

1. ION MASS SPECTROMETRY AND RELATED TRACE GAS DETECTION IN THE STRATOSPHERE

Etienne Arijs,
Dennis Nevejans, Johan Ingels, Didier Fussen,
Piet Frederick, Crist Amelynck

Belgisch Instituut voor Ruimte Aeronomie
Ringlaan 3, B-1180 Brussel

ABSTRACT

An overview of the research work in stratospheric ion mass spectrometry, modeling and laboratory work on stratospheric ion chemistry and related trace gas detection 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 (CH_3CN), which is compared with model calculations.

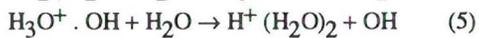
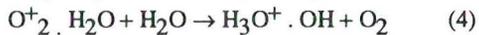
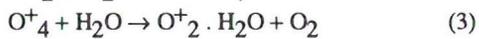
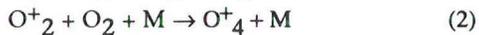
From the negative ion composition data, showing the presence of NO_3^- and HSO_4^- cluster ions, the density of sulfuric acid in the stratosphere is inferred.

The results obtained have led to a consistent picture of the stratospheric ion chemistry as far as concerns the major positive and negative ions.

Finally some present and future research efforts concerning the possible use of ion mass spectrometry for selective stratospheric trace gas detection are briefly described.

INTRODUCTION

Whereas, at altitudes above 50 km the ionization in the Earth's atmosphere is provoked by energetic particles and solar UV radiation, the main ionization source in the stratosphere is galactic cosmic radiation. Due to the high energy of the cosmic rays the ionization in the stratosphere is non-selective and yields mainly N_2^+ and O_2^+ as well as electrons as primary charged particles. The electrons attach very rapidly to molecular oxygen and as a result the rarefied "stratospheric plasma" consists of positive and negative ions. As a result of the weak 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 $5 \times 10^{-7} cm^{-3}s^{-1}$ at 25 km)^[2], the ion density in the stratosphere is very low. Application of the simple steady state equation ($Q = \alpha n^2$), indicates that the ion density n at 25 km is about $3,200 cm^{-3}$. Thus nominal ion concentrations are expected in the stratosphere. The corresponding lifetime being very long ($\tau = 1/\alpha n$), the ions can make many collisions with neutrals before disappearing through ion-ion recombination. Some of these collisions result in ion - molecule reactions changing the nature of the ions. For the positive ions some typical ion - molecule reactions are:



Reactions (1 to 5) are the start of a rather complicated reaction chain for the positive ions, the description of which is beyond the scope of this report and which is discussed to full extent in the literature ^[3,4,5]. This reaction chain is completed in a short time, compared to the long ion lifetime and converts the primary N_2^+ and O_2^+ ions into the so-called hydronium ions or proton hydrates (PH), represented by the formula $\text{H}^+(\text{H}_2\text{O})_n$, 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 above was already known before 1977 and had been derived from laboratory work about possible stratospheric ion-molecule reactions or from theoretical studies extrapolating the experimental results obtained at higher altitudes, such as mass spectrometry measurements in the D-region of the ionosphere ^[6].

However, no experimental data for the stratospheric ion composition were available 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 summarized in this report. 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 discussed.

EXPERIMENTAL

The experimental problem, encountered in the early stage of this research, was sampling thermalized ions from a relatively high pressure gas (stratospheric pressures are of the order of a few millibars) and leading them into a *balloon-borne* mass spectrometer, functioning at high vacuum. This problem, solved straightforward in the laboratory by differential pumping, is rather troublesome in a balloon-borne experiment, considering that the instrument has to be limited in weight and power consumption. 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, the weight limit was 350 kg in Europe). Nevertheless it should be kept in mind that the instrument apart from containing the mass spectrometer and the pumping system, should contain adequate electronics and must be powered by batteries. Furthermore appropriate provisions should be made to recover the instrument undamaged after the balloon flight, requiring a mounting in a special mechanical support structure capable of withstanding the landing shock. All this means extra, but necessary weight. The final instrument, overcoming these problems evolved from a series of extensive laboratory tests and several balloon flights, and is described briefly hereafter (details can be found in the literature ^[7,8,9]).

The heart of a typical payload as developed at our institute is shown in figure 1, which represents the high vacuum part of the instrument.

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

On the bottom of the cryopump, an electrically insulated *sampling* flange is mounted, which, by remote control, can be put on different voltages (*draw-in potentials*) to attract ions. A small hole with a diameter of about 0.2 mm is drilled in its central part, 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 and 45 km), a pyrotechnical opening device activated by telecommand re-

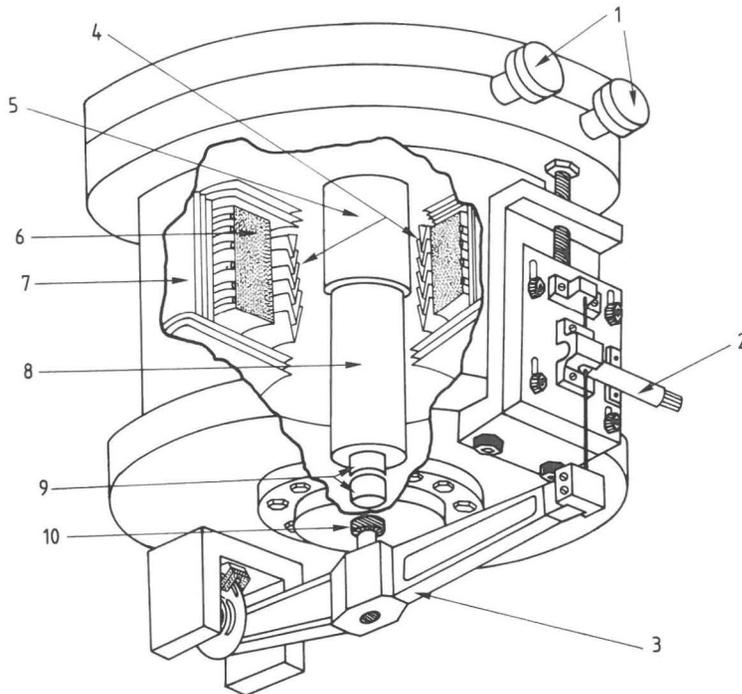


Figure 1: High vacuum part of the balloon-borne mass spectrometer . 1. Sampling orifice; 2. Electrostatic ion lens; 3. Quadrupole mass filter; 4. Electron multiplier; 5. Liquid helium reservoir; 6. Aluminized glass fiber superinsulation; 7. Chevron baffles or thermal shields; 8. Opening device; 9. Pyrotechnical cable cutter; 10. Liquid helium inlet and gaseous helium outlet.

moves 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 focused 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 pulse, which is counted by a pulse discriminator and counter connected to an onboard microprocessor. The latter builds up the ion spectra sent to the ground station by telemetry.

