

## Stratospheric positive ion composition measurements, ion abundances and related trace gas detection

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**Abstract** Positive ion spectra obtained from measurements with a balloon-borne mass spectrometer during three balloon flights are critically investigated and compared with other data. Ion abundances for proton hydrates  $[H^+(H_2O)_n]^{+}$  ions at different stratospheric temperatures are compared, as well as the abundances of non proton hydrates  $H^+X(H_2O)_m$ , X being most likely  $CH_3CN$ .

The detection of trace gases from ion composition measurements is discussed and an upper limit for the number densities of minor constituents such as  $NH_3$  and  $CH_3OH$  is estimated at 35 km. Although sodium compounds cannot be responsible for the major positive ions, a closer investigation of high resolution daytime spectra suggests a small contribution of sodium in daytime ion chemistry.

### 1. INTRODUCTION

Recently the identification of positive ions in the stratosphere has been possible by rocket-borne and balloon-borne mass spectrometers (ARNOLD *et al.*, 1977; ARIJS *et al.*, 1978; ARNOLD *et al.*, 1978). It has been shown that the major positive ions can be classified into two main groups. The first one, which could be expected from models extending the D-region ion chemistry (FERGUSON, 1974), is the group of the proton hydrates (PH) and contains the ions of the form  $H^+(H_2O)_n$ . The second family has been called the 'non proton hydrates' (NPH) and groups the ions of the form  $H^+X(H_2O)_m$ . Their origin has been explained by ion-molecule reactions of the PH with a trace gas X, with a number density of the order of  $10^5 \text{ cm}^{-3}$  and with a proton affinity larger than that of water (ARNOLD *et al.*, 1978). Recent high resolution measurements (ARIJS *et al.*, 1980) have shown unambiguously that the mass of X was 41, excluding  $NaOH$ , previously proposed (FERGUSON, 1978). An alternative proposal of  $MgOH$  (MURAD and SWIDER, 1978; FERGUSON, 1979) could also be rejected since no major ion clusters containing the Mg isotopes were detected (ARIJS *et al.*, 1980). The unambiguous determination of the mass of X (41 amu) was confirmed later on by ARNOLD *et al.* (1981) who also showed the absence of ions due to Mg isotopes.

Thus the most likely candidate for X remained  $CH_3CN$ , as originally suggested by ARNOLD (1978). Recent laboratory measurements (SMITH *et al.*, 1981; BÖHRINGER and ARNOLD, 1981) as well as a detailed study of ion abundances (ARNOLD *et al.*, 1981) seem to reinforce this suggestion. The fractional ion abundances reported so far however (ARNOLD *et al.*, 1981), only deal with one measurement, performed during

one particular daytime flight in November 1977. In the present paper ion abundances measured during different flights at different periods of the year and consequently at different stratospheric temperatures are compared. Thus additional information concerning the nature of X is obtained and some hypotheses, put forward in an earlier paper (ARNOLD *et al.*, 1981) are checked. Furthermore, the relative ion abundances of the stratospheric positive ions are also discussed in view of recently performed laboratory studies. Finally, minor mass peaks, not taken into account before, as well as some differences between nighttime and daytime positive ion composition data, are demonstrated and analyzed.

### 2. EXPERIMENTAL

The balloon-borne payload has been briefly described before (ARIJS *et al.*, 1980) and will be described to a larger extent later on. It consists of a quadrupole mass filter, mounted into a high speed cryopump (INGELS *et al.*, 1978). The associated electronics are microprocessor controlled (NEVEJANS *et al.*, 1981) resulting in a great flexibility of the instrument. Several modes of operation are possible, such as positive and negative ion sampling and in flight calibration. In each mode, the resolution and mass domain can be chosen by remote control. Stratospheric ions are sampled through a 0.2 mm hole drilled in a stainless steel flange of 0.1 mm thick. This flange is electrically insulated from the gondola and can be biased with respect to it with a draw-in potential between -5 and +5 V. The optimum value of this draw-in potential is determined either by remote control or automatically by the microprocessor. It has been shown by BÖHRINGER and

ARNOLD (1979), that such low draw-in potentials hardly induce any ion cluster break up at the high pressure side of the draw-in plate. At the low pressure side of the aperture the sampled ions are focussed into the mass filter by means of an electrostatic lens. The ion optical system consists of a small cylindrical lens (1 cm diameter and 1 cm long) mounted at 0.8 cm from the inlet orifice (0.02 cm diameter) and followed by a conventional electron impact ion source (Finnigan model 400), which can be used as a lens element or as an ion source for testing.

