1. Stratospheric ion formation and conversion

High energy radiation of different forms (energetic particles from the solar wind, X-rays and UV photons from the Sun and cosmic rays) results in ionization of a fraction of the Earth’s atmosphere giving rise to the ionosphere, a rarefied plasma surrounding our planet.

Above 50 km altitude this plasma consists of positive ions and free electrons, the latter determining the important role of the ionosphere in the reflection and propagation of radio waves. It has therefore been extensively studied by ground-based radio sounding techniques and other experimental methods (1).

Under normal conditions however, only cosmic rays penetrate into the atmosphere below 50 km and almost all other ionizing radiation is absorbed above. Thus the main ionization source in the stratosphere, which extends from about 15 to 50 km, is galactic cosmic radiation which is sufficiently energetic to provoke partial ionization of all gases. Nitrogen and oxygen being the most abundant gases, the primary charged particles in the stratosphere are therefore mainly N₂ and O₂ as well as electrons.

Whereas in the ionosphere the concentration of electrons is adequate to influence radio waves, the electron density is negligible in the stratosphere. This is due to the high gas number density in this region of the atmosphere which provides ample collisions between oxygen molecules and electrons for electron attachment to molecular oxygen and formation of O₂ ions. As a result the stratospheric charge carriers are positive and negative ions. The concentration of the stratospheric ions is extremely low compared to the neutral density. Considering as an example at 25 km the simple steady state equation \( Q = \alpha \times n^2 \), expressing that in equilibrium the ionization rate \( Q \) equals the loss through ion- ion recombination \( (\alpha \times n^2) \) and using measured values of \( Q \) (only 5 ion pairs cm\(^{-3}\)s\(^{-1}\) at 25 km) (2) and of the ion-ion recombination coefficient \( \alpha \) (about \( 5 \times 10^{-7} \) cm\(^3\)s\(^{-1}\) at 25 km)(3), leads to an ion density \( n \) of about 3,200 cm\(^{-3}\) at 25 km, compared to a neutral density of \( 8.4 \times 10^{17} \) cm\(^{-3}\) at the same altitude.

The lifetime of the stratospheric ions \( (\tau = 1/\alpha n) \) is very long and numerous collisions with neutrals occur before the charged particles disappear through ion-ion recombination.

A number of these collisions involve ion-molecule reactions modifying the nature of the ions. Some typical reactions for the positive ions are:

\[
\begin{align*}
N_2^+ + O_2 & \rightarrow O_2^+ + N_2 \quad (1) \\
O_2^+ + O_2 + M & \rightarrow O_2 + M \quad (2) \\
O_2^+ + H_2O & \rightarrow O_2^+H_2O + O_2 \quad (3) \\
O_2^+H_2O + H_2O & \rightarrow H_3O^+.H_2O \quad (4) \\
H_3O^+.OH + H_2O & \rightarrow H^+(H_2O)_{12} + OH \quad (5)
\end{align*}
\]

These reactions are the onset of a reaction sequence for the positive ions, shown in Figure 1 and discussed in full detail in the literature (4,5,6). The time to complete this reaction sequence is short compared to the ion life time.

The final result is a conversion of the primary N₂ and O₂ ions into the so-called hydronium ions or proton hydrates \((PH)\), represented by the formula \(H^+(H_2O)n\ (1 \leq n \leq 4)\), which were believed to be the terminal positive ions in the stratosphere.

It is remarkable that gases with an extremely low concentration in the stratosphere or so called trace gases (such as water present only in the ppm level) play an important role in the final nature of the ions. This is due to the very long ion lifetime which enhances the probability for collisions and reaction with these trace gases.

Another reaction chain (Figure 2), involving minor constituents such as NO, NO₂ and HNO₃ converts the primary O₂ ions into NO₃ \((HNO_3)n\) clusters.

