Positive and negative ions in the stratosphere

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ABSTRACT. Ion sources and sinks in the altitude region between 10 to 50 km are briefly reviewed. Up to 1977 only total ion density measurements and mobility data were available for the stratosphere.

Recent *in situ* data obtained with balloon-borne mass spectrometers have revealed the nature of the most abundant ions in the stratosphere.

Proton hydrates, i.e. ions of the form $H^+(H_2O)_n$ and non proton hydrates, resulting from ion-molecule reactions of minor constituents with $H^+(H_2O)_n$ ions were found as positive ions. The major negative ions were NO_3^- and HSO_4^- cluster ions.

The experimental method and the results of recent measurements will be discussed as well as the ion chemistry leading to the terminal cluster ions which were observed.

Key words : aeronomy, stratosphere, ions, trace species.

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INTRODUCTION

Until recently our knowledge of the charged particles in the stratosphere had progressed rather slowly. The main reasons for this were the absence of any effect on radio wave propagation and the difficulties of performing *in situ* composition measurements, due to the high gas number density in this part of the atmosphere. Nevertheless a knowledge of the number density and the nature of the charged species in the altitude region from 10 to 50 km is indispensable for an understanding of atmospheric electricity problems. When, about five years ago the first stratospheric ion composition data became available, it became clear that the ion composition was strongly related to minor constituents and the possibility of detecting trace gases with very low concentrations (such as sulfuric acid), so far not measured, was demonstrated.

The important role that trace gases play in processes of general interest (such as the ozone layer problem) and the possible role of ions in aerosol formation (which in turn may influence the earth's radiation budget) renewed the interest in stratospheric ions.

Furthermore, it was recognized that an understanding of the ion chemistry in the stratosphere can contribute to enlarge our information on the thermochemistry of ion-molecule interactions in general.

It is the aim of the present paper to review our current knowledge of stratospheric ions. Although emphasis will be given to recent composition data, a review will be presented of the so-called bulk properties of the stratospheric charged medium. This was felt as a necessity in view of recent new data and the important role that these properties play in the interpretation and use of ion composition data as a diagnostic tool in trace gas analysis.

BULK PARAMETERS OF THE STRATOSPHERIC CHARGED MEDIUM

Ionization sources in the stratosphere

The ionization sources in the atmosphere have been the subject of many studies, especially with respect to their possible role in atmospheric electricity and dependent sun-weather relationships. An excellent survey of most recent work in this field can be found in several review papers, which are brought together in the proceedings of the NASA workshop on the « Middle Atmosphere Electrodynamics » (Maynard, 1979).

For the purpose of the present discussion, however, we will restrict ourselves to those ionization sources, which are active in the stratosphere or altitude region between 15 and 50 km.

The principal source of ionization under normal conditions in the altitude range of 15 to 50 km is provided by galactic cosmic rays. The nature of cosmic rays (being high energetic particles) results in a non selective ionization in contrast with the H Lyman-α

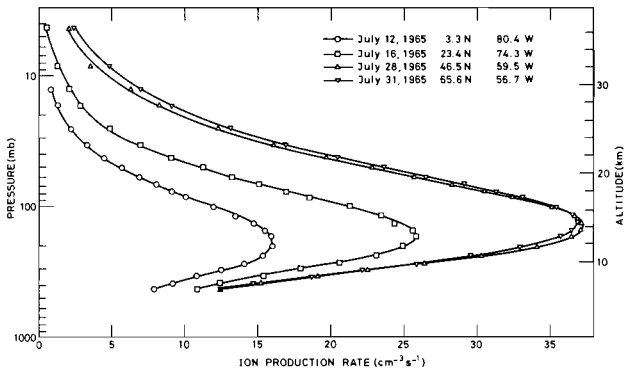

Figure 1
Rate of production of ion pairs by cosmic rays as compiled from data of Neher (1967) *for solar minimum at different latitudes.*

ionization in the *D*-region e.g., which is only ionizing NO and certain metal atoms.

Furthermore, virtually no absorption of the ionizing radiation occurs, so that in the stratosphere the ionization rate merely depends on the total gas number density. Only at altitudes below 15 km a marked mass absorption of the cosmic rays occurs, giving rise to decrease in ionization with decreasing altitude. The latter effect is illustrated in figure 1, which is based on the ballon measurements of Neher (1967).

The galactic cosmic ray flux on the earth's atmosphere is mainly affected by two factors, namely the geomagnetic field and the solar activity.

The earth's magnetic field causes a deflection of the incoming particles of the cosmic ray shower and, therefore, an increase of about 60 % of the ionizing radiation intensity is found at geomagnetic latitudes larger than 70° (Sandström, 1965). At lower latitudes only particles with energies larger than about 15 GeV are reaching the atmosphere. As a result of the higher penetration depth of these high energy particles the maximum in the ionization rate *versus* altitude curve (fig. 1) shifts to lower heights for lower geomagnetic latitude.

Cosmic ray intensity is also controlled by solar activity currently observed by sunspot number variation. An 11-year cycle is found in the ionization rate which is anticorrelated with the sunspot number variations. This effect is clearly illustrated on figure 2, which is taken from Pommerantz and Duggal (1974). The mechanism, however which is controlling the correlation between solar activity and cosmic ray intensity is at present not fully understood.

Besides the long term variations of stratospheric ionization, short time fluctuations may occur during PCA (Polar Cap Absorption) events, which are due to the penetration of high energetic particles ejected during Solar Flares (Solar cosmic rays) into the earth's atmosphere. This effect however is mostly limited to high latitudes. It is, as can be seen from figure 3 (after Goldberg, 1979) quite dramatic and can alter the ion production by a factor of 10000 at 40 km.

Apart from the non selective ionization produced by cosmic rays the attention has been drawn very recently (Aikin, 1981) to an ionization source which should be active in the upper part of the stratosphere and the lower part of the mesosphere (40 to 70 km) and which may result in ion production several times of that due to cosmic rays. It consists of photoionization of metal compounds originating from meteoric debris. No experimental data however are available to demonstrate the effect of such an ionization source.

For the purpose of the present discussion we will, therefore, accept that stratospheric ionization is non selective and rather constant at mid-latitudes.

