

## MASS SPECTROMETRIC MEASUREMENTS OF STRATOSPHERIC IONS

E. Arijs, D. Nevejans and J. Ingels

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

### ABSTRACT

Recent 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 non proton hydrates of the form  $H^+X_m(H_2O)_z$ . The data analysis allows a derivation of the vertical mixing ratio profile of X (most probably  $CH_3CN$ ), which is compared with recent model calculations. From negative ion composition data, showing the presence of  $NO_3^-$  and  $HSO_4^-$  cluster ions, the density of sulfuric acid in the stratosphere is deduced. The implications of these findings on our understanding of the sulfur chemistry is briefly treated.

Finally some other aspects such as contamination, cluster break up and the use of stratospheric ion mass spectra for determination of thermochemical data and other minor constituents are discussed.

### INTRODUCTION

The study of the ion composition of the lower ionosphere, has made enormous progress since the pioneering work of Narcisi et al. /1,2/. Since then, in situ measurements with rocket borne mass spectrometers /3,4,5/ associated with laboratory work /6,7/ and modelling efforts /8,9/ have enabled a fairly good understanding of the ion chemistry in the altitude range from 100 to 60 km and showed that neutral trace species play a key role in the ion composition of the lower atmosphere.

Extending the existing work down to the stratosphere /9,10/ allowed to predict that the primary ions formed by cosmic rays in the stratosphere, will rapidly convert to ions with a totally different identity through ion-molecule reactions, involving minor constituents with very low concentrations. Once these reactions and their rate constants are known, a detailed knowledge of the ion composition can be used to determine these trace species and their mixing ratios. Conversely, the measurement of the ion composition can lead to the derivation of thermochemical and kinetic data of the appropriate ion-molecule reactions. Lately, it was also pointed out /11,12/ that stratospheric ions may play a role in the nucleation and formation of aerosols. Thus, the previous considerations justify as a logical step, the extension of ion composition measurements into the stratosphere.

The associated technical problems are very difficult, due to the high gas number densities at lower altitudes. However, such measurements have become feasible recently, mainly as a result of the development of powerful and light weight cryopumping systems, enabling a vacuum below  $10^{-4}$  Torr in the mass spectrometer, in spite of a high ambient pressure.

It is the purpose of this paper to review stratospheric ion mass spectrometry, emphasizing the obtained results and their discussion.

The description of the instruments, primarily consisting of a quadrupole mass filter, built into a high speed liquid helium or neon pump and the associated electronics, has been given in detail elsewhere /13,14,15/.

In view of the limited space available, it is not possible to treat all the aspects of the subject in detail, but we have tried to make the reference list as complete as possible. Earlier reviews have also been given by Arnold /16/, Ferguson and Arnold /17/ and Arijs /18/.

### POSITIVE ION COMPOSITION OF THE STRATOSPHERE

The first positive ion composition data of the stratosphere resulted from measurements with rocket borne instruments by Arnold et al. /19/ and showed the existence of two major ion families. The first one, identified as  $H^+(H_2O)_n$  ions or proton hydrates (PH), was expected

from models based on laboratory measurements and extensions of the understanding of the D-region ion chemistry /9,10,20/. The second one contains ions with masses  $29 \pm 1$ ,  $42 \pm 1$ ,  $60 \pm 1$  and  $80 \pm 1$  amu, termed non proton hydrates (NPH), which become dominant below 40 km. It was established that this group resulted from reactions of PH with an unknown trace gas X. Originally  $\text{CH}_2\text{O}$  was proposed, which was rejected later as a result of laboratory work /21/.

Since rocket flights allow only a short sampling time, thereby hampering the use of high resolution, and also induce shock waves, causing dissociation of cluster ions, further efforts to identify X were performed with balloon borne instruments.

The first positive ion mass spectra obtained from balloon flights in the stratosphere were reported almost simultaneously by three groups /22,23,24/. The major ions observed are summarized in table 1. From this it was concluded /23/ that all NPH cluster ions could be represented by  $\text{H}^+\text{X}_n(\text{H}_2\text{O})_m$  where X had a mass number of  $41 \pm 1$  amu, a proton affinity substantially higher than that of water and an atmospheric number density of approximately  $10^5 \text{ cm}^{-3}$ . Arnold et al. /23/ subsequently suggested acetonitrile ( $\text{CH}_3\text{CN}$ ) for X. Because of the difficulty of conceiving a viable production method of  $\text{CH}_3\text{CN}$  in the stratosphere and inspired by the existence of a sodium layer in the upper atmosphere /25/, Ferguson proposed NaOH for X /26/. Subsequent model calculations of Liu and Reid /27/ and laboratory data of Märck et al. /28/ and Perry et al. /29/ gave more credibility to this hypothesis. In 1979 it was pointed out /30/ that the NPH could also be fitted by  $\text{Mg}^+(\text{OH})_n$  although this possibility was excluded later by laboratory measurements /31/.

The first high resolution mass spectra of positive ions in the stratosphere, reported in 1980 by Arijs et al. /32/ showed unambiguously that X had mass 41 and that no Mg isotopes could be detected. This ruled out both the NaOH and MgOH hypotheses and gave credit again to the original  $\text{CH}_3\text{CN}$  proposal.

More arguments<sup>3</sup> in favour of this candidate were brought by laboratory experiments /33,34/ and by inspections of the fractional abundances of positive ions observed around 35 km /35,36/.