In this region a combination of rather high pressure and high field strength may exist. In the laboratory pressures of the order of  $4 \times 10^{-3}$  Torr have been measured with a minaturized ionization gauge at distances of 1 cm behind the inlet hole, when the pressure above the sampling aperture was 5 Torr. It is therefore expected that weakly bound clusters, such as PH will partly break up due to energetic collisions of electric field accelerated ions with neutrals. Such an electric field induced collisional dissociation has been observed by ARNOLD *et al.*, (1981) and consequently these authors have applied a correction factor, deduced from laboratory measurements, to the PH cluster abundances observed.

In order to investigate which correction factors should be applied for our instrument, extensive laboratory studies have been performed. The stratospheric plasma has been simulated by ionizing a nitrogen-nitric oxide gas mixture (typically 1% NO in  $N_2$ ) at pressures between 3 and 5 Torr with UV irradiation (the 129.6 nm line of a xenon RF excitation). The  $NO^+$  primary ions created by photoionization are quickly converted through a series of ion molecule reactions to ion clusters such as  $NO^+(H_2O)_n$  and  $H^+(H_2O)_n$ . By adding sufficient water vapor to the gas mixture, the PH become the dominant ions. These ions are sampled then with the same mass spectrometer used for the *in situ* measurements. The relative abundances of the PH have been measured as a function of the focus potential (potential of the first lens element). Since the voltages applied on all other lens elements are smaller than 1 V and since these elements are at larger distances from the sampling hole (thus at lower pressures), it has been assumed that there is no electric field induced collisional break up at 0 V focus potential. The results of such a set of measurements are shown in Fig. 1. The relative abundance of mass 73 decreases at higher focus potentials and reduces to about 90% of its undisturbed value at the normally applied potential of -65 V. The contribution of dissociation products from higher PH to mass 73 can be neglected since the signals of mass 91 and 109 are one order of magnitude lower at least.

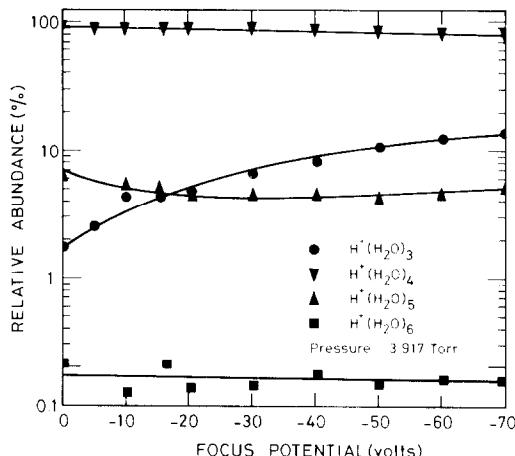


Fig. 1. Fractional PH abundance versus focus potential.

Mass 91 is dissociated for about 20% at -65 V focus potential. The rather constant abundance of mass 109 is strange, but it should be noted that the count rate at this mass was very low and unstable. Therefore dissociation effects are easily masked. The field induced collisional dissociation modifies the abundances of mass 73 and 91 by no more than 20%, which is for some measurements within the experimental error. However, due to this effect, the observed abundance for the lower order PH ions (mass 55), present at small concentrations, may be an order of magnitude too high.

As far as possible, the abundances for PH reported in this paper, will be corrected for these dissociation effects.