Recently a parametrization of the cosmic ray ion-pair production rate has been reported by Heaps (1978). An empirical formula was found for the ion-pair production rate which was fitting to within 10 % with most of the experimental data. Figure 4 shows a comparison of recent experimental data (Gringel *et al.*, 1978*a*) with the formula

$$Q = (A + B \sin^4 \Lambda)\, N_0^{\gamma} N^{n} \quad (\mathrm{cm}^{-3}\,\mathrm{s}^{-1}) \qquad (1)$$

which is valid through the 30-18 km altitude range A and B are constants depending on solar activity as given by Heaps (1978) and

$$N_0 = 3.03 . 10^{17}\ \mathrm{cm}^{-3} \qquad (2)$$

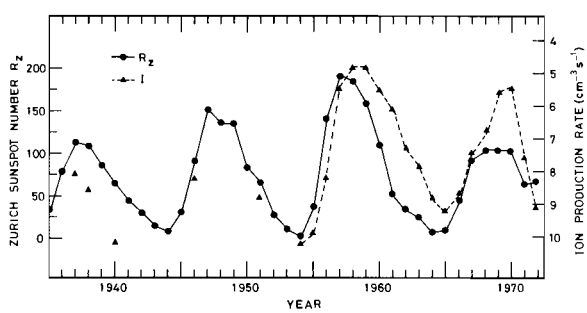

Figure 2
Ion-pair production at 27 km altitude normalized to the latitude of Thule (Greenland) for the last solar cycles and Zurich sunspot number. Note the inversion of vertical axes to demonstrate the anticorrelation (after Pomerantz and Duggal, 1974*).*

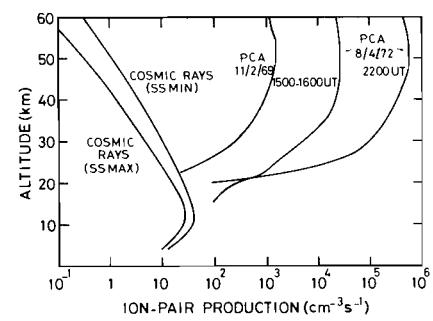

Figure 3
Ion production rate during two PCA events compared to normal galactic cosmic ray production after Herman and Goldberg (1978).

$$n = 0.6 + 0.8 \cos \Lambda \quad (3)$$

and

$$\gamma = 1 - n. \quad (4)$$

For Λ the appropriate value of the geomagnetic latitude of Laramie (Wyoming) was inserted.

As it can be seen in figure 4, reasonable agreement is found between the measured and calculated values.

Ion sinks in the stratosphere

The main sink for ions in the stratosphere is recombination. Since the electrons formed in the primary ionization process rapidly attach to electronegative gases (mainly oxygen) the rarified plasma in the stratosphere consists of positive and negative ions. Therefore the ion loss process is ion-ion recombination. It has been customary to make a distinction between two body and three body recombination.

Above 30 km binary recombination is dominant. This process has been studied rather extensively (Smith and Church, 1976; Smith and Church, 1977; Smith *et al.*, 1976 and Smith *et al.*, 1981) and values of the binary recombination rate coefficient α_2 have been determined experimentally for various types of ions. Values between 5.8×10^{-8} cm^3 s^{-1} and 6.6×10^{-8} cm^3 s^{-1} were reported for ions which have the same nature as those actually found in the stratosphere (Smith *et al.*, 1981). The temperature dependence of α_2 was found to be $T^{-1/2}$ (Smith and Church, 1977).

Much less is known about the three body recombination mechanism which becomes the most effective one in the lower part of the stratosphere.

Experimental laboratory data are sparse but the existing ones (Fisk, 1967; Mahan, 1973) suggest values for the three body recombination coefficient α_3 of about 2×10^{-25} ([M] cm^6 s^{-1}, [M] being the density of the third body in units of cm^{-3}) and a strong temperature dependence (T^{-3} or T^{-4}). Relying upon their own measurements of α_2 and the above mentioned data for α_3 Smith and Church (1977) calculated the total recombination coefficient α_T in the atmosphere up to 80 km altitude. Their results are represented in figure 5.

Also shown in figure 5 are some data on α_T as available in the literature. It should be noted that most of these data were based on a combination of experimental and theoretical results existing at the time.

The only points of figure 5 based on *in situ* experiments are those of Gringel *et al.* (1978*b*) and Rosen and Hofman (1981), the last ones being the most reliable ones since ion densities as well as ionization rate were measured simultaneously for their derivation.

Very recently Smith and Adams (1982) have found a parametrization for the total ion recombination α_T of the form :

$$\alpha_T = 1.63 \times 10^{-5} \exp(-h/7.38) + 5.25 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \quad (5)$$

where h is expressed in km.

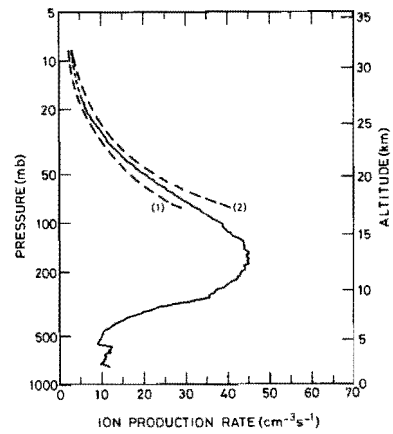

Figure 4
Ionization rate as given by Heap's parametrization (Heaps, 1978*) during solar maximum* (1) *and solar minimum* (2) *compared to experimental data of Gringel* et al. (1978*a*).

This expression which is valid in the altitude region 10 to 60 km is claimed to be accurate to better than ± 50 %.

Recent theoretical progress (Bates, 1982) has shown that the total ion-ion recombination coefficient α_T must be represented by

$$\alpha_T = \alpha_3 + \Delta\alpha_2 \quad (6)$$

where α_3 is the three body recombination coefficient and $\Delta\alpha_2$ is regarded as an enhancement due to the binary channel. This enhancement is pressure and temperature dependent.

Computer simulations have allowed a calculation of α_T in the altitude region 0 to 40 km (Bates, 1982) and these results are also shown in figure 5.

In view of some approximations used in the calculations of Bates (such as the derivation of an effective polarizability from a rather uncertain empirical relationship between ion mass and ion mobility) and the uncertainty of 50 % on the parametrization of Smith and

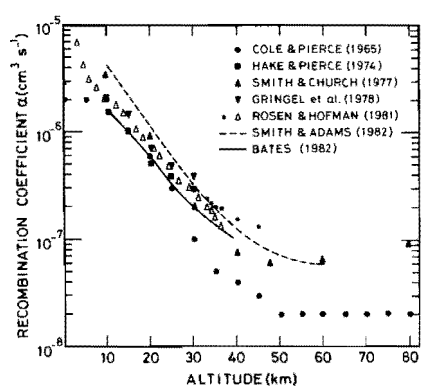

Figure 5
Different values of total ion-ion recombination coefficient as published in the literature. It should be noted that the data of Cole and Pierce (1974) *are less accurate due to an underestimation of the binary recombination rate coefficient.*

Adams, the agreement between both approximations for α_T and the data of Rosen and Hofman (1981) is reasonable.

In general it can therefore be stated that the ion-ion recombination coefficient between 10 and 40 km is known within a factor of two.