The above described conversion schemes for the primary ions were already suggested before any experimental data on the stratospheric ion composition were available and had been derived from laboratory work on possible atmospheric ion-molecule reactions or from models extrapolating the results of mass spectrometry measurements in the lower part of the ionosphere (D-region) (7).
For the stratospheric ion composition however, no experimental in-situ data were available before 1977. This was partly due to a lack of motivation, caused by the negligible effect of the low stratospheric charged particle concentration on radio wave propagation, but mainly to the experimental difficulties associated with ion sampling in a mass spectrometer from a relatively high pressure medium such as the stratosphere.

Nevertheless the knowledge of the ion composition and associated ion chemistry is required to fully understand atmospheric processes and more important, it can lead to the detection of stratospheric trace gases. Therefore a project was started in the early seventies at our institute aiming the development of a balloon-borne mass spectrometer to measure the ion composition in the stratosphere. The results obtained within this project so far are summarized hereafter and future possible perspectives are discussed.

2. Experimental results

From 1972 up to 1977 a series of laboratory tests and a few technological balloon flights led to the realization of a balloon-borne instrument for the measurement of positive as well as negative ions. The instrument, fully described in the literature (8, 9, 10), consists of a quadrupole mass spectrometer built into a liquid helium cryopump and its associated electronics. The ions are sampled into the mass filter through a small aperture (diameter 0.2 mm) in an electrically insulated stainless steel flange. The signals of the mass spectrometer detector are treated by pulse counting techniques and the complete instrument is microprocessor controlled. Three types of instruments were developed with increasing performances (mass domain and resolution) from generation to generation.

Since 1977 several balloon flights were performed with these ion mass spectrometers to determine the natural stratospheric ion composition. All flights were realized in Europe, at the CNES launching base in Aire-sur-l'Adour or Gap-Tallard (France). Only two groups were successfully active in this field; the team of our institute (BISA), and the one of the Max-Planck-Institut für
The reaction rate coefficient $k_1$ and the recombination coefficient $\alpha$ have been measured in the laboratory (12), whereas the total negative ion number density $n^-$ can be estimated from previous parameterization studies based on in-situ measurements of total ion densities (14). Thus the number density and consequently the mixing ratio of acetonitrile can be deduced from the observed ratio $[\text{NPH}]/[\text{PH}]$ in a mass spectrum, since ion densities can be derived from the peak heights in the spectra.

Figure 4 represents the mixing ratio profile of CH$_3$CN as derived by this method for the different balloon flights performed by the BISA and MPIH teams. This mixing ratio profile suggests that acetonitrile is released at the Earth’s surface, diffuses into the atmosphere and is destroyed on its way up.

A literature search has shown that acetonitrile is indeed emitted in the atmosphere through anthropogenic activities (mainly industry and car exhaust) and that it can reach the stratosphere through diffusion, where it is destroyed by photodissociation and reaction with hydroxyl radicals. Subsequent model calculations based on estimations of the emission rate, measured reaction rates and photodissociation coefficients resulted in stratospheric CH$_3$CN concentrations which were in reasonable agreement with the data obtained from ion mass spectrometry, after correction for collision induced dissociation or CID (15). These CID effects are due to partial break-up of the ions in the sampling region of the mass spectrometer, where the pressure is still rather high and where considerable electric fields are used to accelerate the ions into the mass filter. Such CID gives rise to partial reconversion of NPH to PH, if the CH$_3$CN ligands are broken off from the NPH.

2.1. Positive ions and related trace gases

The very first spectrum obtained by a balloon borne instrument of stratospheric positive ions is shown in Figure 3. This spectrum, only of moderate resolution, not only demonstrates the existence of the predicted PH (H$^+$H$_2$O) with n=2,3,4, but it also shows another unexpected ion family, which can be represented by H$^+$Xm(H$_2$O) (X having a mass of 41 u). This group, called the non proton hydrates (NPH) was found to be due to ion-molecule reactions of the PH with an unknown trace gas X. Subsequent higher resolution measurements of our team (11) and laboratory work (12, 13) showed that this molecule was acetonitrile (CH$_3$CN).