With an outside pressure of several millibars, the cryopump maintains a vacuum of the order of 10^{-5} 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 aluminum 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 80C86*) 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 programmes, 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 (*SIT-TEL TMTC*), which is delivered by the balloon launching organization (*CNES, Centre National d'Etudes Spatiales, Division Ballons, France*).

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

RESULTS

Since 1977 a series of 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 m³) 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 ^[10], Ferguson and Arnold ^[9], Arijis ^[4, 5] and Arijis et al. ^[11]). We will therefore only give a concise description here and merely focus on the implications for trace gas detection.

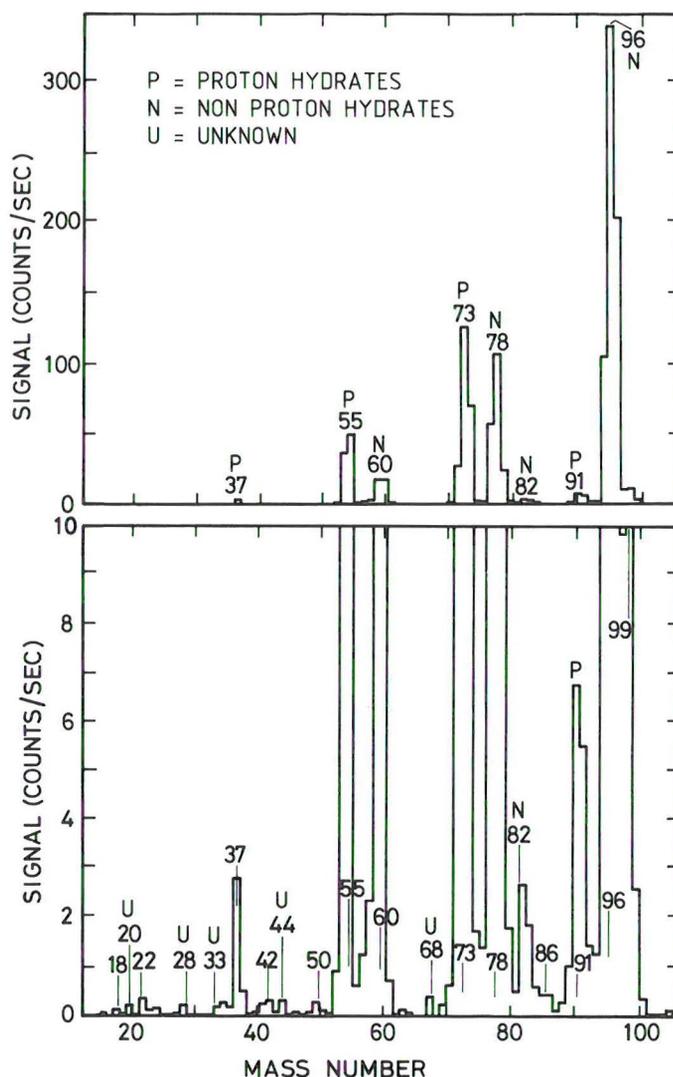


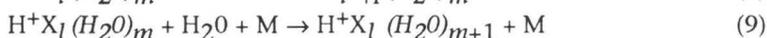
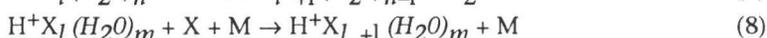
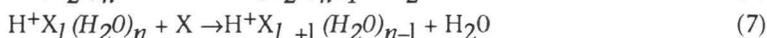
Figure 2: First mass spectrum obtained in the stratosphere with a balloon-borne instrument on 30 September 1977 at an altitude of 35 km. The spectrum was recorded during nighttime and the mass range was limited to 110 amu.

1 POSITIVE IONS

A typical spectrum of positive ions obtained at 35 km altitude is represented in figure 2, showing the very first spectrum obtained with a balloon-borne instrument in the stratosphere ^[12].

This spectrum, recorded at moderate resolution, clearly reveals the major positive ions present in the stratosphere.

Apart from the minor mass peaks, indicated as unknown in figure 2, the major positive ions belong to two main families, which can be represented by $H^+(H_2O)_n$ and $H^+X_l (H_2O)_m$, where X has mass 41. These mass determinations were confirmed later by high resolution data of our group ^[13] and results of the MPIH group ^[14, 15]. As expected from previous modeling work, one major ion group consists of the proton hydrates (PH). Apart from this, however, another group is found, called the non proton hydrates (NPH), the presence of which was explained by ion-molecule reactions of the type:



where M is a third body reaction partner (typically oxygen or nitrogen), not participating in the reaction, but carrying the energy excess. To allow for switching reactions (6) and (7) to take place, the molecule X must have a proton affinity larger than that of water. According to later laboratory work ^[16, 17] and in-situ experiments ^[18, 19], CH_3CN or acetonitrile seems to be the most likely candidate for X.

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

$$k[X][PH] = \alpha[NPH][n^-] \quad (10)$$

where square brackets denote number densities.

In equation (10) k is the reaction rate coefficient for switching reactions of type (6) and (7), 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 ^[16] and n^- can be estimated from previous parameterization studies based on in-situ measurements of total ion densities ^[20]. 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_3CN as derived with formula 10 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

$$\alpha = 6 \times 10^{-8} \times (300/T)^{1/2} + 1.25 \times 10^{-25} \times [M] \times (300/T)^4 \quad (11)$$

where [M] is the total density of the neutral molecules and T the temperature. Expression 11 results in values of α which are in reasonable agreement ^[21] with laboratory data ^[16], theoretical values ^[22] and recent in-situ measurements ^[23].

