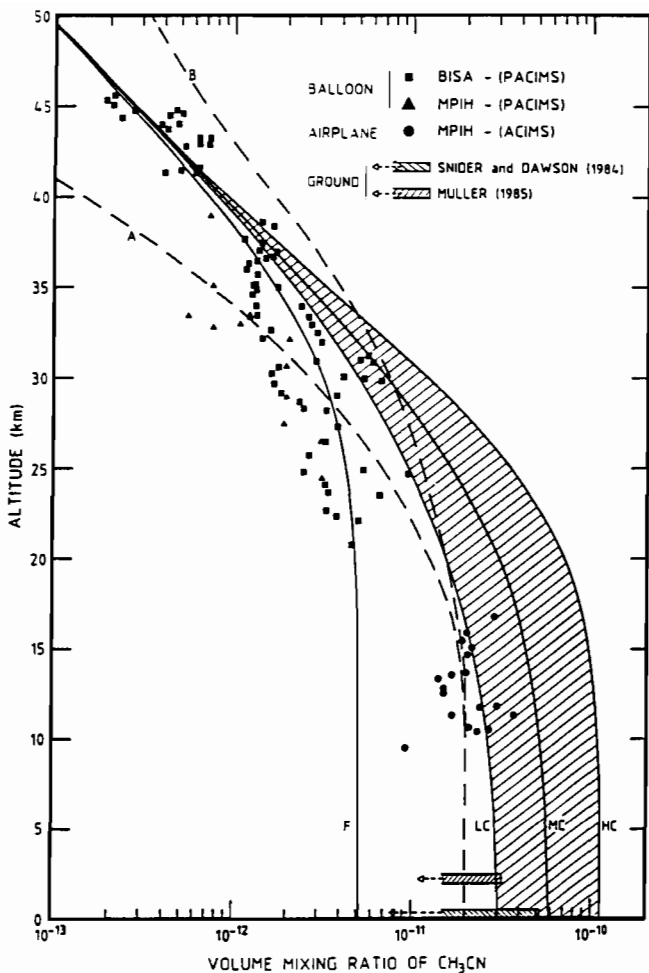
FIG. 3: Volume mixing ratio of acetonitrile versus altitude.

Comparison of experimental data obtained by mass spectrometry and models. PACIMS means "Passive Chemical Ionization Mass Spectrometry" (method explained in section 3.1). ACIMS is "Active Chemical Ionization Method" (see section 5). Possible corrections are indicated and results of ground based measurements obtained with other techniques are also shown. For details see text.

Recently acetonitrile has also been measured in the troposphere by the *MPIH* group using aircraft-borne active chemical ionization mass spectrometry *(ACIMS)*, a method which we will return to in section 4 [24]. The data of the *MPIH* group are consistent with the results of Snider and Dawson and the estimation for the upper limit of the CH_3CN mixing ratio, deduced by Muller [25] from infrared spectra obtained at Kitt Peak Observatory.
In order to explain the mixing ratio profile shown in figure 3 modelling efforts were made at our institute [26, 27]. Two typical results of these theoretical investigations are represented by curves A and B in figure 3. The major difference between both curves is that for the main destruction process of acetonitrile, i.e. reaction with hydroxyl radicals, reaction rate coefficients from different laboratory measurements were used [27]. The

yearly global emissions (or quantity of material released over the whole Earth per year) required to obtain an acceptable fit between the model results and the experimental data are in reasonable agreement with estimations of the releases from possible sources, such as car exhaust gases, direct releases from industry and biomass burning [27].

Also shown in figure 3 is a least square fit (curve F) through all the balloon data. As can be seen for altitudes larger than 30 km. this fit lies within the two model curves A and B, which are themselves in agreement with the airplane and ground data. Below 30 km however the agreement between the theory and the fit to the balloon data is unsatisfactory. The reason for this has recently been discovered and is due to experimental problems. Laboratory and in flight tests [28, 29] have indeed shown that when the ambient pressure is above a certain value (which is the case below 30 km.), the sampled ions undergo too many collisions in the jet expansion region just behind the sampling orifice of the instrument. Due to the accelerating electric fields induced by the ion lens, some of these collisions are so energetic that the ions are breaking up into fragments. Such collision induced dissociation (CID) may result in the loss of a CH_3CN ligand and some NPH can be reconverted to PH, thus falsifying the *[NPH]/[PH]* ratio to be used in equation (5). Preliminary laboratory work [28] indicated that the correction for CID are of the right order of magnitude to explain the discrepancies observed in figure 3.