By adding  $CH_3CN$  vapor to the gas mixture, the NPH ions observed in the stratosphere were also measured in the laboratory. Measurements to investigate the field induced collisional break up of these NPH were started but were very difficult to interpret. This was due to signal instability caused by desorption and adsorption of  $CH_3CN$  vapor on the walls of the instrument. These difficulties were especially severe at low focus potentials, where a long integration time was needed to build up a spectrum, because of the weak signals. However indications are present that similar break up effects exists as for PH ions.

### 3. RESULTS AND DISCUSSION

#### 3.1. Measurements

The results discussed hereafter have been obtained during three stratospheric balloon flights. The first one took place on 30 September 1977. All measurements were performed at float altitude (35 km) after sunset.

Table 1. Mass numbers, identification and fractional abundances of major ions observed around 35 km altitude

Mass number (amu)	Identification $X = 41$ amu	Measured fractional abundance		
		MPI (Nov 77)	June 80	Sept. 80
55	$H^+(H_2O)_3$	0.034 (-)	0.55 (0.023)	0.031 (-)
73	$H^+(H_2O)_4$	0.268 (0.213)	0.296 (0.322)	0.371 (0.384)
78	$H^+X(H_2O)_2$	0.072	0.084	0.067
91	$H^+(H_2O)_5$	0.089 (0.178)	0.028 (0.034)	0.067 (0.085)
96	$H^+X_2(H_2O)_3$	0.196	0.444	0.304
101	$H^+X_2(H_2O)_4$	0.107	0.035	0.067
114	$H^+X(H_2O)_4$		0.009	
119	$H^+X_3(H_2O)_2$	0.161	0.049	0.068
137 $\pm$ 1	$H^+X_2(H_2O)_3$	0.044		
142 $\pm$ 1	$H^+X_3(H_2O)$	0.029		0.025

The corrected values, taking into account cluster break up are shown in parentheses.  
Horizontal bar (-) means abundance below detection limit.

Preliminary data of this flight were already reported (ARIJS *et al.*, 1978). The second flight was realized on 16 June 1980 and lasted 8 hours, thus permitting to obtain nighttime as well as daytime spectra at 34 km. The last flight happened on 18 September 1980 and resulted in nighttime data at 35 km altitude. All flights were performed in southern France at about 44°N (flight 1 and 3: Aire-sur-l'Adour; flight 2: Gap-Tallard). For the discussion of ion abundances the June 80 and September 80 data only will be used. They will be compared with the data of the Max Planck Institut für Kernphysik (Heidelberg) which were reported by ARNOLD *et al.* (1981) termed MPI group hereafter. These data were obtained in November 1977 and a stratospheric temperature of 227 K was reported for that particular flight. In this way, data at different temperatures (summer, autumn and winter data) are compared.

The positive ions observed in these recent balloon flights are shown in Table 1, together with the measured abundance. The abundances corrected for field induced collisional cluster break up are given in parentheses. It should be noted that the June 80 data were obtained at high resolution (constant peak width mode), where the transmission of the quadrupole mass filter depends upon the ion mass. Therefore the abundances of the higher masses may be somewhat larger for this flight than those mentioned. The September 80 abundance data however were obtained at low resolution, where the transmission of the quadrupole is supposed to be near 100% and mass independent. All mass numbers up to mass 119 have been determined unambiguously, with a technique described earlier (ARIJS *et al.*, 1980). Mass 137 has not been observed by our group, thus the error of  $\pm 1$  amu, stated by the MPI group has been adopted. The error

on mass 142 is also  $\pm 1$  amu in our measurements, since this mass was observed only in low resolution spectra.