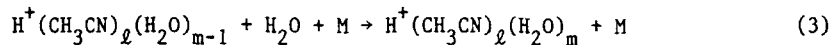
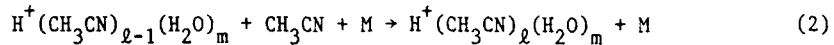
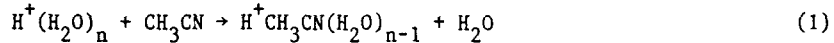
Although recently the presence of  $\text{CH}_3\text{CN}$  in the stratosphere was questioned by Ballenthin /37/ as a result of the in situ measurement of the isotopic mass peaks of mass 78 [ $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_2$ ], a careful check during a recent balloon flight realized by our group, has not allowed to confirm his statement.

TABLE 1 Observed positive ions in the stratosphere

Ref 19	Mass (in amu)			Proposed Ion Clusters
	24	22	23	
$19 \pm 2$		$20 \pm 3$		$\text{H}^+(\text{H}_2\text{O})$
$29 \pm 2$		$29 \pm 3$		?
$37 \pm 2$		$37 \pm 3$		$\text{H}^+(\text{H}_2\text{O})_2$
$42 \pm 2$		$43 \pm 3$		$\text{H}^+\text{X}$
		$50 \pm 3$		?
$55 \pm 2$		$55 \pm 3$	55	$\text{H}^+(\text{H}_2\text{O})_3$
$60 \pm 2$		$60 \pm 2$		$\text{H}^+\text{X}(\text{H}_2\text{O})$
	73	$73 \pm 2$	$73 \pm 1$	$\text{H}^+(\text{H}_2\text{O})_4$
$80 \pm 2$		$78 \pm 2$	$78 \pm 2$	$\text{H}^+\text{X}(\text{H}_2\text{O})_2$
		$82 \pm 2$		$\text{H}^+\text{X}_2$
	91	$91 \pm 2$	$91 \pm 1$	$\text{H}^+(\text{H}_2\text{O})_5$
		$96 \pm 2$	$96 \pm 1$	$\text{H}^+\text{X}(\text{H}_2\text{O})_3$
		$99 \pm 2$	$100 \pm 1$	$\text{H}^+\text{X}_2(\text{H}_2\text{O})$
	109	$109 \pm 2$		$\text{H}^+(\text{H}_2\text{O})_6$
			$114 \pm 2$	$\text{H}^+\text{X}(\text{H}_2\text{O})_4$
			$118 \pm 1$	$\text{H}^+\text{X}_2(\text{H}_2\text{O})_2$
			$136 \pm 2$	$\text{H}^+\text{X}_2(\text{H}_2\text{O})_3$
			$140 \pm 2$	$\text{H}^+\text{X}_3(\text{H}_2\text{O})$

Since 1977, several mass spectra of the positive ions in the stratosphere have been obtained /38-41/ in the altitude region from 20 to 45 km. The measured fractional abundances of the NPH ions are summarized in figure 1.

Accepting that NPH are formed through the reactions



and assuming that the major sink for NPH is ion-ion recombination and that reconversion from NPH to PH can be neglected, the  $\text{CH}_3\text{CN}$  number density can be derived from the steady state equation

$$[\text{CH}_3\text{CN}] = \frac{\alpha [n_-] [\text{NPH}]}{k_1 [\text{PH}]} \quad (4)$$

Here square brackets denote number densities,  $\alpha$  is the ion-ion recombination coefficient,  $[n_-]$  the total negative ion density and  $k_1$  the rate coefficient for reactions of type (1). The recombination rate coefficient  $\alpha$  being known /33,42,43/ and taking  $k_1$  from laboratory measurements by Smith et al. /33/, the mixing ratio of  $\text{CH}_3\text{CN}$  can be calculated from the data points of figure 1. The result is shown in figure 2.

To explain the presence of acetonitrile in the stratosphere two different hypotheses have been put forward. Murad et al. /44/ propose an in situ formation mechanism based on the reactions :

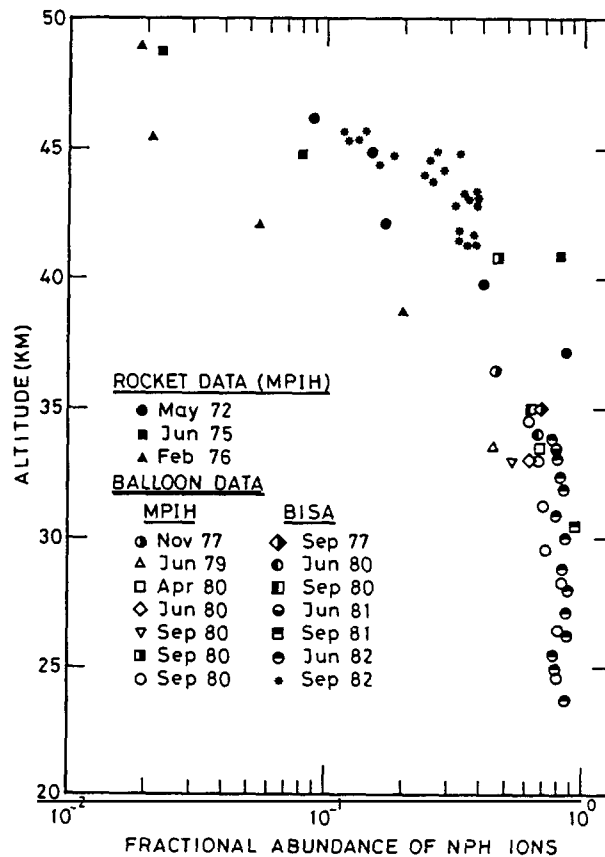


Fig. 1. Fractional abundance of  $\text{H}^+(\text{CH}_3\text{CN})_m(\text{H}_2\text{O})_{\ell}$  ions as measured during different balloon- and rocket flights.