The total negative ion density was derived from

$$[n^+] = [n^-] = (Q/\alpha)^{1/2} \quad (12)$$

where Q was taken from a parameterization of Heaps ^[24].

The mixing ratio profile of CH_3CN as shown in figure 3 suggests that this gas 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 ^[18], who detected acetonitrile at ground level by an independent method. The results of these authors are also included in figure 3.

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 discuss in section 4 ^[25]. The MPIH-data are consistent with the results of Snider and Dawson and the CH_3CN upper limit estimation deduced by Muller ^[26] from infrared spectra obtained at Kitt Peak Observatory.

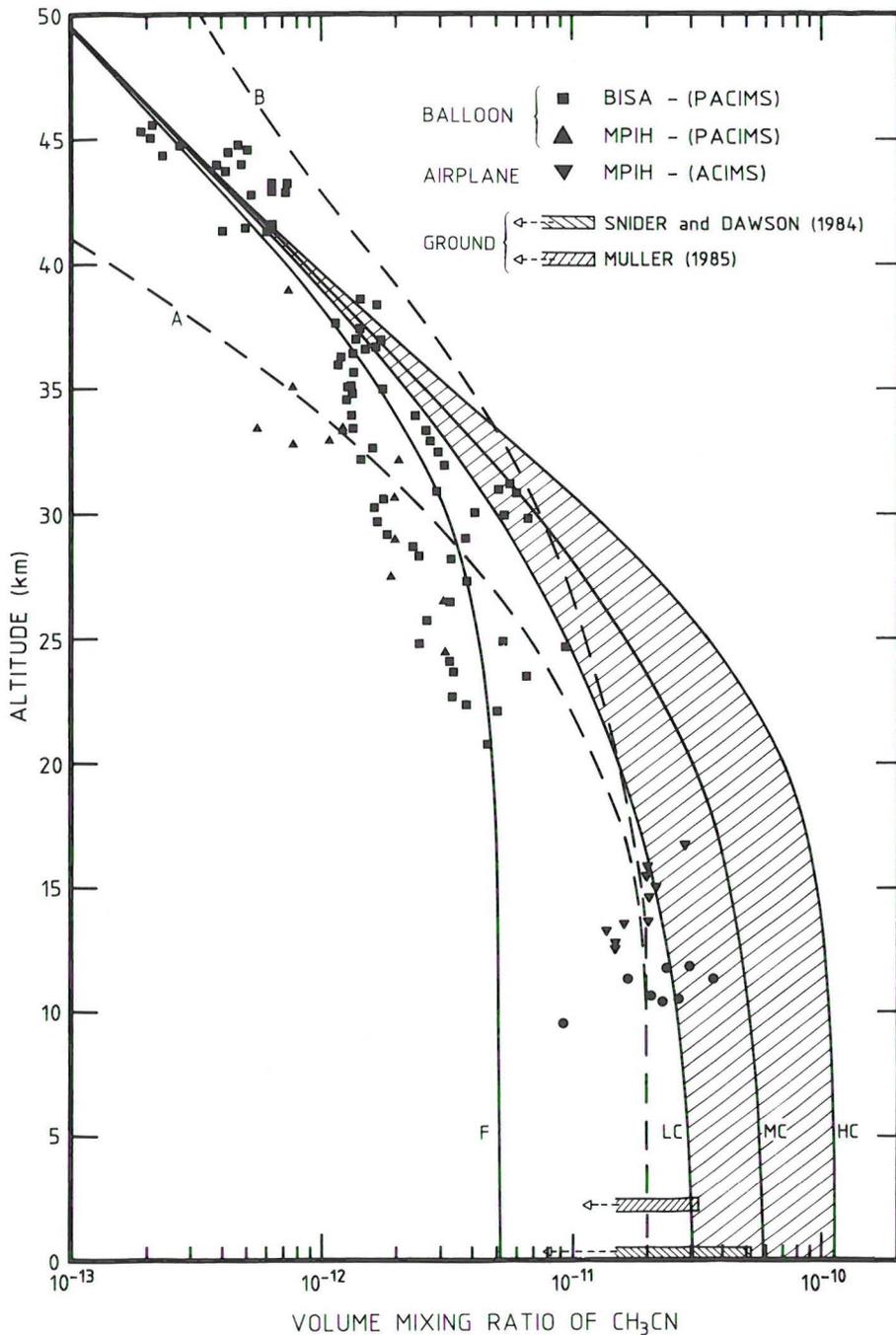


Figure 3 : Comparison of experimental data obtained by mass spectrometry and models. PACIMS means "Passive Chemical Ionization Mass Spectrometry" (method explained in section 3.1). ACIMS is "Active Chemical Ionization Method" (see section 5). Possible corrections are indicated and results of ground based measurements obtained with other techniques are also shown. For details see text.

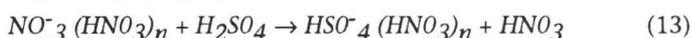
To explain the mixing ratio profile shown in figure 3, modeling efforts were made at our institute ^[27, 28]. Two typical results of these theoretical investigations are represented by curves A and B in figure 3. The major difference between both curves is that for the main destruction process of acetonitrile, i.e. reaction with hydroxyl radicals, reaction rate coefficients from different laboratory measurements were used ^[28]. 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 ^[28] and the recent calculation of Hamm et al ^[29, 30].

Also shown in figure 3 is a least square fit (curve F) through all the balloon data. As can be seen for altitudes above 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 is now believed to be due to experimental problems. Laboratory and in flight tests ^[31, 32] 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 ^[31] indicated that the corrections 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 ^[33]. 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 $\sigma(NPH) = 1/2 \times \sigma(NPH)$, $\sigma(NPH) = \sigma(NPH)$ or $\sigma(NPH) = 2 \times \sigma(NPH)$. As seen in figure 3 the agreement between balloon data and model calculations becomes more acceptable now.