### 3.2. Proton hydrates

From the foregoing measurements, it is obvious that masses 55, 73 and 91 belong to the PH group. In Table 2 the relative distribution for the PH of our most recent two balloon flights are shown, together with the data of the MPI group. Since no temperature measurement was performed in our balloon flights no direct comparison with the hydrate distribution derived from thermochemical data can be done. However, relying upon the certainty that masses 55, 73 and 91 belong to the PH group, the relative abundances can be used to derive an atmospheric temperature. To do so the theoretical relative abundances of  $H^+(H_2O)_4$ —mass 73 and  $H^+(H_2O)_5$ —mass 91 were calculated as a function of temperature, using the thermochemical data of KEBARLE (1977) and assuming a constant mixing ratio of water of 3 ppm at 35 km altitude. The results of such a calculation are pictured in Fig. 2. The experimental data, corrected for electric field induced collisional cluster break-up, are then fitted to these curves. The June 80 and the September 80 data can be fitted rather well using temperatures of 239 K and 232 K respectively. The error on these deduced temperature values may be rather large ( $\pm 2$  K), but within the uncertainties the obtained temperatures are in good agreement with the temperatures tabulated in the U.S. Standard Atmosphere (1966) for the same period of the year. As known (NEY *et al.*, 1961), direct atmospheric temperature measurements may suffer from considerable errors. As large as 10 degrees deviation from air temperature, due to the absorbance

Table 2. Measured proton hydrate distribution and expected theoretical values

Mass number (in amu)	MPI—data		Our data			
	November 77 Exper.	Theor.	June 80 Exper.	Theor.	September 80 Exper.	Theor.
55	—	0.001	0.145 (0.06)	— 0.02	0.066 ( )	— 0.003
73	0.544	0.63	0.781 (0.85)	0.90	0.791 (0.82)	0.811
91	0.456	0.36	0.074 (0.09)	0.08	0.134 (0.18)	0.182

Tabulated are relative abundances  $[H^+(H_2O)_n]/\Sigma[H^+(H_2O)_i]$ . The corrected values taking into account cluster break up are shown in parentheses.

of solar radiation and to the emission of IR radiation by the temperature sensor have been reported. In fact a comparison of the relative PH abundances of the MPI group with the theoretical curves seem to indicate that such errors may have influenced their temperature measurements and that the actual stratospheric temperature may have been somewhat lower than 227 K in November 1977. On the other hand some uncertainties on thermochemical data used in deriving the theoretical distributions should also be taken into account. In view of all these considerations and for the purpose of further discussions the temperature values of 227, 232 and 239 K will be adopted for the MPI, June 80 and September 80 data respectively.

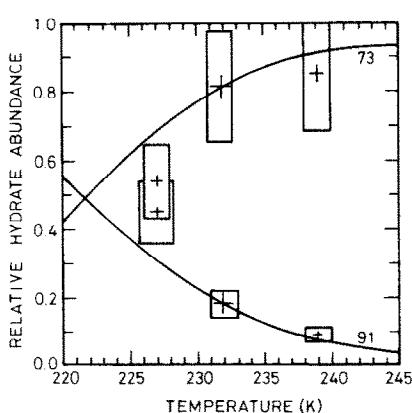
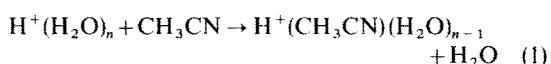


Fig. 2. Measured relative abundances for  $H^+(H_2O)_4$  (mass 73) and  $H^+(H_2O)_5$  (mass 91) compared with calculated abundances versus temperature. The error rectangles were obtained accepting an error of  $\pm 1$  K on temperature and 20% on the abundances. The rectangle for mass 91 of the MPI data is only somewhat larger to distinguish it from the 73 rectangle.

### 3.3. Major non proton hydrates

Apart from the PH the other major ions can be represented by the formula  $H^+X_i(H_2O)_m$ . These ions are formed through reactions of PH with a molecule X and subsequent association of X and/or ligand exchange of X with  $H_2O$ . In view of the recent *in situ* measurements (ARIJS *et al.*, 1980) and the detailed reconsiderations of formerly measured abundances (ARNOLD *et al.*, 1981) the original suggestion for X, namely  $CH_3CN$  has become topical again. Support for this suggestion was brought by recent laboratory measurements of BÖHRINGER and ARNOLD (1981). Recently SMITH *et al.* (1981) have measured the rate constant for the reaction:



and values as high as  $4 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$  have been found. Using the recombination coefficients also measured by these authors (SMITH *et al.*, 1981), an estimation for the number density of X can be made, assuming X being  $CH_3CN$ . From continuity considerations it follows that