Another sink for charged species in the stratosphere may be ion annihilation by aerosol particles (Zikmunda and Mohnen, 1972), but very little is shown about the contribution of this mechanism to the total ion losses. The efficiency of ion annihilation through the attachment at aerosols is believed to be low in the stratosphere, although good estimations are not available because of the lack of knowledge of the size distributions of aerosol particles.

Ion densities

Once the ionization rate is known as a function of altitude and assuming mutual recombination to be the only ion sink, the ion density profile can be calculated from the simple steady state formula

$$Q = \alpha n^+ n^- . \qquad (7)$$

Several such calculations have been performed although most of the early models related to higher altitude regions and were more concerned with the production of the electrons in the atmosphere and the resultant absorption of radio waves (Webber, 1962; Cole and Pierce, 1965).

Figure 6 shows a calculation performed by Reid (1979). This result is compared with some of the many experimental data (Paltridge, 1965; Bragin, 1967; Rose *et al.*, 1972 and Widdel *et al.*, 1977). As can be seen the general trend of the experimental data, which were all obtained with Gerdian condensers is in reasonable agreement with the modelling result. However strong fluctuations and extreme deviations are observed. These were formerly ascribed to either imperfect modelling, due to an incomplete knowledge of the ion chemistry (Bragin *et al.*, 1966) or to effects of ion annihilation by aerosols or attachment of ions on particles (Paltridge, 1966; Morita *et al.*, 1971).

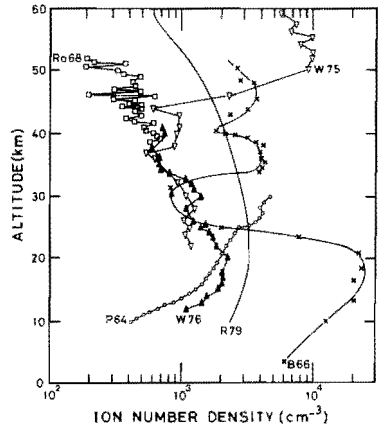

Figure 6
Ion densities versus *altitude as measured by different authors. P64 : measurement performed on* 13 *Feb.* 1964 *by Paltridge* (1965), *B* 66 *: Bragin* (1967) *on* 19 *April* 1966 *; Ro* 68 *: Rose* et al. (1972) *on* 15 *May* 1968 ; *W* 75 *: Widdel* et al. (1977) *on* 7 *June* 1975. *R* 79 *is a model calculation by Reid* (1979).

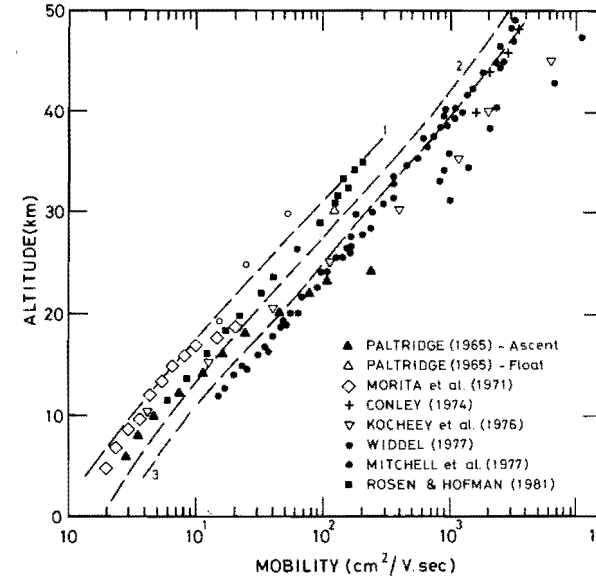

Figure 7
Ion mobilities versus *altitude from different sources. Curves* 1, 2 *and* 3 *are calculated from* $K = K_0 \frac{760}{p} \frac{T}{273.16}$ *for* K_0 0.92; 1.94 *and* 2.7 *respectively. Pressure p and temperature T* versus *altitude were taken from the U.S. standard atmosphere of* 1967.

Recently, however, Rosen and Hofman (1981) have measured ion densities systematically with a Gerdian condenser operating in the saturation mode and based on the design of Kroenig (1960). By using a lobe pump to draw air though the ion collector a constant and well known flow rate was obtained. The ion density profiles thus obtained were much smoother than those of figure 6 and were quite repeatable over a 2 years period.

It is, therefore, believed now that the strong fluctuations can be attributed to poorly known and variable air flow in the older Gerdian condensers.

ION COMPOSITION OF THE STRATOSPHERE

Early information and indirect data

A global picture of the ionized component of the stratosphere does not only contain an overview of the ion sources and sinks and ion densities, but requires a full understanding of the ion chemistry.

In order to comprehend the chemistry of charged particles it is of an absolute necessity to know the ion composition.

The most direct way to obtain this information is to perform ion mass spectrometry measurements in the same way as those made in the *D*-region (Narcisi and Bailey, 1965; Narcisi *et al.*, 1972; Arnold and Krankowsky, 1977 and Zbinden *et al.*, 1975).

In view of the experimental difficulties, related to stratospheric ion mass spectrometry, which will be

described hereafter, no such measurements were reported until 1977.

Therefore, the first data concerning the ion composition of the stratosphere were indirect data and were derived from mobility measurements or modelling efforts. Before giving an overview of the most recent mass spectrometry data, we will, therefore, briefly review these early indirect data.

Ion mobility data in the stratosphere

Mobility data were mostly obtained at the same time as ion density measurements. In fact both kinds of information (ion densities and ion mobilities) are derived from conductivity measurements with a Gerdian condensor (Conley, 1974) or similar probe.

By using a Gerdian condensor in the « ohmic » region, mobility and ion density can be derived from voltage-current characteristics.

Some ion mobility data as observed by different authors (Paltridge, 1965; Morita *et al.*, 1971; Conley, 1974; Kockeev *et al.*, 1976; Widdel *et al.*, 1976; Mitchell *et al.*, 1977 and Rosen and Hofman, 1981) in the altitude region 5 to 50 km are summarized in figure 7. In the polarization limit the mobility K of ions with mass m is given by the Langevin formula (McDaniel, 1973)

$$K = \frac{13 \cdot 896}{\alpha^{1/2} M^{1/2}} \left(1 + \frac{M}{m}\right)^{1/2} (\mathrm{cm^2\,V^{-1}\,s^{-1}}) \qquad (8)$$

and

$$K = K_0 \cdot \frac{760}{p} \cdot \frac{T}{273 \cdot 16} \qquad (9)$$

where α is the polarizability of the gas in $Å^3$, m the ion mass in $g.mole^{-1}$, M the mass of the neutrals (also in $g.mole^{-1}$) in which the ions are moving, p the pressure in torr and T the temperature in Kelvin.