2 NEGATIVE IONS

The first stratospheric negative ion composition data obtained by the MPIH team ^[34] with a balloon-borne instrument, showed the presence of two major negative stratospheric ion families. Whereas the first one, the $NO_3^-(HNO_3)_n$ cluster ions, were predicted by laboratory work ^[35] and extrapolations from D-region ion chemistry, the second family was unexpected. The ions of this group can be represented by $R^-(HR)_l(HNO_3)_m$, R having a mass of 97 amu. Arnold and Henschen ^[34] suggested that these ions were formed through reactions of $NO_3^-(HNO_3)_n$ ions with sulfuric acid and hence proposed H_2SO_4 for HR. This gas was expected in the stratosphere as a result of the photo-chemical oxidation of sulphur compounds (mainly SO_2) but had never been measured before 1978. To check the previous hypothesis, the rate constants of the reaction



were measured in the laboratory by Viggiano et al. ^[36]. Values of 2.6×10^{-9} , 2.3×10^{-9} and $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ were found for $n = 0, 1$ and 2 respectively.

In 1980 the BISA team ^[37] recorded the first high resolution negative ion spectra around 35 km. These data, a typical sample of which is shown in figure 4, allowed an unambiguous mass identification and confirmed the H_2SO_4 hypothesis.

Negative ion spectra, obtained in the altitude range from 20 to 45 km by our group and the MPIH team ^[38-46], show that the major negative ions over the whole altitude range are cluster ions with cores of NO_3^- or H_2SO_4 . Fractional ion abundance variations with altitudes are caused by the sulfuric acid altitude dependent concentration in the stratosphere.

Through a similar steady state treatment as for positive ions, the number density of H_2SO_4 , converting NO_3^- clusters into H_2SO_4 clusters, can be derived from:

$$k_2[H_2SO_4][n_N] = \alpha[n_S][n^+]$$

Here n^+ is the total positive ion density, $[H_2SO_4]$ the sulfuric 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 results inferred with this method by our group is represented in figure 5.

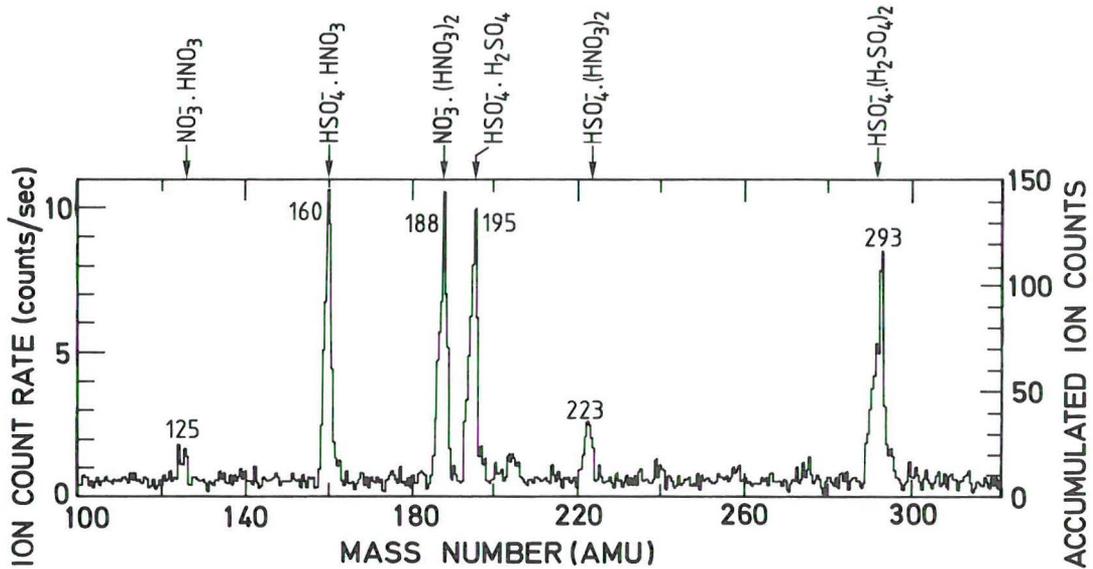


Figure 4 : Typical nighttime spectrum for negative ions obtained near 35 km altitude. Mass numbers, as well as ion identification are indicated.

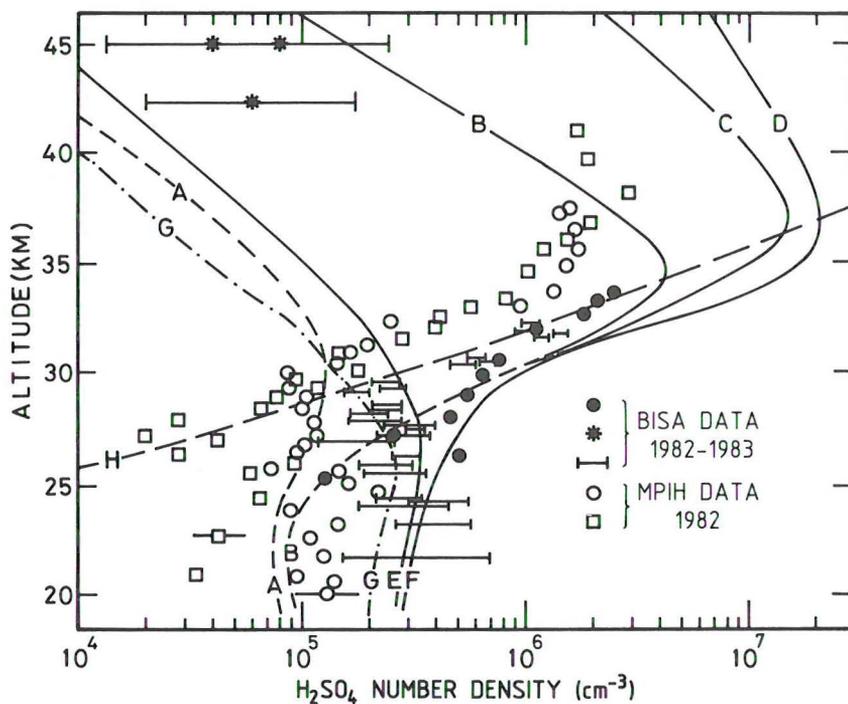


Figure 5 : Stratospheric H_2SO_4 concentrations as derived from negative ion mass spectra, compared to model calculations (curves A and B). Curve H is a representation of the H_2SO_4 vapor pressure (expressed as a number density) taking into account the temperature gradient in the stratosphere.