Recently a theoretical study of CID was done by our group [30]. Unfortunately CID cross sections of NPH $\sigma(NPH)$ are not known and therefore the correction to be applied to curve F can only be estimated. It turns out however that curve F shifts to LC, MC or HC depending on whether we put $\sigma(NPH) = 1/2 \times \sigma(PH)$, $\sigma(NPH) = \sigma(PH)$ or $\sigma(NPH) = 2 \times \sigma(PH)$. As seen in figure 3 the agreement between balloon data and model calculations becomes more acceptable now.

3.2 Negative ions

The first stratospheric negative ion composition data obtained with a balloon borne instrument were reported by Arnold and Henschen [31]. They showed that two major negative ion families are present in the stratosphere. The first one consists of $NO_3^-(HNO_3)_n$ cluster ions, as predicted by laboratory work [32] and extrapolations from D-region ion chemistry. The second family however was unforeseen and its members could be represented by $R^-(HR)_l(HNO_3)_m$, R having a mass of 97 amu. Arnold and Henschen [31] suggested that the latter group of ions resulted from reactions of $NO_3^-(HNO_3)_n$ ions with sulphuric acid and hence proposed H_2SO_4 for HR. This gas is indeed formed in the stratosphere through photochemical oxidation of SO_2. The rate constants of the reaction

$$NO_3^-(HNO_3)_n + H_2SO_4 \rightarrow HSO_4^-(HNO_3)_n + HNO_3 \qquad (14)$$
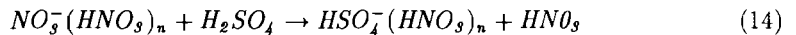
have been measured in the laboratory by Viggiano et al. [33, 34]. Values of 2.6×10^{-9}, 2.3×10^{-9} and $1.1 \times 10^{-9} cm^3 s^{-1}$ were found for n = 0, 1 and 2 respectively.

In 1980, Arijs et al. [35] measured the first high resolution spectra of negative ions around 35 km. A typical spectrum of these measurements is shown in figure 4.
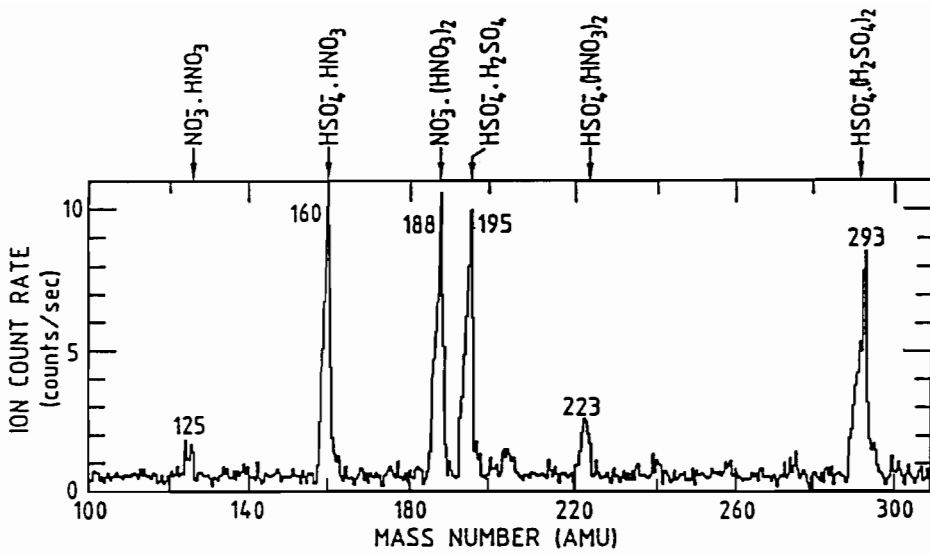
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FIG. 4.: Negative ion spectrum.

Typical nighttime spectrum for negative ions obtained near 35 km. altitude. Mass numbers, as well as ion identification are indicated.

These data allowed an unambiguous mass identification of the major ions and confirmed the H_2SO_4 hypothesis.

Negative ion spectra have now been obtained in the altitude range from 20 to 45 km. by our group and the *MPIH* team [36 – 44]. They all show that the major negative ions over the whole altitude range are cluster ions with cores of NO_3^- or HSO_4^-. Variations of the fractional ion abundances with altitudes are caused by variations of the sulphuric acid concentration in the stratosphere.

By using a similar steady state treatment as for positive ions, the number density of H_2SO_4, converting NO_3^- clusters into HSO_4^- clusters, can again be deduced from:

$$k_2[H_2SO_4][n_N] = \alpha[n_S][n^+] \tag{15}$$

where n^+ is the total positive ion density, $[H_2SO_4]$ the sulphuric acid number density, k_2 the rate coefficient of reaction (14) and $[n_N]$ and $[n_S]$ the total number densities of NO_3^- or HSO_4^- clusters respectively.