Reaction (5) however is probably much slower than deduced by Murad et al. /44/. If fast enough to explain the data of figure 2, it should represent a major sink of HCN and the measured values of HCN should be very difficult to explain /45/. Furthermore the reaction



most likely is fast enough to destroy all  $\text{CH}_2\text{CN}$  before it can form any acetonitrile.

At present it seems therefore more realistic to accept the model of Brasseur et al. /46/ who assume a surface emission of  $\text{CH}_3\text{CN}$ , followed by upward diffusion and destruction by OH in the stratosphere. Recent measurements of  $\text{CH}_3\text{CN}$  at ground level /47,48/ seem to plead for this proposal, although some problems remain to be solved, such as possible tropospheric wash out and a detailed investigation of emission sources.

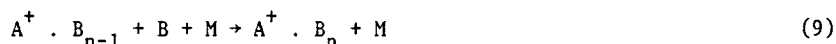
Also shown in figure 2 for comparison is a model calculation, assuming no wash out (which seems to be likely /48/) and a global yearly emission of  $2.3 \times 10^{10}$  g  $\text{CH}_3\text{CN}$ . This low emission can be accounted for by sources such as biomass burning, industrial releases and car gas exhaust.

Although  $\text{CH}_3\text{CN}$  may not have a large impact on major aeronomic problems such as ozone depletion, its derivation is a nice example of the use of ion mass spectra for the detection of trace gases at the ppt level and it clearly illustrates the power of the method.

An inspection of minor mass peaks in positive ion spectra /36,49/ shows the potential of the detection of other trace gases among which Na, Al,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{COH}$ , HCN,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_2\text{O}_2$ ,  $\text{CH}_4\text{S}$ ,  $\text{C}_2\text{H}_6\text{O}$ ,  $\text{CH}_3\text{NO}_2$  and  $\text{C}_2\text{H}_5\text{NS}$  are possible candidates. Apart from  $\text{CH}_3\text{OH}$ , which seems to be clearly present, the mentioned molecules are rather speculative and more measurements are needed to establish their role in the stratospheric ion chemistry.

It should also be stressed that contamination caused by outgassing from balloon and gondola, may give rise to some additional artificial mass peaks /15,40,41/, resulting in possible misinterpretation of the data. The use of valve controlled balloons, allowing a slow descent and consequently a fresh air flow around the instrument and of nighttime flights, with no heating of the payload by solar radiation, should minimize contamination.

Another effect hampering full exploitation of stratospheric ion composition data is cluster break up or collision induced dissociation. It especially limits the use of the so-called equilibrium method, in principle allowing the derivation of either trace gas concentrations or thermochemical data from the measurement of fractional ion abundances. This method is based on the fact, that when cluster ions  $\text{A}^+ \text{B}_n$  are formed by a reaction



the abundance ratio of the ions of the family  $\text{A}^+ \text{B}_n$  can be written as :

$$[\text{A}^+ \text{B}_n] / [\text{A}^+ \text{B}_{n-1}] = K p(\text{B}) \quad (10)$$

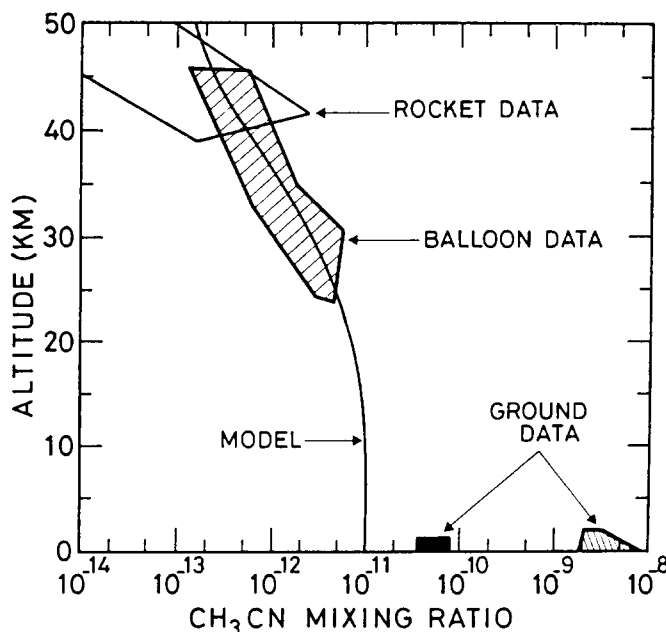


Fig. 2.  $\text{CH}_3\text{CN}$  mixing ratios, as inferred from positive ion composition data and as measured by other techniques /47,48/, compared to a recent model calculation for a global emission of 0.023 MT/yr and no wash out /46/.

where  $p(B)$  is the partial pressure of B and K is the equilibrium constant given by

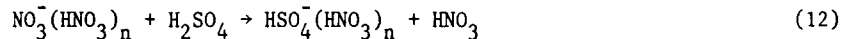
$$-RT \ln K = \Delta H_o - T\Delta S_o = \Delta G_o \quad (11)$$

In principle if  $\Delta G_o$  is known,  $p(B)$  can be derived from  $[A^+B_n]/[A^+B_{n-1}]$  or conversely if  $p(B)$  is measured independently  $\Delta G_o$  can be calculated.