In principle formulae (8) and (9) allow a derivation of m from K. It can be calculated however that a mass resolution of 10 amu requires a precision of about 1.5 % on K. In view of the fact that already p and T are mostly not measured with this precision and in view of the spreading of the points on figure 7 it is very unlikely that mobility data can give sufficient information on the ion mass.

The use of other K *versus* m relationships leads to the same conclusion.

Therefore more direct measurements such as mass spectrometry data are needed.

Modelling efforts

In order to understand the ion chemistry of the *D*-region numerous laboratory studies of ion-molecule reactions were undertaken during the last 15 years.

Progress in laboratory techniques (Ferguson *et al.*, 1969, McDaniel *et al.*, 1970, Adams and Smith, 1976) has allowed a measurement of most critical reaction rate constant. Compilations of these results may be found in Ferguson (1973) and Albritton (1978).

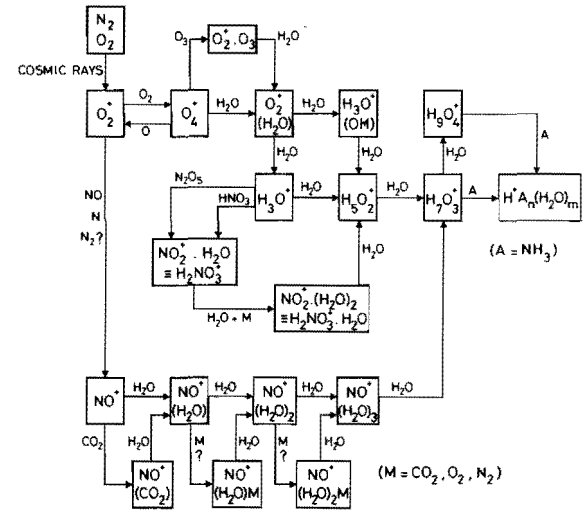

Figure 8

Reaction scheme leading to positive ions in the stratosphere as proposed by models before 1977 *(adapted from Ferguson,* 1974*).*

Based upon these laboratory measurements several models of the ion chemistry in the earth's atmosphere were developed (Fehsenfeld and Ferguson, 1969; Mohnen, 1971; Thomas, 1974; Reid, 1976). Most of these models however relate to the *D*-region. Ferguson (1974) however extrapolated his model into the stratosphere. The reaction schemes as proposed before 1977 are shown in figures 8 and 9.

In the positive ion chemistry the conversion of the primary ions (N_2^+ and O_2^+) to proton hydrates $[H^+(H_2O)_n]$ (hereafter PH) is very efficient and there seems to be no alternative to their production in the stratosphere (Dotan *et al.*, 1978).

It was realized however that the presence of trace gases with a proton affinity larger than the proton affinity of water could give rise to a continuation of the ion-molecule reaction chain and lead to cluster ions of the form $H^+A_n(H_2O)_m$. For A molecules such as NH_3 were proposed.

For the negative ion chemistry, cluster ions with NO_3^- cores were expected. Although originally hydrates of NO_3^- were predicted, it was shown later on by laboratory

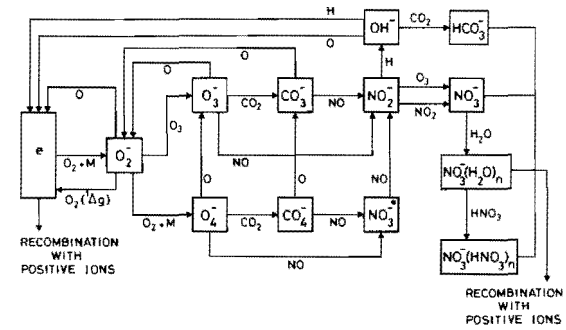

Figure 9

Stratospheric negative reaction scheme from model before 1977 *after Ferguson* (1974).

measurements (Fehsenfeld *et al.*, 1975) that HNO_3 displaces H_2O in the NO_3^- hydrates. The presence of HNO_3 being shown in the stratosphere (Ackerman, 1975), ions of the type $NO_3^-(HNO_3)_n$ were therefore expected.

In situ ion composition measurements

Positive ion composition

The first stratospheric mass spectrometric measurements of positive ions were reported by Arnold *et al.* (1977). The data, which were obtained on the downleg portion of three rocket flights extended from 55 down to 35 km and revealed the existence of ions with mass numbers 19, 29, 37, 42, 55, 60, 73 and 80 all with ± 2 amu, uncertainty. Relying on high resolution measurements at higher altitude the ions with mass numbers 19, 37, 55 and 73 were identified as PH, which was in good agreement with previous models. Below 40 km however the dominant ions (29, 42, 60 and 80 ± 2 amu) had mass numbers, which did not correspond to PH and consequently they were called non proton hydrates (NPH). To explain their presence a simple model was proposed, which was based on neutral model calculations (Stewart and Hoffert, 1975) and laboratory measurements (Karpas and Klein, 1975) and which involved the irreversible reactions of PH with formaldehyde (CH_2O).

A verification of this hypothesis by subsequent laboratory measurements (Fehsenfeld *et al.*, 1978) showed that although the reaction

$$H^+(H_2O) + CH_2O \rightarrow CH_2OH^+ + H_2O \qquad (9')$$

was fast (a reaction rate coefficient of 2.2×10^{-9} cm^3 s^{-1} was reported) hydrates of protonated formaldehyde rapidly converted to PH. The thermochemical data obtained for the reaction of CH_2O with PH indicated that formaldehyde could not be the source of the NPH ions observed in the stratosphere.

A danger inherent to the first observations of Arnold *et al.* (1977) is the possibility of ion fragmentation, due to the use of rockets (shock-wave). Furthermore, only a short measuring time is available during a rocket flight. Therefore, in order to obtain a reasonable height resolution, only limited mass resolutions, resulting in confortable signals, can be used with a rocket-borne mass spectrometer. The main problem with rocket-borne instruments is the decrease of sensitivity with increasing air density due to collisional ion loss in the instrument.

It was, therefore, obvious to try to repeat the measurements with a balloon-borne instrument.

The development of such an instrument, however, poses some serious problems among which the design of a good pumping system with a long standing time is one of the most critical ones.

Balloon-borne ion mass spectrometers have been developed in the mid seventies at several places (Arijs *et al.*, 1975; Arnold *et al.*, 1978; Olsen *et al.*, 1978). They consist of a high speed cryopump in which a quadrupole mass filter is built. The stratospheric ions are sampled through a small orifice, and focused by an electrostatic lens into the mass filter. After mass filtering they reach a high gain electron multiplier, the signals of which are treated by pulse counting. A more detailed description of these instruments is beyond the scope of this work and is given in detail elsewhere (Arijs *et al.*, 1975; Arijs and Nevejans, 1975 and Ingels *et al.*, 1978; Olsen *et al.*, 1978).