Also shown in figure 5 is the envelope of all measurements of H_2SO_4 by ion mass spectrometry, including those of the MPIH group (two full lines E1 and E2), the vapor pressure of H_2SO_4 calculated as explained in detail elsewhere^[44] (curve H) and two typical model calculations by Turco et al.^[47] (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.

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



The main loss processes for sulfuric acid vapor are interaction with aerosols. Above 35 km, the measurements seem to suggest a good agreement with curve B, obtained through modeling and assuming a loss of H_2SO_4 by reaction with smoke particles, caused by a downward metal flux of $10^6 \text{ cm}^{-2} \text{ s}^{-1}$ from meteoric debris^[47].

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^[40, 45] 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:

$$[NO_3^- (HNO_3)_2] = K \times [NO_3^- (HNO_3)] \times p(HNO_3) \quad (18)$$

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:



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^[11] are, compared to model calculations and other experimental results obtained by optical methods^[48], only valid for altitudes above 30 km. The reason for this is probably 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).

RECENT WORK AND FUTURE PERSPECTIVES

It has been shown in the previous sections that apart from giving a better insight into the stratospheric ion chemistry, ion mass spectrometry has allowed the derivation of the concentration of at least three trace gases, namely CH_3CN , H_2SO_4 and HNO_3 . Although acetonitrile does not play a major role in any of the important atmospheric cycles, attention has been paid to it, merely to obtain a consistent picture of the positive stratospheric ion chemistry^[28, 31].

Sulfuric acid however is a much more important trace gas, since it is believed to be one of the precursors 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^[49, 50]. Strong volcanic eruptions can en-

hance 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 sulfuric acid in the stratosphere is therefore extremely important.

Presently however the method for derivation of trace gas concentrations from ion mass spectrometry, although very sensitive, suffers from several drawbacks, such as:

- the method is limited to those gases, which participate in 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 (reconversion of NPH to PH for instance) and needs to be studied
- 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 .

Some years ago the MPIH group has developed a new method for the derivation of trace gases from ion mass spectrometry, called ACIMS^[51]. 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. The ion source of the MPIH group is based upon the ionization of the ambient air by a high frequency high voltage discharge and produces mainly CO_3^- ions and its clusters as precursor ions, which react with HNO_3 to produce NO_3^- ions. This technique, allowing the derivation of nitric acid concentrations with only little disturbance by CID effects, is very promising and has recently given evidence for the coupling between denitrification and polar stratospheric cloud formation^[52], two important phenomena in the ozone hole mechanism.

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

1. 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 . This effort should eventually result in a new instrument capable of detecting positive and negative ions with an enhanced sensitivity, higher resolution and less CID effects.
2. 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^[35, 53], 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.

Both points have been the subject of two projects, partially financed by the Commission of the European Communities (CEC) and undertaken in a collaboration between the Belgian Institute for Space Aeronomy (Brussels, Belgium), the "Laboratoire de Physique et Chimie de l'Environnement du CNRS (Orléans, France) and the "Physikalisches Institut" of the University of Bern (Switzerland).

The realization of a new generation of balloon-borne ion mass spectrometers based upon the combination of a double focusing "Mattauch-Herzog" magnetic mass analyzer and a detector allowing the simultaneous detection of a mass spectrum on the focusing plane^[54] was performed within the SIDAMS project (CEC contract STEP0009M(A)) and has proceeded in two steps. In a first step a positive ion instrument was constructed and tested, and in a second step a similar apparatus for negative ions was realized. Both mass spectrometers were tested in technological balloon flights and although for the measurement of the natural ions some sensitivity improvements are required, the instruments seem to be quite suitable for the ACIMS method, from the point of view of technical performance, speed, sensitivity and resolution.

The second phase of the new research encloses the development of ion sources for the production of Cl_n^- and I_n^- ions, the realization of the associated balloon-borne electronics (hard and software) and the

coupling of these ion sources to the mass spectrometer, developed in the first phase. Two balloon flights for the testing of the new unit in the stratosphere are also planned. This phase is now under development within the CEC project MACSIMS (CEC contract EV5VCT920062), started in 1993.

The application of the ACIMS method also requires some laboratory work for the study of ion-molecule reactions. For this purpose a new laboratory instrument, a flow tube coupled to a quadrupole mass spectrometer has been built in our institute. With this instrument a number of reactions, which have not been measured before, but the understanding of which is necessary for the exploitation of the ACIMS method, have been studied. For the reactions of I, F, Br^- and $HFBr$ with Cl_2 ^[55] and for those of nitric acid with di- and trichloride ions, di- and triiodide ions and with CO_4^- in the gas phase ^[56], previously unknown rate coefficients have been measured.

CONCLUSIONS

The efforts of the mass spectrometry team of the Belgian Institute for Space Aeronomy have, through a series of experiments with in-house designed and built balloon-borne ion mass spectrometers, resulted in a fairly complete and previously unknown data set on the ion composition of the Earth's atmosphere in the altitude region 25 to 40 km. This data set, which is in good agreement with the results obtained by the only other group doing similar work (the Max-Planck-Institut für Kernphysik in Heidelberg, Germany), has allowed an understanding of the ion chemistry in the stratosphere. It has been found that the ion composition of the stratosphere is mainly controlled by the presence of trace gases with very low concentrations. For the positive ions the controlling gas is acetonitrile. The behavior of this gas, which was not expected in the stratosphere, has also been studied in our institute through modeling efforts, which included the positive ions. The results of these models, based upon available laboratory data, are in good agreement with our observations and lead to a consistent picture of the positive stratospheric ion chemistry. Furthermore it has been shown that ion mass spectrometry can be a very powerful tool for trace gas detection down to the ppb level.

For the negative ion chemistry, the major controlling trace gases are nitric acid and sulfuric acid. The ion mass spectra obtained by our group have allowed the derivation of the concentration profile of H_2SO_4 , which together with the results of the MPIH team, are the only data yet available about this constituent in the stratosphere. Although some uncertainties remain about the negative ion chemistry, due to incomplete models and insufficient laboratory data, a better understanding of the underlying processes has been obtained.