A compilation of the recent results thus obtained by our group is shown in figure 5. Also shown in figure 5 is the envelope (two full lines E1 and E2) of all measurements of H_2SO_4 by ion mass spectrometry, including those of the *MPIH* group, the vapour pressure of H_2SO_4 calculated as explained in detail elsewhere [42] (curve H) and two typical model calculations of sulphuric acid concentration profiles by Turco et al.[45] (curves A and B). The agreement between curve H and the measurements in the altitude region from about 28 to 33 km suggests that in this region the H_2SO_4 number density is controlled by the evaporation- recondensation equilibrium of aerosol droplets.
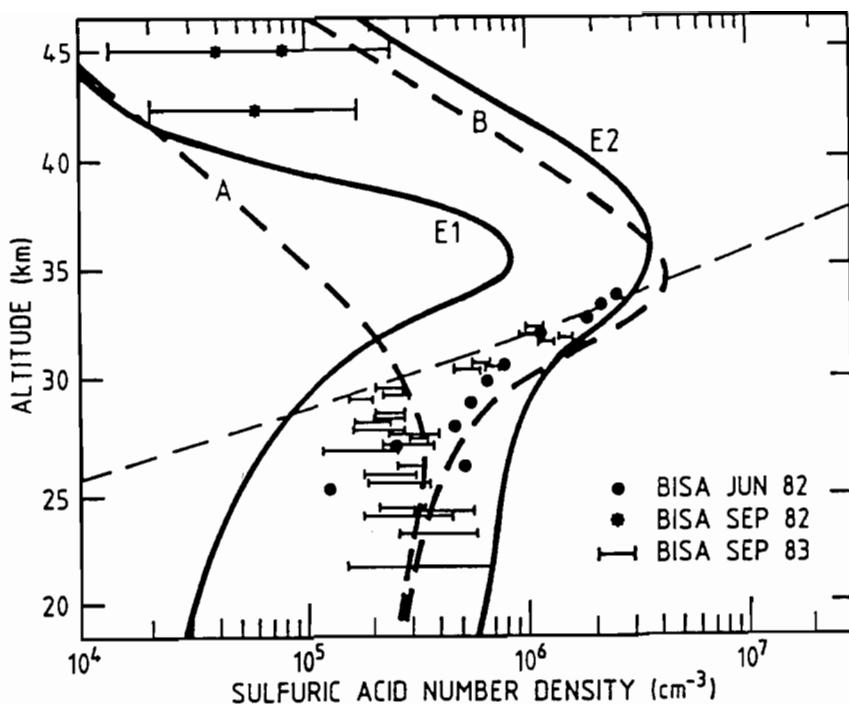
FIG. 5.: Sulfuric acid number density vs. altitude.

Stratospheric H_2SO_4 concentrations as derived from negative ion mass spectra, compared to model calculations (curves A and B). Curve H is a representation of the H_2SO_4 vapour pressure (expressed as a number density) taking into account the temperature gradient in the stratosphere.

Below 28 km, the H_2SO_4 vapour is clearly in supersaturation, suggesting that the liquid-vapour equilibrium is disturbed by the oxidation of SO_2 vapour through the reactions:

$$SO_2 + OH + M \rightarrow HSO_3 + M \tag{16}$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{17}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{18}$$

The main loss processes for sulphuric acid vapour are interaction with aerosols. Above 35 km, the measurements seem to suggest a good agreement with curve B, obtained through modelling and assuming a loss of H_2SO_4 by reaction with *smoke particles*, caused by a downward metal flux of $10^6 cm^2 s^{-1}$ from meteoric debris [45].

Another important trace gas, the concentration of which can also be derived from negative ion composition data is HNO_3. Apart from the steady state method explained in the previous paragraphs for CH_3CN and H_2SO_4, another technique, called the equilibrium

method [37, 46] can be applied here. This method is based on the fact that the number density ratio of two cluster ion species from the same family such as $NO_3^-(HNO_3)$ and $NO_3^-(HNO_3)_2$ is given by:

$$[NO_3^-(HNO_3)_2] = K \times [NO_3^-(HNO_3)] \times p(HNO_3) \qquad (19)$$

where square brackets again denote number densities, $p(HNO_3)$ is the partial pressure of nitric acid and K is the equilibrium constant of the reaction:

$$NO_3^-(HNO_3) + HNO_3 + M \rightleftharpoons NO_3^-(HNO_3)_2 + M \qquad (20)$$
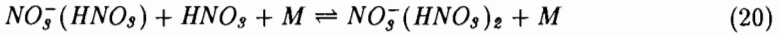
Since K can be derived from laboratory measurements, $p(HNO_3)$ can be inferred from the ratio of the peak intensities observed at mass 188 ($NO_3^-(HNO_3)_2$) and 125 ($NO_3^-(HNO_3)$), observed in the negative ion spectra.