$$[X] = \frac{\alpha \cdot [n][NPH]}{k[NH]} \quad (2)$$

where the square brackets denote number densities, k is the reaction coefficient ( $4 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$ ),  $\alpha$  the recombination coefficient ( $6 \times 10^{-8} \text{ cm}^3 \text{s}^{-1}$ ) and  $[n]$  the total density of negative (or positive) ions. For the MPI, June 80 and September 80  $[NPH]/[PH]$  was found to be 1.54, 1.65 and 1.15 respectively. Thus  $[X] \cong 20 \times [n]$ . With  $[n] \cong 10^3 \text{ cm}^{-3}$ , mixing ratios of the order of 0.1 ppt are obtained. The concentration of X calculated in this way, must be considered as a

lower limit. The derivation of this value is based on the assumption that the NPH are predominantly lost by recombination. If reconversion of NPH to PH is predominant then the continuity equation (2) can be approximated by

$$k_f[X][\text{PH}] = k_r[\text{NPH}][\text{H}_2\text{O}]. \quad (3)$$

Assuming with SMITH *et al.* (1981) that  $k_r < 10^{-4} k_f$ , where  $k_f$  denotes the forward reaction rate constant and  $k_r$  the reverse rate constant, it follows that

$$[X] < 10^{-4} \times [\text{H}_2\text{O}] \cdot [\text{NPH}]/[\text{PH}]. \quad (4)$$

Hence mixing ratios smaller than 0.4 ppb are found. The value of  $[X]$  will depend on whether recombination or reverse reactions are the main loss terms for NPH. This will be considered hereafter.

The NPH ions were divided by ARNOLD (1981) in three subfamilies called A, B and C respectively. Their fractional abundance as well as the abundance of their individual members are shown in Table 3 for the three experiments under discussion.

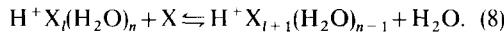
From a steady state treatment of the reactions converting PH to NPH, and assuming recombination to be the predominant loss term it is found that:

$$R_1 = \frac{[\text{NPH}]}{[\text{PH}]} = \frac{[\text{A}] + [\text{B}] + [\text{C}]}{[\text{PH}]} = \frac{k[X]}{\alpha[n]} \quad (5)$$

$$R_2 = \frac{[\text{B}] + [\text{C}]}{[\text{A}]} = \frac{k[X]}{\alpha[n]} \quad (6)$$

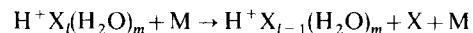
$$R_3 = \frac{[\text{C}]}{[\text{B}]} = \frac{k[X]}{\alpha[n]} \quad (7)$$

where  $k$  is the rate coefficient for switching reactions of the form



It is assumed that  $k$  has the same value for  $l = 0, 1, 2$ . From the fact that  $R_1 \cong R_2$  and  $R_3 < R_1$  (for the MPI data), ARNOLD *et al.* (1981) concluded that the reverse

of the reactions of type (8) were taking place also (at least for  $l = 2$ ). As a critical check they suggest a repetition of the measurements at higher stratospheric temperatures, where  $R_3$  should become even smaller, and  $R_2$  may become smaller than  $R_1$ . Furthermore, BÖHRINGER and ARNOLD (1981) also suggested that thermal dissociation:



may also occur.

Our June 80 and September 80 flights are in fact measurements at more elevated temperatures. As can be calculated from Table 3,  $R_3 = 0.18$  for the September 80 flight, which is higher than the MPI value (0.1). For the June 80 flight  $[\text{C}]$  is below the detection limit of the instrument, due to the high resolution used. A value of  $R_3$  of 0.1 would imply a fractional abundance for the C family of 0.008, which was undetectable because of the low transmission of the quadrupole.

From the observed  $R_3$  values at different temperatures it is not clear whether reverse reactions of type (8) are operative or the rate coefficient  $k$  for the conversion from B to C is 10 times smaller than for the conversion from PH to NPH.

On the other hand our  $R_2$  values (0.429 for September 80 and 0.157 for June 80) which are considerably smaller than  $R_1$  (1.15 for September 80 and 1.64 for June 80) are decreasing with increasing temperature, suggesting that the reverse reactions of type (8) are active for A to B conversion. In this case one would expect the same thing for B to C conversion.