The experimental work of both the MPIH and the BISA teams have opened the way for the development of a new technique for trace gas detection through active chemical ionization. This technique may turn out to be extremely useful for the study of localized phenomena, such as the ozone hole formation, where in-situ probing is the only means for giving information, complementary to remote sensing, required for a full understanding of all phenomena.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the following organisms, which have, in addition to the tutorial authorities, given the financial support to make their research possible:

- "Fonds voor Fundamenteel Onderzoek van het Nationaal Fonds voor Wetenschappelijk Onderzoek (Belgian National Science Foundation) for delivering additional funding throughout the whole period of this research (contracts: 2.0009.79, 2.0095.83, 2.0119.89)
- "Fonds voor Fundamenteel Onderzoek op Ministerieel Initiatief" for the matching funds allowing the partial financing of the SIDAMS and MACSIMS projects (contracts SIMULION 1 and SIMULION 2)
- Commission of European Communities for the contracts STEP0009M(A) for the SIDAMS project and ECSVCT920062 for the MACSIMS project.

REFERENCES

1. H. V. Neher, "Cosmic ray particles that changed from 1954 to 1965," *J. Geophys. Res.*, vol. 72, pp. 1527-1539, 1967.
2. D. Smith and N. G. Adams, "Ionic recombination in the stratosphere," *Geophys. Res. Lett.*, vol. 9, pp. 1085-1087, 1982.
3. E. E. Ferguson and F. Arnold, "Ion chemistry in the stratosphere.," *Acc. Chem. Res.*, vol. 14, pp. 327-334, 1981.
4. E. Arijs, "Positive and negative ions in the stratosphere," *Annales Geophysicae*, vol. 1, pp. 149-162, 1983.
5. E. Arijs, "Stratospheric ion chemistry: present understanding and outstanding problems," *Planet. Space Sci.*, vol. 40, pp. 255-270, 1992.
6. E. E. Ferguson, "Ion chemistry in the normal earth's stratosphere," in *The natural stratosphere of 1974* CIAP Monograph 1, (E. E. Reiter, ed.), (Department of Transportation), pp. 5.425.54, The Scientific Panel on the Natural Stratosphere, Climatic Assessment Program, 1974.
7. J. Ingels, E. Arijs, D. Nevejans, H. J. Forth, and G. Schaffer, «Liquid helium cryopump and reliable opening device for a balloon borne mass spectrometer," *Rev. Sci. Instr.*, vol. 49, pp. 782-784, 1978.
8. D. Nevejans, P. Frederick, and E. Arijs, "Microprocessor based data acquisition and control system for a balloon-borne quadrupole mass spectrometer," *Bull. Cl. Sci. Acad. Roy. Belg.*, vol. 67, pp. 314-332, 1982.
9. D. Nevejans, J. Ingels, and E. Arijs, "Measurement and identification of stratospheric ions with balloon borne instruments," in *Handbook for MAP*, Vol. 15, (D. G. Murcray, ed.), pp. 124-138, Urbana, Illinois: ICSU Scientific Committee on SCOSTEP, 1985.
10. F. Arnold, "The middle atmosphere ionized component," in *Proceedings of the fifth ESAPAC symposium on European Rocket and Balloon Programmes and Related Research*, ESASP 152, (Bournemouth, U.K.), pp. 479-495, European Space Agency, 1980.
11. E. Arijs, D. Nevejans, and J. Ingels, "Mass spectrometric measurements of stratospheric ions," *Adv. Space Res.*, vol. 4, pp. 19-28, 1984.
12. E. Arijs, J. Ingels, and D. Nevejans, "Mass spectrometric measurement of the positive ion composition in the stratosphere," *Nature*, vol. 271, pp. 642-644, 1978.
13. E. Arijs, D. Nevejans, and J. Ingels, "Unambiguous mass determination of major stratospheric positive ions," *Nature*, vol. 288, pp. 684-686, 1980.
14. F. Arnold, H. Böhringer, and G. Henschen, "Composition measurements of stratospheric positive ions," *Geophys. Res. Lett.*, vol. 5, pp. 653-656, 1978.
15. F. Arnold, G. Henschen, and E. E. Ferguson, «Mass spectrometric measurements of fractional ion abundances in the stratosphere -Positive ions," *Planet. Space Sci.*, vol. 29, pp. 185-193, 1981.
16. D. Smith, N. G. Adams, and E. Alge, "Ion-ion mutual neutralization and ion-neutral switching reactions of some stratospheric ions," *Planet. Space Sci.*, vol. 29, pp. 449-454, 1981.