Unfortunately the cluster ions  $A^+B_n$  (for the stratosphere  $A \equiv H_3O^+$  or  $H^+CH_3CN$  and  $B = H_2O$ ,  $CH_3CN$  or one of the previously mentioned trace gases) are weakly bound ions and can break up in the mass spectrometer just behind the sampling hole, where the pressure is still relatively high and where electric fields accelerate them into the mass filter. It has been shown /15/ that this collision induced dissociation can falsify measurements largely, especially at lower altitudes. To a certain extent however cluster break up can be simulated in the laboratory /35,36/ and the distribution of positive ions can be used to derive useful data, such as temperature /36/. It is evident however that instrumental refinements to avoid collision induced dissociation as well as further laboratory studies should be made.

#### NEGATIVE ION COMPOSITION OF THE STRATOSPHERE

The first stratospheric negative ion composition data, obtained with a balloon borne instrument by Arnold and Henschen /50/ showed that the major ions are  $NO_3^- \cdot HNO_3$  cluster ions, predicted by laboratory data /51/, and ions of the type  $R(HR)_0(HNO_3)_m$ . For  $HR$ , Arnold and Henschen suggested  $H_2SO_4$ , formed through photochemical oxydation of  $SO_2$  in the stratosphere /52/. The rate constants of the reactions,



were subsequently measured in the laboratory by Viggiano et al. /53,54/ and turned out to be fast ( $2.6 \times 10^{-9}$ ,  $2.3 \times 10^{-9}$  and  $1.1 \times 10^{-9}$   $cm^3 s^{-1}$  for  $n = 0, 1$  and  $2$  respectively).

In 1980, the first high resolution measurements of negative ion composition around 35 km by Arijis et al. /55/, allowed an unambiguous mass determination of the major ions and confirmed the  $H_2SO_4$  hypothesis. Since then, negative ion spectra were obtained in the altitude range from 20 to 45 km /56-62/, which showed that the major ions over the whole altitude region were  $NO_3^-$  and  $HSO_4^-$  core ions.

A typical fractional abundance measurement by the Heidelberg group of both ion families is shown in figure 3. The measurements of the Belgian group are rather similar, though a higher fractional abundance of  $HSO_4^-$  core ions is observed below 30 km.

Above 40 km, the  $HSO_4^-$  core ions redisappear slowly /61/ and at 45 km even  $CO_3^-$  ions are observed, indicating that stratospheric ion chemistry merges with D-region ion chemistry in that region.

Variations with altitude of the ion fractional abundances as shown in figure 3 are caused by the variation of sulfuric acid concentration in the stratosphere. Using a similar steady state treatment as for PH and NPH, the number density of sulfur compounds converting  $NO_3^-$  core ions into  $HSO_4^-$  core ions can be deduced from

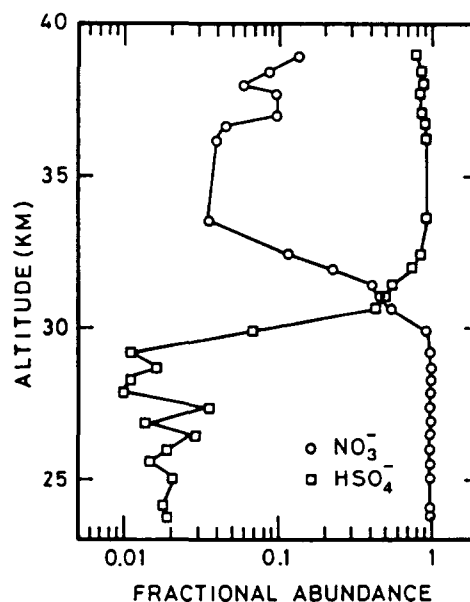


Fig. 3. Fractional ion signal of  $NO_3^-$  and  $HSO_4^-$  core ions versus altitude from a balloon flight of Viggiano and Arnold /57/.

$$k_2 [n_N] [H_2SO_4 + HSO_y] = \alpha [n_+] [n_S] \quad (13)$$

where  $[n_+]$  is the total positive ion density,  $k_2$  the rate coefficient of reaction (12) and  $[n_S]$  and  $[n_N]$  the total number density of  $HSO_4^-$  and  $NO_3^-$  core ions respectively.  $HSO_y$  represents  $HSO_3$ ,  $HSO_5$  and any other sulfur compound giving rise to  $HSO_4^-$  core ions. A compilation of recent results obtained in this way by the Heidelberg and the Belgian group /55,63-68/ is given in figure 4. The number densities shown here, suffer from large errors due to uncertainties in the values of  $\alpha$ ,  $[n_+]$  and  $k_2$  and due to uncertain  $[n_S]$  values, resulting from poor signal strength at lower altitudes. In view of these uncertainties and possible errors on altitude measurement the data of the different groups are in reasonable agreement.

Also shown in figure 4 are some recent model calculations for  $[H_2SO_4]$  by Turco et al. /69/, represented by curves A, B, C and D (full lines above 30 km and dashed lines below). The dot-and-dash line G is a model result for  $[HSO_3]$  /52/. Curves E and F are summations of G + A and G + B (or C, or D) respectively. The dashed line H is a vapour pressure calculation of  $H_2SO_4$  as explained in detail before /65/. 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  $H_2SO_4 + HSO_y$  vapour is clearly in supersaturation. The main loss processes for sulfuric acid vapour are interaction with aerosols; its production being the oxydation of  $SO_2$  vapour through the reactions



Above 35 km, the measurements seem to suggest a good agreement with curve B, obtained by 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 /69/.