Table 1

Major positive ions as observed by early in situ *mass spectrometer measurements at typical balloon float altitudes (35-37 km).*

Mass in amu (1)	(2)	(3)	(4)	Proposed ion clusters
19 ± 2		20 ± 3		$H^+(H_2O)$
29 ± 2		29 ± 3		?
37 ± 2		37 ± 3		$H^+(H_2O)_2$
42 ± 2		43 ± 3		H^+X
		50 ± 3		?
55 ± 2		55 ± 3	55	$H^+(H_2O)_3$
60 ± 2		60 ± 2		$H^+X(H_2O)$
	73	73 ± 2	73 ± 1	$H^+(H_2O)_4$
80 ± 2		78 ± 2	78 ± 2	$H^+X(H_2O)_2$
		82 ± 2		H^+X_2
	91	91 ± 2	91 ± 1	$H^+(H_2O)_5$
		96 ± 2	96 ± 1	$H^+X(H_2O)_3$
		99 ± 2	100 ± 1	$H^+X_2(H_2O)$
	109	109 ± 2		$H^+(H_2O)_6$
			114 ± 2	$H^+X(H_2O)_4$
			118 ± 1	$H^+X_2(H_2O)_2$
			136 ± 2	$H^+X_2(H_2O)_3$
			140 ± 2	$H^+X_3(H_2O)$

(1) Arnold *et al.* (1977).
(2) Olsen *et al.* (1978).
(3) Arijs *et al.* (1978, 1979).
(4) Arnold *et al.* (1978).

The first positive ion mass spectra obtained with a balloon-borne instrument at an altitude of 35 km covered the mass range 0-109 amu (Arijs *et al.*, 1978) and revealed the existence of PH with mass 19, 37, 55, 73, 91 and 109 amu and NPH with mass 42, 60, 78 and 96 amu. The uncertainties on the reported mass numbers was ± 2 or ± 3 amu. Some minor mass peaks, (table 1) apparently not belonging to the previously mentioned series were also detected, but only analysed later on. The existence of NPH in the stratosphere was confirmed later on by data obtained with a similar instrument at 37 km altitude (Arnold *et al.*, 1978), but, due to the higher mass range, ions up to mass 140 amu were measured.

The mass numbers as observed in the first rocket and balloon flights are summarized in table 1. From the above data it was concluded (Arnold *et al.*, 1978) that the major ions at 35-37 km altitude were PH and NPH, which could be represented by $H^+X_l(H_2O)_m$ where X should have

— a mass number of 41 ± 1 amu,
— an atmospheric number density of about 10^5 cm^{-3} at 35 km,
— and a proton affinity larger than 175 kcal.mole^{-1}.

On the base of these conclusions, Ferguson (1978) proposed NaOH as a candidate for X. This hypothesis, which was relying on the expected existence of NaOH, resulting from a reaction chain starting at the atmospheric sodium layer (Richter and Sechrist, 1979), was backed up by calculations of Liu and Reid (1979) and laboratory measurements of Märck *et al.* (1980). Although the diffusive chemical model of Liu and Reid (1979) did not take into account loss processes for NaOH, which would give rise to other sodium compounds such as NaCl (Murad and Swider, 1979), it was shown by laboratory measurements (Perry *et al.*, 1980) that practically all sodium compounds existing in the stratosphere would give rise to $Na^+(H_2O)_n$ ions.

Another possible candidate which was put forward for X was MgOH (Murad and Swider, 1979) although it was excluded later on by laboratory measurements (Ferguson *et al.*, 1981).

Therefore NaOH remained the most likely candidate for X until 1980. In that year the first high resolution mass spectra of positive ions became available (Arijs *et al.*, 1980). A typical spectrum from this flight is shown in figure 10. From these data it was shown unambiguously that the mass of X was 41 amu, and, since no Mg isotopes were detected, the NaOH and MgOH hypotheses were rejected and, CH_3CN, the candidate proposed for X by Arnold *et al.* (1978) became topical again.

This suggestion was strengthened by a careful inspection of ion fractional abundances (Arnold *et al.*, 1981*a*), laboratory measurements (Smith *et al.*, 1981; Böhringer and Arnold, 1981) and an inspection of mass peaks due to heavy isotopes (Arijs *et al.*, 1982*a*).

The major observed stratospheric positive ions can therefore be represented by $H^+(H_2O)_n$ and $H^+X_l(H_2O)_m$, X being most probably CH_3CN. At present the source of CH_3CN in the stratosphere is not yet clear.

Recent studies of the fractional ion abundances of PH and NPH have led to an estimation of the mixing ratio of CH_3CN in the stratosphere at typical balloon float altitudes as well as at lower altitudes (Arnold *et al.*, 1981*a*; Henschen and Arnold, 1981*a*; Arijs *et al.*, 1982*a*; Arijs *et al.*, 1982*c*).

A typical result of such estimations is shown in figure 11. Although *in situ* production mechanism for CH_3CN was proposed (Murad and Swider, 1982) the CH_3CN profiles of figure 11 seem to suggest a source term of CH_3CN in the troposphere followed by an upward diffusion and photochemical destruction at higher altitudes. In the derivation of the CH_3CN mixing ratios, it was assumed that the main loss process for NPH is recombination. It has been shown, however, that reverse switching reactions

$$H^+X_l(H_2O)_m + X \rightleftarrows H^+X_{l+1}(H_2O)_{m-1} + H_2O \qquad (10)$$

or thermal dissociation

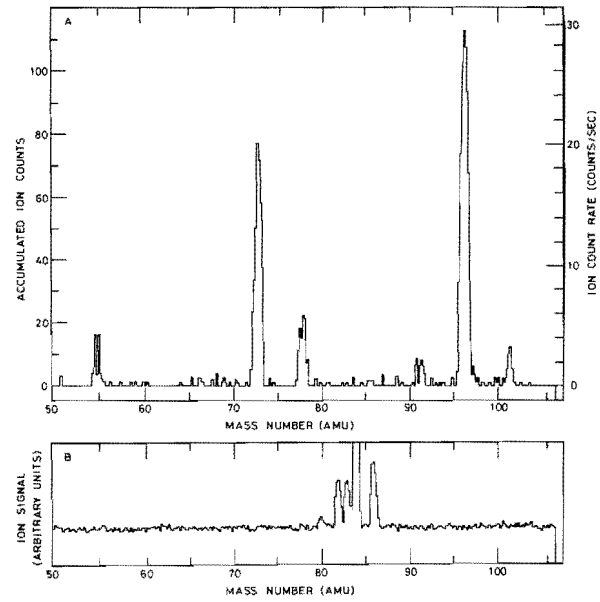

Figure 10

a) High resolution positive ion mass spectrum obtained at 34 km altitude in the mass domain 50-106 amu (Arijs et al. *,1980). The peak width is constant over the mass range and equals 0.9 amu.*

b) In flight calibration obtained in the same mass domain, showing clearly the krypton isotopes. This spectrum was taken just before the spectrum of figure 10a by putting on an ion source and injecting krypton into the instrument.

$$H^+X_{l+1}(H_2O)_m + M \rightarrow H^+X_l(H_2O)_m + X + M \qquad (11)$$

may be occurring (Böhringer and Arnold, 1981; Arnold *et al.*, 1981*a*; Arijs *et al.*, 1981*a*).