17. H. Böhringer and F. Arnold, «Acetonitrile in the stratosphere : implications from laboratory studies," *Nature*, vol. 290, pp. 321-322, 1981.
18. J. R. Snider and G. A. Dawson, "Surface acetonitrile near Tucson, Arizona," *Geophys. Res. Lett.*, vol. 11, pp. 241-242, 1984.
19. H. Schlager and F. Arnold, "Balloon-borne fragment ion mass spectrometry studies of stratospheric positive ions: unambiguous detection of $H+(CH_3CN)l(H_2O)m^-$ clusters.," *Planet. Space Sci.*, vol. 33, pp. 1363-1366, 1985.
20. J. M. Rosen and D. J. Hofman, "Balloon-borne measurements of the small ion concentration," *J. Geophys. Res.*, vol. 86, pp. 7399-7405, 1981.
21. E. Arijs, D. Nevejans, J. Ingels, and P. Frederick, "Positive ion composition measurements between 33 and 20 km altitude," *Annales Geophysicae*, vol. 1, pp. 163-168, 1983.
22. D. R. Bates, "Recombination of small ions in the troposphere and lower stratosphere," *Planet. Space Sci.*, vol. 30, pp. 1275-1282, 1982.
23. J. M. Rosen and D. J. Hofman, "Balloon-borne measurements of electrical conductivity, mobility and the recombination coefficient," *J. Geophys. Res.*, vol. 86, pp. 7406-7410, 1981.
24. M. G. Heaps, "Parametrization of the cosmic ray ionpair production rate above 18 km.," *Planet. Space Sci.*, vol. 26, pp. 513-517, 1978.
25. G. Knop and F. Arnold, "Stratospheric trace gas detection using a new balloon-borne ACIMS method: acetonitrile, acetone and nitric acid.," *Geophys. Res. Lett.*, vol. 14, pp. 1262-1265, 1987.
26. C. Muller, "Acetonitrile in the earth's atmosphere: an upper limit deduced from infrared solar spectra," *Bull. Cl. Sci. Acad. Roy. Belg.*, vol. 61, pp. 225-229, 1985.
27. G. Brasseur, E. Arijs, A. De Rudder, D. Nevejans, and J. Ingels, "Acetonitrile in the atmosphere," *Geophys. Res. Lett.*, vol. 10, pp. 725-728, 1983.
28. E. Arijs and G. Brasseur, «Acetonitrile in the stratosphere and implications for positive ion composition," *J. Geophys. Res.*, vol. 91, pp. 4003-4016, 1986.
29. S. Hamm, G. Helas, and P. Warneck, "Acetonitrile in the air over Europe," *Geophys. Res. Lett.*, vol. 94, pp. 483-486, 1989.
30. S. Hamm and P. Warneck, "The interhemispheric distribution and the budget of acetonitrile in the troposphere," *J. Geophys. Res.*, vol. 95, pp. 20593-20606, 1990.
31. E. Arijs, D. Nevejans, and J. Ingels, "Stratospheric positive ion composition measurements and acetonitrile detection: a consistent picture ?," *Int. J. Mass Spect. Ion Proc.*, vol. 81, pp. 15-31, 1987.
32. H. Schlager and F. Arnold, "On stratospheric acetonitrile detection by passive chemical ionization mass spectrometry," *Planet. Space Sci.*, vol. 35, pp. 715-725, 1987.
33. D. Fussen, E. Arijs, and D. Nevejans, "The effect of collisionally dissociation in balloon borne stratospheric mass spectrometry of positive ions," *Int. J. Mass Spect. Ion Proc.*, vol. 91, pp. 301-316, 1989.

34. F. Arnold and G. Henschen, "First mass analysis of stratospheric negative ions," *Nature*, vol. 275, pp. 521-522, 1978.
35. F. C. Fehsenfeld, C. J. Howard, and A. L. Schmeltekopf, "Gas phase ion chemistry of HNO₃," *J. Chem. Phys.*, vol. 63, pp. 2835-2841, 1975.
36. A. A. Viggiano, R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, "The role of H₂SO₄ in stratospheric negative ion chemistry," *J. Geophys. Res.*, vol. 85, pp. 4551-4555, 1980.
37. E. Arijs, D. Nevejans, P. Frederick, and J. Ingels, "Negative ion composition measurements in the stratosphere," *Geophys. Res. Lett.*, vol. 8, pp. 121-124, 1981.
38. F. Arnold and R. Fabian, "First measurements of gas phase sulphuric acid in the stratosphere," *Nature*, vol. 283, pp. 55-57, 1980.
39. A. A. Viggiano and F. Arnold, "The first height measurement of the negative ion composition of the stratosphere," *Planet. Space Sci.*, vol. 29, pp. 895-906, 1981.
40. E. Arijs, D. Nevejans, P. Frederick, and J. Ingels, "Stratospheric negative ion composition measurements, ion abundances and related trace gas detection," *J. Atmos. Terr. Phys.*, vol. 44, pp. 681-694, 1982.
41. A. Viggiano, A., H. Schlager, and F. Arnold, "Stratospheric negative ions Detailed height profiles," *Planet. Space Sci.*, vol. 31, pp. 813-820, 1983.
42. E. Arijs, D. Nevejans, J. Ingels, and P. Frederick, "Negative ion composition and sulfuric acid vapour in the upper stratosphere," *Planet. Space Sci.*, vol. 31, pp. 1459-1464, 1983.
43. F. Arnold and S. Qiu, "Upper stratosphere negative ion composition measurements and inferred trace gas abundances," *Planet. Space Sci.*, vol. 32, pp. 169-177, 1984.
44. E. Arijs, D. Nevejans, J. Ingels, and P. Frederick, "Sulfuric acid vapour derivations from negative ion composition data between 25 and 34 km," *Geophys. Res. Lett.*, vol. 10, pp. 329-332, 1983.
45. A. A. Viggiano and F. Arnold, "Stratospheric sulfuric acid vapour: new and updated measurements," *J. Geophys. Res.*, vol. 88, pp. 1457-1462, 1983.
46. S. Qiu and F. Arnold, "Stratospheric in-situ measurements of H₂SO₄ and HSO₃ vapors during a volcanically active period," *Planet. Space Sci.*, vol. 32, pp. 87-95, 1984.
47. R. P. Turco, O. B. Toon, P. Hamill, and R. C. Whitten, "Effects of meteoric debris on stratospheric aerosols and gases," *J. Geophys. Res.*, vol. 86, pp. 1113-1128, 1981.
48. M. M. Abbas, V. G. Kunde, J. C. Brasunas, and J. R. Herman, "Nighttime reactive nitrogen measurements from stratospheric infrared thermal emissions," *J. Geophys. Res.*, vol. 96, pp. 10,885-10,897, 1991.
49. M. J. Molina, T. L. Tso, L. T. Molina, and F. C. Y. Wang, "Antarctic stratospheric chemistry of chlorine nitrate, hydrogen chloride and ice: release of active chlorine," *Science*, vol. 238, pp. 1253-1257, 1987.
50. P. J. Crutzen and F. Arnold, "Nitric acid cloud formation in the cold antarctic stratosphere: a major cause for the springtime ozone hole," *Nature*, vol. 324, pp. 651-655, 1986.