The data derived in this way however [10] are, compared to model calculations and other experimental results obtained by optical methods [47], only valid for altitudes above 30 km. The reason for this is again CID which reconverts $NO_3^-(HNO_3)_2$ ions back into $NO_3^-(HNO_3)$ ions in the mass spectrometer sampling region. For this reason the equilibrium method has not been fully exploited.

As will be explained in the next section nitric acid concentrations can be more accurately derived from active chemical ionization mass spectrometry (ACIMS).

4   Conclusions and future perspectives

It has been shown that from the spectra of natural stratospheric ions obtained hitherto, the concentration of at least three kind of trace gases can be derived, namely CH_3CN, H_2SO_4 and HNO_3. Although acetonitrile does not play an important role in any of the major atmospheric cycles, attention has been paid to it, merely to obtain a consistent picture of the positive stratospheric ion chemistry [27, 28].

Sulphuric acid however is a much more important trace gas, since it is the precursor of aerosols, which, in the stratosphere, consist of microscopic droplets or crystals of a mixture of water and H_2SO_4. These aerosols may have an impact on the Earth's radiation budget and thus on our climate. Furthermore aerosols are considered as the seat for some heterogeneous reactions which are believed to be responsible for the Antarctic ozone hole formation [50, 51]. Strong volcanic eruptions can enhance the concentration of sulphur compounds in the stratosphere considerably, and as a result of the oxidation of these sulphur compounds, the H_2SO_4 number density can also increase significantly, leading to a high aerosol concentration. It can therefore be speculated that some of the heterogeneous reactions which cause the ozone depletion at the South Pole may occur at other latitudes. A study of sulphuric acid in the stratosphere is therefore extremely important.

So far only the major mass peaks of ion spectra have been used for the derivation of trace gas profiles. An investigation of the lower part of figure 2 however, shows that the minor mass peaks (indicated as *unknown* in figure 2) can be assigned to some other trace gases. For instance the masses indicated as 33, 50, 68 and 86 are, due to the low signal, very difficult to identify and may in reality be 33, 51, 67 (and/or 69) and

85 (and/or 87). In this case they could be due to protonated methanol cluster of the form $H^+.CH_3OH(H_2O)_n$ (methanol in the stratosphere being a result of the oxidation of methane). Also negative ion spectra show several smaller peaks [37], which are due to so far undetected gases. It is therefore evident that if more sensitive ion mass spectrometers can be developed, a wealth of information may be inferred from ion mass spectrometery. Presently however the method for derivation of trace gas concentrations from ion mass spectrometry, although very sensitive, suffer from several drawbacks, such as:

• the method is limited to those gases, which intervene in the final stages of the ion-molecule reaction chain, leading to the terminal ions

• cluster break up of the sampled ions just behind the sampling hole of the mass spectrometer can lead to falsified results (re-conversion of *NPH* to *PH* for instance) and need to be studied more in detail before using results of more sensitive instruments

• the exploitation of ion mass spectra strongly depends upon the availability of laboratory data, such as reaction rate constants of appropriate ion-molecule reactions and thermochemical data. Therefore laboratory studies should be performed in parallel with in- situ measurements.

Recently the *MPIH* group has developed a new method for the derivation of trace gases from ion mass spectrometry, called *ACIMS* [49]. This method relies upon the reactions of atmospheric trace gases with ions produced by an external ion source, mounted in front of the mass spectrometer, leading to specific product ions. From the relative abundance of the signals of the precursor and product ions in the spectra obtained with the ion source, the mixing ratios of the reactive trace gases can be determined. This technique is very promising and has allowed recently to give evidence for the coupling between denitrification and polar stratospheric cloud formation [52], two important phenomena in the ozone hole formation.

In view of the previous considerations the future research in ion mass spectrometry at our institute is oriented towards two major directions:

• The development of a novel balloon borne mass spectrometer *SIDAMS* based upon the combination of a Mattauch-Herzog filter with a simultaneous ion detection system [53]. This effort should result in a new instrument capable of detecting positive and negative ions with an enhanced sensitivity, higher resolution and less *CID* effects.

• Development of new selective ion sources to be used with the new mass spectrometer for *ACIMS* application to the detection of HNO_3 and N_2O_5, two trace gases playing an important role in the ozone hole formation. The innovation of our *ACIMS* technique lies in the fact that an ion source will be developed, which produces mainly Cl^- and I^- ions. The Cl^- ions react both with HNO_3 and N_2O_5, whereas I^- only reacts with N_2O_5. Both reactions result in NO_3^- core ions. Since the reaction rate coefficients of the three ion-molecule reactions involved have been measured in the laboratory [32, 54], the HNO_3 and N_2O_5 concentrations can be derived from the abundance ratios $[NO_3^-]/[Cl^-]$ and $[NO_3^-]/[I^-]$ measured with the ion mass spectrometer equipped with the selective ion source.

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