![Figure 3: First mass spectrum obtained at 35 km altitude with a balloon borne ion mass spectrometer on 30 Sep. 1977.](image-url)
2.2. Negative ions and trace gas detection

The first spectra of stratospheric negative ions measured by the MPIH group indicated that the final nature of these ions was not only determined by the presence of nitric acid vapor, but also by sulfuric acid, which was expected as a minor constituent in the stratosphere as a result of the oxidation of sulfur compounds emitted by human activities and volcanoes.

High resolution spectra obtained by the BISA group, an example of which is shown in Figure 5, have confirmed this hypothesis and showed that the major negative ions in the stratosphere were clusters with either NO$_3$ or HSO$_4$ as core ion. The existence of the sulfate ions was explained by conversions of the type

\[ \text{NO}_3 (\text{HNO}_3)_n + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4 (\text{HNO}_3)_n + \text{HNO}_3 \]  

(7)

and further replacements of HNO$_3$ ligands by H$_2$SO$_4$, as well as additional clustering of sulfuric acid.

The negative ion mass spectra contained the first clear experimental evidence for the existence of sulfuric acid as a trace gas in the stratosphere.

Again the sulfuric acid concentration can be derived from the abundance ratio of the sulfate and nitrate ions, using a similar procedure as for acetonitrile. In this case the steady state equation becomes:

\[ k_2 [\text{H}_2\text{SO}_4][n^+] = \alpha [n_0][n^+] \]  

(8)

Here [n$^+$] is the total positive ion density, [H$_2$SO$_4$] the sulfuric acid number density and k$^2$ the rate coefficient of the reactions converting nitrate to sulfate ions, which were measured in the laboratory by Viggiano et al. (16).

The total number densities of NO$_3$ or HSO$_4$ clusters, [nN]...
and \([n_3]\) respectively, can again be deduced from the ion spectra. The results of such derivations are shown in Figure 6.

![Figure 6: Sulfuric acid concentrations as derived from negative ion mass spectra compared to model calculations (curves A and B).](image)

Although these data show a large scatter, a clear trend is noticed in the profile as shown by the envelope of all data points represented by the dotted lines of Figure 6. For comparison’s sake two model calculations by Turco et al. (17) are also shown in this figure. As can be seen the agreement is reasonable, taking into account the scatter and error on the experimental data and the strong dependency of the theoretical profile upon different parameters (the difference between the model curves A and B lays in the use of different vapor pressures of \(H_2SO_4\) and different meteoric metal fluxes, neutralizing sulfuric acid).

Whereas the derivation of the acetonitrile profile is merely a demonstration of the power and sensitivity of the method of inferring trace gas concentration from ion spectra, the sulfuric acid results are much more important. In fact the measurement of the ion composition is, even up to now, the only method of determining sulfuric acid in the stratosphere. Furthermore \(H_2SO_4\) is a much more important minor constituent than \(CH_3CN\) because it is believed to play an important role in aerosol formation, in turn can result in heterogeneous chemical processes having a large impact on the ozone equilibrium. The data on sulfuric acid have given a better insight into the photochemistry of this molecule.

In principle it is even possible to derive from ion mass spectra the concentration of nitric acid, another gas playing an important role in the ozone cycle. However this derivation is not based upon the conversion of one ion family to another (such as PH to NPH or nitrate to sulfate ions), but on the relative abundances of members of the same family.

Indeed knowing the enthalpy and entropy changes for conversions of the type

\[
NO_3^- (HNO_2) + HNO_3 + M \leftrightarrow NO_3^- (HNO_3)_2 + M
\]

one can derive the nitric acid concentration from the ratio of the signal at mass 188 \((NO_3(HNO_3)_2)\) and 125 \((NO_3HNO_3)\), as observed in spectra like the one of Figure 5. Unfortunately due to CID effects resulting in partial conversion of \(NO_3(HNO_3)_2\) to \(NO_3HNO_3\) in the mass spectrometer itself, this method is less accurate than presently existing optical methods for nitric acid.

### 3. New perspectives for ion mass spectrometry

Apart from having given a better insight into the implied ion-molecule chemistry, ion mass spectrometry measurements in the stratosphere have led to a new method for trace gas detection.