Thus, it is not excluded that part of the loss of NPH is reconversion to PH. Therefore it is safe, only to give the number density of X by

$$2 \times 10^4 \text{ cm}^{-3} < [X] < 7 \times 10^7 \text{ cm}^{-3} \quad (9)$$

around 35 km.

The fact that the  $R_1$  values for different flights at

Table 3. Relative hydrate distributions of non proton hydrates

Sub-family	Core ion	Flight	Total fractional abundance	Relative abundance			
				$[\text{H}^+ \text{X}_l(\text{H}_2\text{O})_m]/\sum_j [\text{H}^+ \text{X}_j(\text{H}_2\text{O})_j]$	$m=1$	$m=2$	$m=3$
A	$\text{H}^+ \text{X}$	MPI	0.26	—	0.269	0.731	—
		June 80	0.537	—	0.157	0.826	0.017
		Sept. 80	0.371	—	0.181	0.819	—
B	$\text{H}^+ \text{X}_2$	MPI	0.31	0.344	0.516	0.141	—
		June 80	0.084	0.42	0.58	—	—
		Sept. 80	0.135	0.496	0.504	—	—
C	$\text{H}^+ \text{X}_3$	MPI	0.03	1.00	—	—	—
		June 80	—	—	—	—	—
		Sept. 80	0.025	1.00	—	—	—

different temperatures seem to be independent of temperature (within the experimental errors) suggests that reconversion from NPH to PH seems unlikely. This also follows from considerations of the laboratory measurements of SMITH *et al.* (1981). Therefore it is more probable that [X] is closer to the lower limit than to the upper limit indicated in Equation (9). In any case extremely low number densities are found for X or CH<sub>3</sub>CN. It is obvious that with such low number densities X or CH<sub>3</sub>CN may originate from different sources. Apart from the sources already speculated on earlier (ARIJS *et al.*, 1980; SMITH *et al.*, 1981), CH<sub>3</sub>CN may be produced by aeroplane flights above the tropopause or it may even reach the stratosphere as a result of surface production. Acetonitrile is indeed a frequently used industrial solvent and according to CRUTZEN (1981) it is one of the products of biomass burning in the tropics. It is not excluded that it may reach the stratosphere in the low concentrations needed to explain the conversion from PH to NPH, even though it is highly soluble in water and thus susceptible to washing out by rain.

Recently studies of clustering equilibria for H<sup>+</sup>(CH<sub>3</sub>CN)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub> ions have been made in the laboratory by BÖHRINGER and ARNOLD (1981). From these results, the abundance ratios of the different hydrates of the different families can be calculated. Those abundances are summarized in Table 4, as well as the water concentrations deduced from them. As can be seen, experimental data are in reasonable agreement with laboratory studies, implying that the observed NPH mass numbers and abundances can be explained by mixed clusters of the form H<sup>+</sup>(CH<sub>3</sub>CN)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>. BÖHRINGER and ARNOLD (1981) also made a comparison of the predicted H<sup>+</sup>(CH<sub>3</sub>CN)<sub>n</sub>H<sub>2</sub>O<sub>m</sub> distributions as deduced from their laboratory measurements and those measured in the stratosphere, without however taking into account

our June 80 results, and came to the same conclusion.

The use of *in situ* ion composition measurements as a method for trace gas analysis has been reported previously (FERGUSON, 1979; ARNOLD and FABIAN, 1980; ARNOLD *et al.*, 1981).

From foregoing considerations, some conclusions can be drawn already about the validity of using stratospheric ion measurements as an analytical method for trace gas detection. Taking into account the different water vapor mixing ratios we obtained (Table 4) as well as the different uncertainties on the laboratory data, the method can hardly be considered as an exact quantitative one. However the power of this method lies in the fact that trace gases, which due to their low number density cannot be identified by other means, can be detected if they play a role in the final ion chemistry. When better laboratory data (e.g. rate coefficients, recombination rates and equilibrium constants) become available as well as complete sets of *'in situ'* data, the method can become an attractive analytical tool. Conversely the method may also be used to derive fundamental data such as kinetic or equilibrium data on ion molecule reactions under conditions which cannot be simulated in the laboratory.