Recently it became possible to deduce  $HSO_3$  number densities from steady state considerations about ions containing  $HSO_3$  ligands /70,71/ as well as  $SO_2$  concentrations from ion composition measurements /61/. These data /68,73/ show that  $H_2SO_4$  has a much larger photodissociation coefficient than accepted in the models so far. Furthermore the oxydation mechanism of  $SO_2$  is not clear yet /73/ and therefore it seems premature to draw definite conclusions. Anyhow, negative ion composition data have delivered the first data on  $H_2SO_4$  vapour concentrations in the stratosphere and provide a powerful tool for a further understanding of sulfur chemistry in the stratosphere.

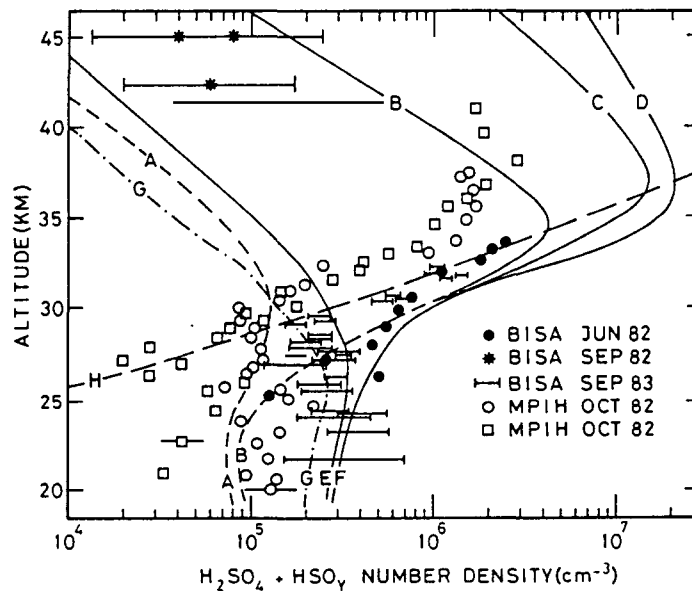


Fig. 4.  $H_2SO_4 + HSO_y$  number densities obtained from different in situ measurements and from different model calculations.

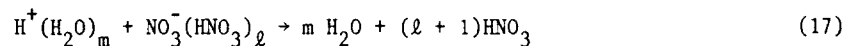
Nitric acid is another important trace gas, where of the concentration can be derived from negative ion composition data. Both the equilibrium method /59,74/ and the steady state method /57,58,62/ have been applied. Below 30 km, cluster break up disturbs the measurements /72/ severely and the inferred  $\text{HNO}_3$  mixing ratios are much too low. Above this altitude however ion composition data may turn out to be a useful method for  $\text{HNO}_3$  derivations. The values obtained and summarized in figure 5, are in reasonable agreement with previously measured data or model calculations /75/ within the experimental errors above 30 km.

The measurement of minor ion abundances with more sensitive instruments can open the way for the detection of many other trace gases such as  $\text{HCl}$ ,  $\text{HOCl}$  and  $\text{HCN}$  /58,59/ although contamination is a serious problem here. More laboratory measurements should also be performed to obtain kinetic and thermochemical data about the ion-molecule reactions with these species.

As stated in the introduction, these data can also be deduced from in situ ion mass spectrometric probings, using the stratosphere as a laboratory. Again contamination and especially cluster break up, inhibit this kind of measurements. Nevertheless, for cluster ions such as  $\text{HSO}_4^-$  core ions, where no laboratory data at all are available some first approximative thermochemical data can be inferred from the ion abundances obtained at high altitudes where cluster break up has a minor effect. This has been done by the Heidelberg group /56,62,70/ and extensive lists of  $\Delta G_0$  and  $\Delta H_0$  values can be found in the appropriate references.

#### MULTI-ION COMPLEXES AND ION NUCLEATION

Ions in the stratosphere are believed to disappear under normal conditions by recombination processes such as :



It was pointed out by Ferguson /76/ however, that for high values of  $(\ell + m)$ , reactions such as (17) can become endothermic and stable solvated ion pairs can be produced. According to Arnold /12/, the condition for such a polyion formation is :

$$E_A + S_- > \text{IP} - S_+ + E_C \quad (18)$$

where  $E_A$  is the electron affinity of the negative ion core, IP the ionization potential of the positive ion core,  $S_-$  and  $S_+$  are the total solvation energies of the negative and positive cluster ions and  $E_C$  the energy released on formation of a chemical bond. The solvation energies  $S$  can be derived from the free energy differences  $\Delta G$  as inferred from laboratory measurements or stratospheric ion composition data. From this Arnold /70/ concluded that the region around 30 km contains enough higher order cluster ions to be favourable for polyion formation.

These polyions can be the basis for aerosol formation through ion induced nucleation mechanisms.

Recently, the ion nucleation rate was calculated by Arnold /77/. It appeared that ion nucleation can be an efficient source for condensation nuclei, in the 27-37 km altitude region, especially during periods of short temperature changes in the stratosphere. These

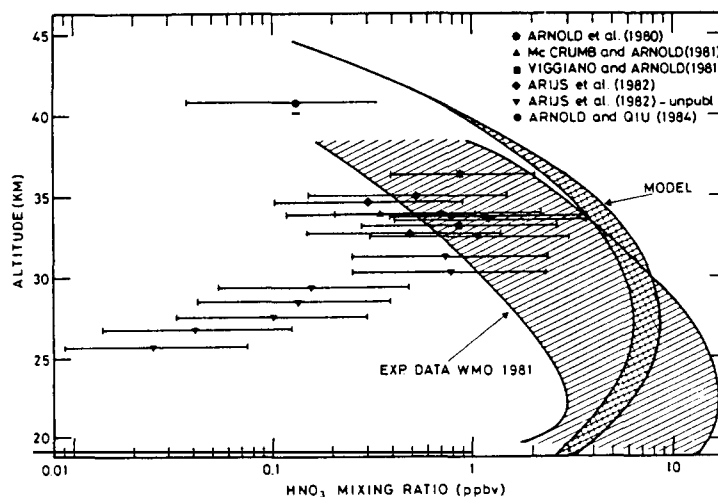


Fig. 5. Nitric acid mixing ratios deduced from negative ion composition measurements, compared to other measurements and model calculations.

calculations however are only first order approximations and more extensive model treatments are needed. Definite experimental evidence for the existence of polyions or multi-ion complexes has not yet been found /40,78/ although recently Hofman and Rosen /79/ were able to explain condensation nuclei events with the model developed by Arnold /77/.