The profiles of two minor constituents, which had not been detected before, have been derived from the data, the most important one being sulfuric acid.

The above described methods can however, only be applied to trace gases playing an important role in the ion chemistry of the natural ions and are hampered by CID effects. Recently however the MPIH group has introduced a new method called Active Chemical Ionization Mass Spectrometry or ACIMS (18). In this method an ion source is mounted at the extremity of a so called “flow tube”, which is coupled to the ion mass spectrometer. Through a gas flow, created by a small turbine the ions formed by the ion source are guided to the mass spectrometer, reacting on their way with trace gases. From the measurement of relative abundances of product ions (formed through reactions with minor constituents) and source ions the concentration of the reactive trace gases can be deduced if the residence time of the ions in the flow tube and the appropriate reaction rates are known. Through the proper choice of the source ions this method can extend the range of gases which can be detected by ion mass spectrometry. So far the MPIH group has used several source ions \((CO_3^-, CO_3^-(H_2O)n\) and \(NO_3^-(H_2O)n\)) to measure \(HNO_3\), HCN and HCl in the stratosphere.

Our team has focused its efforts towards the development of an ACIMS instrument with an ion source, producing alternately \(O^+\) and \(I^-\) (19). The \(O^+\) 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

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reaction rate coefficients of the ion-molecule reactions involved have been measured in the laboratory (20, 21), the HNO₃ and N₂O₅ concentrations can be derived from the abundance ratios [NO₃]/[Cl⁻] and [NO₃]/[I⁻]. The major innovation of this method lies in the possibility of N₂O₅ measurements, which is a key gas in the ozone depletion mechanism and of which only few data are available. In addition the ACIMS method allows measurements during nighttime, which is excluded by the present optical methods. The development of the instrument has shown however that next to Cl⁻ and I⁻, also polyhalide ions Cl₂⁻ and I₂⁻ are produced in the ion source. Laboratory measurements of the additional ion-molecule reactions have therefore been necessary (22, 23).

In parallel a new balloon-borne magnetic mass spectrometer with enhanced sensitivity, higher resolution and less CID effects and based upon the combination of a Mattauch-Herzog filter with a simultaneous ion detection system has been constructed (24).

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The new mass spectrometer has been tested in technological balloon flights in 1991 and 1992. Recently (May 1994) the first model of the combined ACIMS instrument (ion source for Cl⁻ ions only and new magnetic mass spectrometer) has been launched. The data of this successful flight are now being analyzed and preliminary results on a nitric acid profile between 32 and 22 km show that the technique is promising.

4. Conclusions

A series of experiments with balloon-borne ion mass spectrometers, designed and built in house, 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. These data, in good agreement with the results obtained by the Max-Planck-Institut für Kernphysik in Heidelberg, led to a better understanding of the ion chemistry in the stratosphere. It was found that the ion composition of the stratosphere is controlled by the presence of trace gases with very low concentrations. For the positive ions the controlling gas is acetonitrile, which was not expected in the stratosphere. The results of modeling efforts concerning this gas, including positive ions, are in good agreement with our observations and provided a consistent picture of the positive stratospheric ion chemistry. Furthermore the power of ion mass spectrometry as a method for trace gas detection down to the ppb level was demonstrated.

For the negative ion chemistry, the controlling minor constituents are nitric acid and sulfuric acid. Ion mass spectra of BISA and MPIH have allowed the derivation of the concentration profile of H₂SO₄, which are the only data yet available about this gas in the stratosphere. In spite of some uncertainties about the negative ion chemistry, due to incomplete models and lack of laboratory data, this resulted in a better understanding of the underlying processes.

The experimental work of both the MPIH and the BISA team have opened the way for the development of a new technique for trace gas detection through active chemical ionization. This method may turn out to be extremely useful for the study of local phenomena, such as the ozone hole formation, where in-situ probing can complement remote sensing, to come to a better insight in the processes controlling the behavior of our atmosphere.

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