All the arguments proposed above do not really provide direct proof for X being CH<sub>3</sub>CN. In fact, it can only be shown that CH<sub>3</sub>CN cannot be excluded, where NaOH and MgOH can, and that it remains a viable candidate for X.

A method however, which would give more direct information about the nature of the unknown molecule X, would be to investigate the abundances of NPH mass peaks due to the presence of heavy isotopes. The most abundant NPH peak in the positive ion spectrum is located at mass 96. If X is CH<sub>3</sub>CN, one expects from the abundances of the isotopes <sup>13</sup>C, <sup>2</sup>H, <sup>17</sup>O and <sup>15</sup>N a peak at mass 97 with a

Table 4. Comparison of abundance ratios obtained from laboratory data and *in situ* measurements of NPH

Abundance ratio	Laboratory data	MPI	<i>In situ</i> data	
			June 80	Sept. 80
[96]/[78]	$1.7 \times 10^{-11} [\text{H}_2\text{O}]$	2.7 ( $1.6 \times 10^{11}$ )	5.3 ( $3 \times 10^{11}$ )	4.5 ( $2.7 \times 10^{11}$ )
[119]/[101]	$3.5 \times 10^{-12} [\text{H}_2\text{O}]$	1.5 ( $4.3 \times 10^{11}$ )	1.4 ( $4 \times 10^{11}$ )	1.0 ( $2.8 \times 10^{11}$ )
[114]/[96]	$2.2 \times 10^{-14} [\text{H}_2\text{O}]$	..	0.02 ( $9 \times 10^{11}$ )	
[137]/[119]	$4.7 \times 10^{-16} [\text{H}_2\text{O}]$	0.27 ( $5.7 \times 10^{13}$ )		

Ions are referred to by mass number. The deduced H<sub>2</sub>O number density is indicated in parentheses.

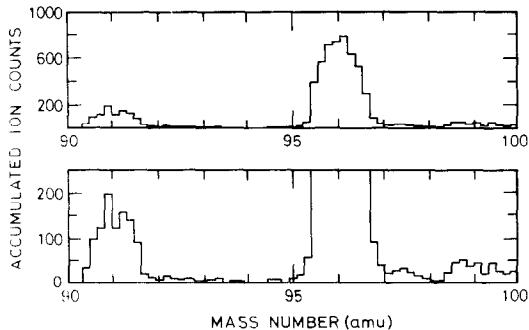


Fig. 3. Detailed mass spectrum obtained in the constant peak width mode around mass 96, obtained at 35 km.

peakheight of about 2.8% of peak 96. Similarly, one expects 0.6% at mass 98 due to  $^{18}\text{O}$ .

In order to verify this, a small domain (90–100 amu) has been scanned for a very long time in the June 80 flight. Data of about 248 scans have been accumulated to obtain the spectra shown in Fig. 3. As can be seen a mass peak is indeed present at mass 97 but its form is not well pronounced due to incomplete statistics. Furthermore this small peak is overlapped by the tail of the large peak 96. Nevertheless an estimation of the peak height is possible and shows that the abundance is about 3% of the peak 96. For the peak at mass 98 only an upper limit of 1% can be estimated for its abundance ratio.

Although not being a full proof evidence, the abundance ratio of the mass peaks due to heavy isotopes, gives strong supplementary support for mass 96 being  $\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_3$  and thus for the identification of X as acetonitrile.

#### 3.4. Minor non proton hydrates

So far only major mass peaks have been reported and discussed in the literature. While analyzing our most recent mass spectra however, it became clear that apart from PH and NPH due to X ( $\text{CH}_3\text{CN}$ ) another series with structure  $\text{H}^+\text{Y}(\text{H}_2\text{O})_k$  was present in the positive ion spectrum (ARIJS *et al.*, 1980). Evidence for such a series has also been found by BÖHRINGER and ARNOLD (1981). To obtain more information about these clusters we decided to reconsider some of our earlier results of the September 1977 flight. To do so, all positive ion spectra, which were obtained with the same resolution in that flight have been summed to one spectrum, shown in Fig. 4. A blown up version of this spectrum (Fig. 4b), clearly demonstrates the existence of many minor peaks.