51. F. Arnold and G. Knop, «Stratospheric trace gas detection using a new balloon-borne ACIMS method.», *Int. J. Mass Spectr. Ion Proc.*, vol. 81, pp. 33-44, 1987.
52. H. Schlager and F. Arnold, "Measurements of stratospheric gaseous nitric acid in the winter arctic vortex using a novel rocket-borne mass spectrometric method.," *Geophys Res. Lett.*, vol. 17, pp. 433-436, 1990.
53. J. A. Davidson, A. A. Viggiano, C. J. Howard, I. Dotan, F. C. Fehsenfeld, D. L. Albritton, and E. E. Ferguson, "Rate constants for the reactions of O^+_2 , NO^+_2 , NO^+ , H_3O^+ , CO^+ , NO^+_2 , and halide ions with N_2O_5 at 300 K.," *J. Chem. Phys.*, vol. 68, pp. 2085-2087, 1978.
54. R. Moor, E. Kopp, U. Jenzer, H. Ramseyer, U. Walchli, E. Arijs, D. Nevejans, J. Ingels, D. Fussen, A. Barassin, and C. Reynaud, "UA double focussing mass spectrometer for simultaneous ion measurements in the stratosphere," in *Proceedings of ESAPAC Symposium on European Rocket and Balloon Programmes and Related Research, ESASP219*, (Lahnstein, FRG), pp. 129-134, ESA, April 1989.
55. D. Fussen, C. Amelynck, and E. Arijs, "Rate constant measurements for the ion/molecule reactions of I^- , F^- , Br^- and HFB_r with Cl_2 ," *Int. J. Mass Spectr. Ion Proc.*, vol. 116, pp. 13-22, 1992.
56. C. Amelynck, D. Fussen, and E. Arijs, "Reactions of nitric acid with di-and trichloride ions, di-and triiodide ions and with CO_4 in the gas phase," submitted to *Int. J. Mass Spectr. Ion Proc.*, vol. 135, pp. 13-28, 1994.

BIBLIOGRAPHY

Apart from the articles contained in the section references the following articles were published by the authors in the field of research, discussed in this article.

- E. Arijs, "Effusion of ions through small holes," *Vacuum*, vol. 24, pp. 341-345, 1974.
- E. Arijs, J. Ingels, and D. Nevejans, "A balloon borne quadrupole mass spectrometer for the determination of the ionic composition of the stratosphere," in *Colloque International : Technologie des expériences scientifiques spatiales.*, (Paris), pp. 559-567, Centre National d'Etudes Spatiales, CNES, 1975.
- E. Arijs and D. Nevejans, "Programmable control unit for a balloon borne mass spectrometer.," *Rev. Sci.Instr.*, vol. 46, pp. 1010-1015, 1975.
- D. Nevejans, E. Arijs, and J. Ingels, "Camac controlled system for the measurement of ion mobilities," *J. Phys. E: Sci. Instr.*, vol. 11, pp. 955-959, 1978.
- E. Arijs, J. Ingels, and D. Nevejans, "Positive ion composition measurements in the stratosphere - Experimental aspects and results," in *Proceedings of the 27th annual conference on mass spectrometry and allied topics*, (Seattle, Washington), pp. 474-475, American Society for Mass Spectrometry, 1979.
- E. Arijs, Nevejans, D., and J. Ingels, "Stratospheric positive ion composition measurements, ion abundances and related trace gas detection," *J. Atmos. Terr. Phys.*, vol. 44, pp. 43-53, 1982.
- E. Arijs, D. Nevejans, and J. Ingels, "Positive ion composition measurements and acetonitrile in the upper stratosphere," *Nature*, vol. 303, pp. 314-316, 1983.

- E. Arijs, D. Nevejans, J. Ingels, and P. Frederick, "Negative ion composition and sulfuric acid vapor in the upper stratosphere," *Planet. Space Sci.*, vol. 31, pp. 1459-1464, 1983.
- J. Olbregts, G. Brasseur, and E. Arijs, "Reaction of acetonitrile and chlorine atoms," *J. Photochem.*, vol. 24, pp. 315-322, 1984.
- E. Arijs, D. Nevejans, J. Ingels, and P. Frederick, "Recent stratospheric negative ion composition measurements between 22 and 45 km," *J. Geophys. Res.*, vol. 90, pp. 5891-5896, 1985.
- J. Ingels, D. Nevejans, and E. Arijs, "Vertical distribution of acetonitrile in the atmosphere," in *Handbook for MAP, volume 18*, (S. Kato, ed.), pp. 426-430, Urbana, Illinois: ICSU Scientific Committee on SCOSTEP, 1985.
- G. Brasseur, R. Zellner, A. De Rudder, and E. Arijs, "Is hydrogen cyanide (HCN) a progenitor of acetonitrile (CH₃CN) in the atmosphere." *Geophys. Res. Lett.*, vol. 12, pp. 117-120, 1985.
- J. Ingels, D. Nevejans, P. Frederick, and E. Arijs, "Stratospheric positive ion composition measurements between 22 and 45 km-An updated analysis," *J. Geophys. Res.*, vol. 91, pp. 4017-4024, 1986.
- D. Offerman, H. Rippel, P. Aïmedieu, W. A. Matthews, G. Megie, E. Arijs, Ingels, J., D. Nevejans, W. Attmanspracher, J. M. Cisneros, A. W. Dawkins, D. Demeur, P. Fabian, F. Karcher, G. Froment, V. Langematz, R. Reiter, K. Rothe, U. Schmidt, and R. J. Thomas, "Disturbance of stratospheric trace gas mixing ratios during the MAP/Globus 1983 campaign," *Planet. Space Sci.*, vol. 35, pp. 673-684, 1987.
- J. Ingels, D. Nevejans, P. Frederick, and E. Arijs, "Acetonitrile and sulfuric acid concentrations derived from ion composition measurements during the MAP/Globus 1983 campaign," *Planet. Space Sci.*, vol. 35, pp. 685-691, 1987.
- E. Arijs, E. Kopp, A. Barassin, R. Moor, D. Nevejans, U. Jenzer, U. Walchli, C. Rytz, D. Fussen, C. Reynaud, and E. Neefs, "Trace gas detection through passive and active ion mass spectrometry using a new type of balloon-borne mass spectrometer," in *Proceedings of first European Workshop on Polar Stratospheric Ozone Research, Air Pollution Research Report 34 of the CEC*, (J. A. Pyle and N. R. P. Harris, eds.), (Schliersee, Bavaria), pp. 111-114, Commission of the European Communities and Bundesministerium für Forschung und Technologie, FRG, October 1990.
- E. Arijs, D. Nevejans, J. Ingels, and D. Fussen, "Ion mass spectrometry research at the Belgian Institute for Space Aeronomy," *Physicalia Magazine*, vol. 12S, pp. 109-122, 1990.