If such reactions are possible for $l = 0$, a higher concentration of CH_3CN may be found. Reconversion of NPH to PH, however, seems rather unlikely as an effective loss process for NPH (Arijs *et al.*, 1982*a*).

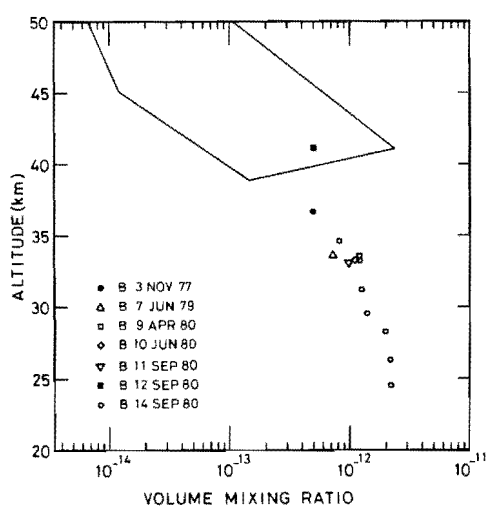

Figure 11

Mixing ratio of CH_3CN versus *altitude as deduced from different balloon and rocket flights (after Henschen and Arnold,* 1981*a).*

Table 2

Minor positive ions recently detected in the stratosphere. The differences on the uncertainties on the ion mass in the measurements of Arijs et al., *is due to poor counting statistics.*

Mass in amu		Tentative identification	
(1)	(2)	(1)	(2)
19±3		$H^+(H_2O)$	
28±2		$H^+ \cdot HCN$	
33±2		H^+CH_3OH	
37	37±1	$H^+(H_2O)_2$	$H^+(H_2O)_2$
42±2	42±1	H^+CH_3CN	H^+CH_3CN
	45±1		$Al(H_2O)$ or $H^+HCN \cdot H_2O$
51±2	49±1	$H^+CH_3OH \cdot H_2O$	$H^+CH_3OH \cdot H_2O$ or $H^+CH_3NH_2H_2O$
	58±1		$Na^+(H_2O)_2$
60	60±1	$H^+CH_3CN(H_2O)_2$	$H^+CH_3CN(H_2O)_2$
	63±1		$Al(H_2O)_2$ or $H^+HCN(H_2O)_2$
69±2	67±1	$H^+CH_3OH(H_2O)_2$	$H^+CH_3OH(H_2O)_2$
77		$Na^+(H_2O)_2$	
	81±1		$Al^+(H_2O)_3$ or $H^+HCN(H_2O)_3$
82±1	83±1	$H^+Y(H_2O)_j$	$H^+(CH_3CN)_2$
87±2	86±1	$H^+CH_3OH(H_2O)_3$	$H^+CH_3OH(H_2O)_3$ or $H^+CH_3NH_2(H_2O)_3$
99±1		$H^+Y(H_2O)_{j+1}$	
	104±1		$AlCH_3CN \cdot (H_2O)_2$ or $H^+HCN \cdot CH_3CN(H_2O)_2$
	110±1		$H^+C_2H_3NS(H_2O)$, $H^+CH_3CN \cdot CH_3OH(H_2O)_2$ or $H^+CH_3CN \cdot CH_3NH_2(H_2O)_2$
117	117±1	$H^+Y(H_2O)_{j+2}$	$H^+CH_3NO_2(H_2O)_3$
	122±1		$H^+CH_3NO_2 \cdot CH_3 \cdot CN \cdot H_2O$
	125±1		$H^+CH_2O_2CH_3CN \cdot (H_2O)_2$, $H^+C_2H_6O \cdot CH_3CN \cdot (H_2O)_2$ or $H^+CH_4S \cdot CH_3CN \cdot (H_2O)_2$
	128±1		$H^+C_2H_3NS(H_2O)_3$

(1) Arijs *et al.* (1982*a*) —Y≡CH_3COH ?
(2) Henschen and Arnold (1981).

Recent studies also revealed that collisional induced cluster break up in the mass spectrometer (Arnold *et al.*, 1981*a*; Arijs *et al.*, 1982*a*) is also falsifying the results.

A detailed study of fractional ion abundances and a comparison with models has, therefore, to take into account this effect and has to await for extensive laboratory measurements of collisional induced dissociation.

Apart from the major positive ions, discussed herefore, many other positive ions have been detected in the stratosphere (Henschen and Arnold, 1981*b*; Arijs *et al.*, 1982*a*). The minor mass peaks as reported so far in the open literature are summarized in table 2, together with their tentative identification. It can be seen from this table that ion compositions offer the possibility of trace gas detection of species so far not measured. It should be noted, however, that signal instabilities, which are very pronounced at low ion count rates, and possible contamination from the balloon hamper the usefulness of the method as a full grown analytical tool.

In the context of the detection of minor ions it is worthwhile to return to the NaOH hypothesis. Since no major ions due to Na^+-cluster ions have been observed, the problem rises what happens to the sodium originating from meteorite ablation. A possible loss mechanism for meteoric sodium is absorption in atmospheric dust and aerosols (Arnold *et al.*, 1981; Arnold and Henschen, 1982). Recent model calculations (Turco *et al.*, 1981) taking into account such removal processes indicate indeed much lower metal vapor concentrations than those found by Liu and Reid (1979). The role of stratospheric ions in aerosol formation has been the subject of many studies (Castleman, 1979, 1982; Mohnen and Kiang, 1976; Chan and Mohnen, 1980). However, the nature and origin of stratospheric condensation nuclei is not known. A possible mechanism for the formation of such condensation nuclei may involve multi-ion complexes (Ferguson, 1979; Arnold, 1980; Arnold, 1982). Recently positively charged particles having masses larger than 327 amu were detected with a balloon-borne ion-mass spectrometer (Arnold and Henschen, 1981). These particles appear to be arranged in a layer peaking around 30 km. Arguments were put forward to interpret these particles as multi-ion complexes and possible condensation nuclei.

As will be pointed out in a contributed paper hereafter (Arijs *et al.*, 1983*a*) however care should be taken with these interpretations in view of possible contamination problems.

Stratospheric negative ion composition measurements

Due to the somewhat larger technical difficulties associated with the detection of negative ions, which are caused by the use of higher high voltages on the detector and associated higher noise levels, the first reports on the negative ion composition in the stratosphere were published somewhat later than those for positive ions. The first mass analysis of stratospheric negative ions (Arnold and Henschen, 1978) revealed the existence of $NO_3^-(HNO_3)_n$ cluster ions, which was expected according to previous models as explained before.