#### CONCLUSIONS

Recent in situ mass spectrometric measurements of positive and negative ions in the altitude region 15 to 45 km, obtained mainly by two groups (Max Planck Institute of Heidelberg and Belgian Institute for Space Aeronomy) have permitted a better understanding of the stratospheric ion chemistry. As far as the formation of major ions is concerned, a consistent picture can now be formed.

Stratospheric ion mass spectrometry also has opened a way for detections of trace gases down to the ppt level. Species e.g.  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{SO}_4$ , not traceable so far, have now been detected. For these gases ion mass spectrometry is the only analytic method available at present. Especially the detection of  $\text{H}_2\text{SO}_4$  is of primary importance for the understanding of the sulfur cycle and the formation of aerosols.

A continuation of in situ data collection and associated laboratory measurements as well as modelling efforts /80,81/ are needed to complete our knowledge of the ion processes in the stratosphere.

#### REFERENCES

1. R.S. Narcisi and A.D. Bailey, Mass spectrometric measurements of positive ions at altitudes from 64 to 112 kilometers, *J. Geophys. Res.*, 70, 3687 (1965).
2. R.S. Narcisi, A.D. Bailey, L.E. Wlodyka and C.R. Philbrick, Ion composition measurements in the lower ionosphere during the November 1966 and March 1977 solar eclipses, *J. Atmosph. Terr. Phys.*, 34, 647 (1972).
3. R.A. Goldberg and A.C. Aikin, Studies of positive ion composition in the equatorial D-region ionosphere, *J. Geophys. Res.*, 76, 8352 (1971).
4. F. Arnold, J. Kissel, D. Krankowsky, H. Wieder and J. Zaehring, Negative ions in the lower ionosphere: A mass-spectrometric measurement, *J. Atmosph. Terr. Phys.*, 33, 1169 (1971).
5. P.A. Zbinden, M.A. Hidalgo, P. Eberhardt and J. Geiss, Mass spectrometer measurements of the positive ion composition in the D- and E-regions of the ionosphere, *Planet. Space Sci.*, 23, 1621 (1975).
6. E.E. Ferguson, Rate constants of thermal energy ion-molecule reactions of aeronomic interest, *Atomic Data and Nucl. Data Tables*, 12, 159 (1973).
7. D.L. Albritton, Ion-neutral reaction rate constants measured in flow reactors through 1977, *Atomic Data and Nucl. Data Tables*, 22, 1 (1978).
8. L. Thomas, Recent developments and outstanding problems in the theory of the D-region, *Radio Science*, 9, 121 (1974).
9. V.A. Mohnen, Discussion of the formation of major positive and negative ions up to the 50 km level, *Pure Appl. Geophys.*, 84, 141 (1971).
10. E.E. Ferguson, Ion chemistry of the normal earth's stratosphere, in "The natural stratosphere of 1974", *CIAP Monograph*, 1, 5.42 (1974).
11. A.W. Castleman, Jr., Nucleation and molecular clustering about ions, *Advances in Colloid and Interface Science*, 10, 73 (1979).
12. F. Arnold, Multi-ion complexes in the stratosphere-implications for trace gases and aerosols, *Nature*, 284, 610 (1980).
13. J. Ingels, E. Arijs, D. Nevejans, H.J. Forth and G. Schaefer, Liquid helium cryopump and reliable opening device for a balloon borne mass spectrometer, *Rev. Sci. Instrum.*, 49, 782 (1978).
14. D. Nevejans, P. Frederick and E. Arijs, Microprocessor based data acquisition and control system for a balloon borne quadrupole mass spectrometer, *Bull. Acad. Roy. Belg. Cl. Sci.*, 68, 314 (1982).
15. D. Nevejans, J. Ingels and E. Arijs, Measurement and identification of stratospheric ions with balloon borne instruments, *MAP Handbook on ballooning techniques*, in press (1984).
16. F. Arnold, The middle atmosphere ionized component, *Proceedings of the Vth ESA-PAC Symposium on European Rocket and Balloon Programmes and Related Research*. Bournemouth, U.K. (ESA, SP-152), 479 (1980).
17. E.E. Ferguson and F. Arnold, Ion Chemistry of the Stratosphere, *Acc. Chem. Res.*, 14, 327 (1981).
18. E. Arijs, Positive and negative ions in the stratosphere, *Annales Geophysicae*, 1, 149 (1983).
19. F. Arnold, D. Krankowsky and K.H. Marien, First mass spectrometric measurements of positive ions in the stratosphere, *Nature*, 267, 30 (1977).
20. F.C. Fehsenfeld and E.E. Ferguson, Origin of water cluster ions in the D region, *J. Geophys. Res.*, 74, 2217 (1969).