Additionally, however, ions of the type

$$R^-(HR)_n(HNO_3)_m$$

were found. Although lack of resolution made it difficult to identify R, Arnold and Henschen (1978) proposed H_2SO_4 as a possible candidate for HR.

Subsequent laboratory measurements (Viggiano *et al.*, 1980) showed that sulfuric acid reacts rapidly with $NO_3^-(HNO_3)$-ions and reaction rate constants were reported for

$$NO_3^- + H_2SO_4 \rightarrow HSO_4^- + HNO_3 \quad (12)$$

$$NO_3^-(HNO_3) + H_2SO_4 \rightarrow HSO_4^- HNO_3 + HNO_3 \quad (13)$$

$$NO_3^-(HNO_3)_2 + H_2SO_4 \rightarrow HSO_4^-(HNO_3)_2 + HNO_3 \quad (14)$$

of 9.7×10^{-10} cm^3 s^{-1}, 8.6×10^{-10} cm^3 s^{-1} and 4×10^{-10} cm^3 s^{-1}, respectively.

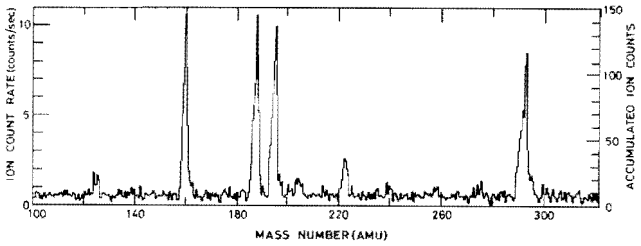

Figure 12
Typical nighttime high resolution spectrum for negative ions obtained near 35 km altitude (Resolution $m/\Delta m \cong 100$) (Arijs et al., 1981*).*

The derivations of these reaction rate constants used a dipole moment of H_2SO_4 of 0.55 Debye. Recently however this dipole moment was measured and found to be 2.725 Debye (Kuczkowski *et al.*, 1981). This increases the rate constants of reactions (12), (13) and (14) by a factor of 2.7 (Viggiano *et al.*, 1982).

In 1980 the first high resolution spectra of stratospheric negative ions (Arijs *et al.*, 1981) allowed an unambiguous mass determination of R and confirmed the H_2SO_4 hypothesis.

A typical negative ion spectrum obtained at 35 km altitude is shown in figure 12.

By using the quadrupole in a « low resolution » mode and relying upon rising mass edge detection, masses as high as 391 $[HSO_4^-(H_2SO_4)_3]$ were detected (Arijs *et al.*, 1981), which were confirmed later by moderate resolution data (Arnold *et al.*, 1982). As a consequence a more detailed reaction scheme for the conversion of NO_3^--ions to HSO_4^- was proposed (Arijs *et al.*, 1981) which is shown in figure 13.

The origin of H_2SO_4 in the stratosphere is, though not completely, far better understood than that of CH_3CN. Sulfuric acid is supposed to originate from the photochemical oxydation of SO_2, OCS and other sulfur gases that reach the stratosphere (Turco *et al.*, 1979). Even with its low number density, sulfuric acid is a very important minor constituent and plays an important role in the formation of stratospheric aerosols (Hamill *et al.*, 1977; Turco *et al.*, 1982). The application of the steady-state continuity equation to the formation and loss mechanism of HSO_4^- ions allows the calculation of the sulfuric acid number density $[H_2SO_4]$, through the formula

$$[H_2SO_4] = \frac{\alpha n^+}{k} \cdot \frac{n(HSO_4^-)}{n(NO_3^-)} \qquad (15)$$

where α_T is the ion-ion recombination coefficient, n^+ the positive ion number density, $n(HSO_4^-)$ and $n(NO_3^-)$ the total number density of all sulfate and nitrite-ions respectively and k the reaction rate constant for reactions of the type (12), (13) and (14). Several derivations of $[H_2SO_4]$ have been published in the past (Arnold and Fabian, 1980; Arijs *et al.*, 1981; Arnold *et al.*, 1981 and Viggiano and Arnold, 1981) and although the early measurements were low compared to model calculations (Turco *et al.*, 1979) more recent data (Viggiano and Arnold, 1982; Arijs *et al.*, 1983*b*) seem

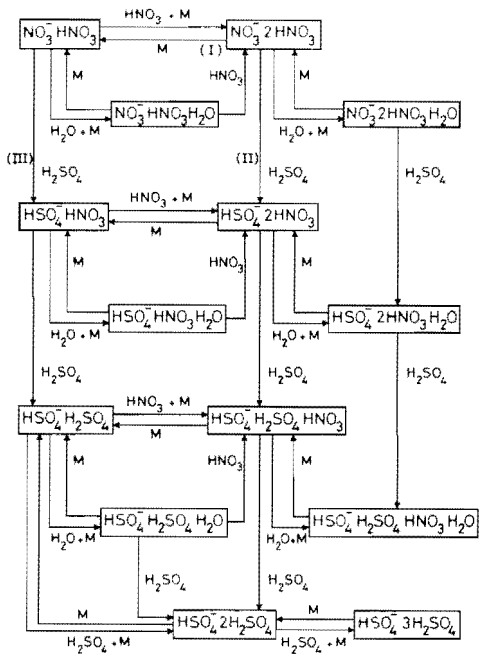

Figure 13
Proposed reaction scheme (Arijs et al., 1981*) for negative ions in the stratosphere. Neutral reaction partners are indicated along the arrows, M means a collision partner. I, II and III are the only reactions studied in the laboratory.*

to be in rather good agreement, as shown in figure 14. Care should be taken, however, in comparing theory and experiment since recent investigations (Arnold *et al.*, 1982) have revealed the existence of HSO_3 in the stratosphere and sulfuric acid vapour concentrations derived from ion-mass spectra include HSO_3, whereas models calculating $[H_2SO_4]$ do not.

By using laboratory data of $NO_3^-(HNO_3)_n$ clustering (Davidson *et al.*, 1977; Wlodeck *et al.*, 1980) and the fractional abundances of $NO_3^- \cdot (HNO_3)_n$-ions in the stratosphere one can also deduce nitric acid concen-

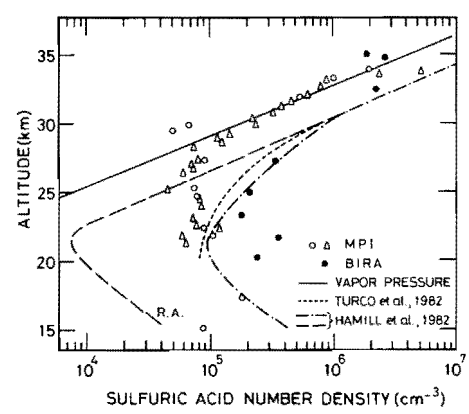

Figure 14
$H_2SO_4 + HSO_4$ *concentrations* versus *height compared to model curves (MPI : Viggiano* et al., 1982*; BIRA : Arijs* et al., 1982*a). The model curves are the* H_2SO_4 *vapour pressure over a* 75 % H_2SO_4/25 % H_2O *mixture (for fall temperatures). The other curves are from Turco* et al. (1981) *and Hamill* et al. (1982) *(RA : radical agglomeration) (after Viggiano and Arnold,* 1982*).*

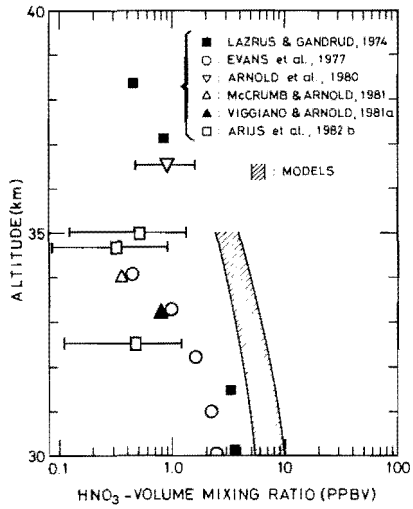

Figure 15
HNO_3 *concentrations* versus *altitude (above 30 km) as measured by different techniques and calculated by current models.*

Table 3
Minor stratospheric negative ions. Unless otherwise specified the uncertainties on the mass numbers is ± 2 amu.

Mass in amu (1)	Mass in amu (2)	Tentative identification (1)	Tentative identification (2)
17		OH^-	
26	26	CN^-	CN^-
42	43	$CN^- \cdot H_2O$	$CN^- \cdot H_2O$
47		NO_2^-	
62	61 ± 1	NO_3^-, CO_3^-	NO_3^-, CO_3^-
67		$NO_2^- \cdot H_2O$	
	80		$NO_3^- \cdot H_2O$, $CO_3^- \cdot H_2O$
87		$NO_3^- \cdot HCN$	
	97 ± 1		HSO_4^-, $NO_3^- \cdot HCl$, $CO_3^- HCl$
101		$NO_2^- \cdot HOCl$, $NO_3^- HCl$	
	109		$NO_3^- \cdot HNO_2$
115		$NO_3^- \cdot HOCl$	
125		$NO_3^- \cdot HNO_3$	
	133		$HSO_4^- \cdot HCl$
144	142	$NO_3^- \cdot HNO_3 \cdot H_2O$	$NO_3^- \cdot HNO_3H_2O$
148	148	$HSO_4^- \cdot HOCl$	$HSO_4^- \cdot HOCl$
173	174	$NO_3^- \cdot HNO_3 \cdot HNO_2$	$NO_3^- \cdot HNO_3 \cdot HOCl$, $HSO_4^- HNO_3 \cdot H_2O$
179		$NO_3^- \cdot HNO_3HOCl$, $HSO_4^- \cdot HNO_3 \cdot H_2O$	
205	206	$NO_3^- \cdot (HNO_3)_2 \cdot H_2O$	$NO_3^- \cdot (HNO_3)_2 \cdot H_2O$
	211		$HSO_4^- \cdot HNO_3 \cdot HOCl$, $HSO_4^- \cdot H_2SO_4 \cdot H_2O$
	231		$HSO_4^- \cdot H_2SO_4 \cdot HCl$
	240		$NO_3^-(HNO_3)_2 \cdot HOCl$, $HSO_4^-(HNO_3)_2 \cdot H_2O$
	248		$HSO_4^- \cdot H_2SO_4 \cdot HOCl$
	259		$HSO_4^- \cdot H_2SO_4 \cdot HNO_3$
275	273	$HSO_4^- \cdot H_2SO_4 \cdot HNO_3 \cdot H_2O$	$HSO_4^-(HNO_3)_2HOCl$, $HSO_4^- \cdot H_2SO_4HNO_3 \cdot H_2O$

(1) Arijs *et al.* (1982*b*).
(2) McCrumb and Arnold (1981).

trations. The results are shown in figure 15 (Arijs *et al.*, 1982*b*). Unfortunately the measured $NO_3^-(HNO_3)_n$-ion abundances are strongly influenced by cluster break up at altitudes below 30 km, which hampers the use of this method at lower altitudes.

Recently minor mass peaks in negative stratospheric ion mass spectra have been investigated. Several ions not belonging to the NO_3^-- or HSO_4^--ion families were observed (Arijs *et al.*, 1982*b*; McCrumb and Arnold, 1981). The power of the use of ion mass spectrometry in detecting trace gases (such as HCl, HOCl a.s.o.) is illustrated by the list of those ions in table 3, although the same remarks concerning signal instabilities and contamination are valid.

CONCLUSIONS

Our knowledge on positive and negative ions in the stratosphere has considerably increased during the last few years. The source of ions is fairly well understood and the information on ion-ion recombination has improved through recent experimental and theoretical work (Smith and Adams, 1982; Bates, 1982).

Due to the *in situ* composition measurements we have obtained a better insight into the ion chemistry in the altitude region from 20 to 35 km altitude. Modelling of stratospheric ion chemistry however is still tentative due to the lack of knowledge of reliable ion-molecule reaction rate constants. Nevertheless it has been possible to use *in situ* ion composition measurements for neutral trace gas analysis for gases such as H_2SO_4 and CH_3CN in the stratosphere.

Another application of stratospheric ion composition measurements (positive as well as negative) is their use as a diagnostic tool for the calculation of thermochemical values of ion-molecule reactions (Arnold *et al.*, 1981*a*, 1981*b*; Arijs *et al.*, 1982*a*, 1982*b*). Although it should be stressed that secondary effects such as pollution by balloon or gondolla, incomplete counting statistics and ion cluster break up may disturb the data. The effect of cluster break up is more pronounced at lower altitudes, which has been clearly shown by height measurements of negative ions from 23 to 39 km (Viggiano and Arnold, 1981).

Future progress in ballooning techniques (valve controlled balloons) and experimental developments (high sensitivity instruments) may help to overcome difficulties of pollution and low counting statistics, as to the understanding of cluster break up extended laboratory measurements will be needed.

It should also be noted that so far only fractional abundances of ions or ion groups have been reported. No data about absolute ion densities have been deduced from mass spectrometer measurements. To do so a careful calibration of the instruments will be necessary, which at present poses some severe problems. However such efforts are clearly needed in the future.

In order to complete the present picture of ion chemistry in the stratosphere the *in situ* measurements must be extended above 35 km and below 20 km altitude and further *in situ* as well as laboratory work will be needed.

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