21. F.C. Fehsenfeld, I. Dotan, D.L. Albritton, C.J. Howard and E.E. Ferguson, Stratospheric positive ion chemistry of formaldehyde and methanol, *J. Geophys. Res.*, 83, 1333 (1978).
22. E. Arijs, J. Ingels and D. Nevejans, Mass spectrometric measurement of the positive ion composition in the stratosphere, *Nature*, 271, 642 (1978).
23. F. Arnold, H. Böhringer and G. Henschen, Composition measurements of stratospheric positive ions, *Geophys. Res. Lett.*, 5, 653 (1978).
24. J.R. Olsen, R.C. Amme, J.N. Brooks, D.G. Murcray, D.A. Steffen, R.E. Sturm and G.E. Keller, Balloon borne ion sampling package, *Rev. Sci. Instrum.*, 49, 643 (1978).
25. G. Megie, F. Bos, J.E. Blamont and M.L. Chanin, Simultaneous nighttime lidar measurements of atmospheric sodium and potassium, *Planet. Space Sci.*, 26, 27 (1978).
26. E.E. Ferguson, Sodium hydroxyde ions in the stratosphere, *Geophys. Res. Lett.*, 5, 1035 (1978).
27. S.C. Liu and G.C. Reid, Sodium and other minor constituents of meteoric origin in the atmosphere, *Geophys. Res. Lett.*, 6, 283 (1979).
28. T.D. Märck, K.I. Peterson and A.W. Castleman Jr., New gas phase inorganic ion cluster species and their atmospheric implications, *Nature*, 285, 392 (1980).
29. R.A. Perry, B.R. Rowe, A.A. Viggiano, D.L. Albritton, E.E. Ferguson and F.C. Fehsenfeld, Laboratory measurements of stratospheric sodium ion reactions, *Geophys. Res. Lett.*, 7, 693 (1980).
30. E. Murad and W. Swider, Chemistry of meteor metals in the stratosphere, *Geophys. Res. Lett.*, 6, 929 (1979).
31. E.E. Ferguson, B.R. Rowe, D.W. Fahey and F.C. Fehsenfeld, Magnesium ion chemistry in the stratosphere, *Planet. Space Sci.*, 29, 479 (1981).
32. E. Arijs, D. Nevejans and J. Ingels, Unambiguous determination of major stratospheric positive ions, *Nature*, 288, 684 (1980).
33. D. Smith, N.G. Adams and E. Alge, Ion-ion mutual neutralization and ion-neutral switching reactions of some stratospheric ions, *Planet. Space Sci.*, 29, 449 (1981).
34. H. Böhringer and F. Arnold, Acetonitrile in the stratosphere-implications from laboratory studies, *Nature*, 290, 321 (1981).
35. F. Arnold, G. Henschen and E.E. Ferguson, Mass spectrometric measurements of fractional ion abundances in the stratosphere-Positive ions, *Planet. Space Sci.*, 29, 185 (1981).
36. E. Arijs, D. Nevejans and J. Ingels, Stratospheric positive ion composition measurements, ion abundances and related trace gas detection, *J. Atmosph. Terr. Phys.*, 44, 43 (1982).
37. J.O. Ballenthin, Positive ion measurements at 38 km altitude, *EOS Trans. Am. Geophys. Union*, 64, 282 (1983).
38. G. Henschen and F. Arnold, Extended positive ion composition measurements in the stratosphere-Implication for neutral trace gases, *Geophys. Res. Lett.*, 8, 999 (1981).
39. F. Arnold and G. Henschen, Positive ion composition measurements in the upper stratosphere-Evidence for an unknown aerosol component, *Planet. Space Sci.*, 30, 101 (1982).
40. E. Arijs, D. Nevejans, J. Ingels and P. Frederick, Positive ion composition measurements between 33 and 20 km altitude, *Annales Geophysicae*, 1, 161 (1983).
41. E. Arijs, D. Nevejans and J. Ingels, Positive ion composition measurements and acetonitrile in the upper stratosphere, *Nature*, 303, 314 (1983).
42. J.M. Rosen and D.J. Hofman, Balloon borne measurements of electrical conductivity, mobility and the recombination coefficient, *J. Geophys. Res.*, 86, 7406 (1981).
43. D.R. Bates, Recombination of small ions in the troposphere and lower stratosphere, *Planet. Space Sci.*, 30, 1275 (1982).
44. E. Murad, W. Swider, R.A. Moss and S. Toby, Stratospheric sources of  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}$ , *Geophys. Res. Lett.*, 11, 147 (1984).
45. R.J. Cicerone and R. Zellner, The atmospheric chemistry of hydrogen cyanide (HCN), *J. Geophys. Res.*, 88, 10689 (1983).
46. G. Brasseur, E. Arijs, A. De Rudder, D. Nevejans and J. Ingels, Acetonitrile in the atmosphere, *Geophys. Res. Lett.*, 10, 725 (1983).
47. K.H. Becker and A. Ionescu, Acetonitrile in the lower troposphere, *Geophys. Res. Lett.*, 9, 1349 (1982).
48. J.R. Snider and G.A. Dawson, Surface acetonitrile near Tucson, Arizona, *Geophys. Res. Lett.*, 11, 241 (1984).
49. G. Henschen and F. Arnold, New positive ion species in the stratosphere, *Nature*, 291, 211 (1981).
50. F. Arnold and G. Henschen, First mass analysis of stratospheric negative ions, *Nature*, 275, 521 (1978).
51. F.C. Fehsenfeld, C.J. Howard and A.L. Schmeltekopf, Gas phase ion chemistry of  $\text{HNO}_3$ , *J. Chem. Phys.*, 63, 2835 (1975).
52. R.P. Turco, P. Hamill, O.B. Toon, R.C. Whitten and C.S. Kiang, A one-dimensional model describing aerosol formation and evolution in the stratosphere : I. Physical processes and mathematical analysis, *J. Atm. Sci.*, 36, 699 (1979).

53. A.A. Viggiano, R.A. Perry, D.L. Albritton, E.E. Ferguson and F.C. Fehsenfeld, The role of  $H_2SO_4$  in stratospheric negative ion chemistry, *J. Geophys. Res.*, 85, 4551 (1980).
54. A.A. Viggiano, R.A. Perry, D.L. Albritton, E.E. Ferguson and F.C. Fehsenfeld, Stratospheric negative ion reaction rates with  $H_2SO_4$ , *J. Geophys. Res.*, 87, 7340 (1982).
55. E. Arijs, D. Nevejans, P. Frederick and J. Ingels, Negative ion composition measurements in the stratosphere, *Geophys. Res. Lett.*, 8, 121 (1981).
56. F. Arnold, R. Fabian, E.E. Ferguson and W. Joos, Mass spectrometric measurements of fractional ion abundance in the stratosphere - Negative ions, *Planet. Space Sci.*, 29, 195 (1981).
57. A.A. Viggiano and F. Arnold, The first height measurements of the negative ion composition of the stratosphere, *Planet. Space Sci.*, 29, 895 (1981).
58. J.L. Mc Crumb and F. Arnold, High-sensitivity detection of negative ions in the stratosphere, *Nature*, 294, 136 (1981).
59. E. Arijs, D. Nevejans, P. Frederick and J. Ingels, Stratospheric negative ion composition measurements, ion abundances and related trace gas detection, *J. Atmosph. Terr. Phys.*, 44, 681 (1982).
60. A.A. Viggiano, H. Schlager and F. Arnold, Stratospheric negative ions - detailed height profiles, *Planet. Space Sci.*, 31, 813 (1983).
61. E. Arijs, D. Nevejans, J. Ingels and P. Frederick, Negative ion composition and sulfuric acid vapour in the upper stratosphere, *Planet. Space Sci.*, 31, 1459 (1983).
62. F. Arnold and S. Qiu, Upper stratospheric negative ion composition measurements and inferred trace gas abundances, *Planet. Space Sci.*, 32, 169 (1984).
63. F. Arnold and R. Fabian, First measurements of gas phase sulfuric acid in the stratosphere, *Nature*, 283, 55 (1980).
64. F. Arnold, R. Fabian and W. Joos, Measurements of the height variation of sulfuric acid vapor concentration in the stratosphere, *Geophys. Res. Lett.*, 8, 293 (1981).
65. 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.*, 10, 329 (1983).
66. A.A. Viggiano and F. Arnold, Extended sulfuric acid vapor concentration measurements in the stratosphere, *Geophys. Res. Lett.*, 8, 583 (1981).
67. A.A. Viggiano and F. Arnold, Stratospheric sulfuric acid vapor: New and updated measurements, *J. Geophys. Res.*, 88, 1457 (1983).
68. S. Qui and F. Arnold, Stratospheric in situ measurements of  $H_2SO_4$  and  $HSO_3$  vapors during a volcanically active period, *Planet. Space Sci.*, 32, 87 (1984).
69. R.P. Turco, O.B. Toon, P. Hamill and R.C. Whitten, Effects of meteoric debris on stratospheric aerosols and gases, *J. Geophys. Res.*, 86, 1113 (1981).
70. F. Arnold, A.A. Viggiano and H. Schlager, Implication for trace gases and aerosols of large negative ion clusters in the stratosphere, *Nature*, 297, 371 (1982).
71. F. Arnold and Th. Buehrke, New  $H_2SO_4$  and  $HSO_3$  vapour measurements in the stratosphere - Evidence for a volcanic influence, *Nature*, 301, 293 (1983).
72. E. Arijs, D. Nevejans, J. Ingels and P. Frederick, Recent stratospheric negative ion composition measurements between 22 and 45 km, Preprints of VII International Conference on Atmospheric Electricity, Albany, N.Y., 8 (1984).
73. S.A. Mc Keen, S.C. Liu, C.S. Kiang, On the chemistry of stratospheric  $SO_2$  from volcanic eruptions, to be published (1984).
74. F. Arnold, R. Fabian, G. Henschen and W. Joos, Stratospheric trace gas analysis from ions:  $H_2O$  and  $HNO_3$ , *Planet. Space Sci.*, 28, 681 (1980).
75. W.M.O. Report n° 311, The Stratosphere 1981, Theory and Measurements, Edited by R. Hudson, pages 1-98 and 1-152 (1981).
76. E.E. Ferguson, Stratospheric ion chemistry related to neutral trace composition, Proc. Nato Advanced Study Institute on Atmospheric Ozone, Algarve, p. 517 (1979).
77. F. Arnold and G. Henschen, Ion nucleation - a potential source for stratospheric aerosols, *Nature*, 299, 134 (1982).
78. F. Arnold and G. Henschen, Mass spectrometric detection of precondensation nuclei in the stratosphere - Evidence for a stratospheric gas to particle mechanism, *Geophys. Res. Lett.*, 8, 83 (1981).
79. D.J. Hofman and J.M. Rosen, Condensation nuclei events at 30 km and possible influences of solar cosmic rays, *Nature*, 302, 511 (1983).
80. G. Brasseur and A. Chatel, Modelling of stratospheric ions: a first attempt, *Annales Geophysicae*, 1, 173 (1983).
81. H. Kawamoto and T. Ogawa, A steady state model of negative ions in the lower stratosphere, *Planet. Space Sci.*, in press (1984).