For the discussion, we shall reject all small peaks lower than 0.1 count per second, which is the noise

level of the ion detector. Furthermore a rather large error on the mass determination induced by the low signal levels will be assumed for the minor peaks. The mass peaks observed are summarized in Table 5.

Apart from the peaks due to  $\text{H}^+(\text{H}_2\text{O})_n$  and  $\text{H}^+\text{X}_k(\text{H}_2\text{O})_m$  there seems to exist a very small group of mass peaks (33, 51, 69 and 87) which is scarcely above the noise background. This ion family may be interpreted as belonging to the hydrates of protonated methanol (PMH). If these mass peaks are real, the abundances of the PMH is certainly not more than 1% of the PH abundance. The reaction rates of the switching reactions of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  in the PH have been measured by the NOAA group in Boulder (FEHSENFELD *et al.*, 1978). Thus a steady state treatment, similar to the one used to derive the number density of X ( $\text{CH}_3\text{CN}$ ), can be applied for the estimation of an upper limit for the number density of methanol at 35 km altitude. It turns out that, if recombination is the main loss term of  $\text{H}^+(\text{CH}_3\text{OH})_k(\text{H}_2\text{O})_m$  ions;

$$[\text{CH}_3\text{OH}] = \frac{\alpha}{k} \frac{[n][\text{PMH}]}{[\text{PH}]}$$

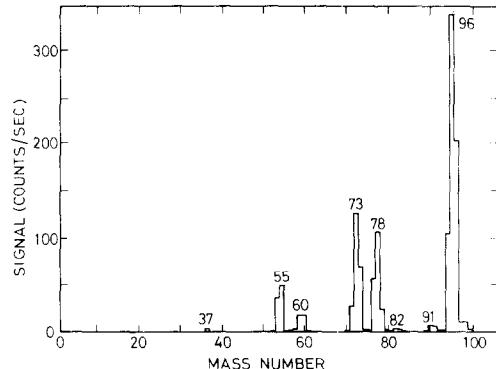


Fig. 4a. Nighttime spectrum in the mass region 0–110 amu obtained at 35 km in September 1977.

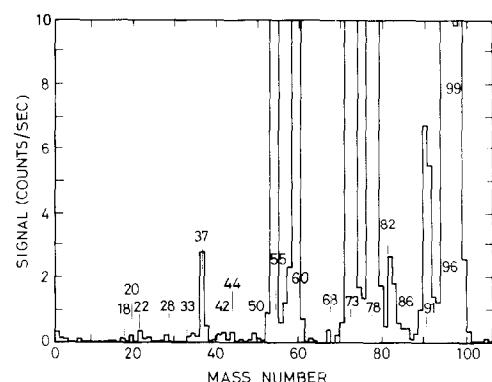


Fig. 4b. Enlarged version of Fig. 4a.

Table 5. Observed mass peaks and tentative identification of major and minor stratospheric positive ions at 35 km

Observed peaks	Assigned mass number	Tentative identification
18,20,22	19±3	H <sup>+</sup> (H <sub>2</sub> O)
28	28±2	H <sup>+</sup> HCN
34	33±2	H <sup>+</sup> CH <sub>3</sub> OH
37	37	H <sup>+</sup> (H <sub>2</sub> O) <sub>2</sub>
42,44	42±2	H <sup>+</sup> CH <sub>3</sub> CN
50	51±2	H <sup>+</sup> CH <sub>3</sub> OH(H <sub>2</sub> O)
55	55	H <sup>+</sup> (H <sub>2</sub> O) <sub>3</sub>
60	60	H <sup>+</sup> CH <sub>3</sub> CN(H <sub>2</sub> O) <sub>2</sub>
68	69±2	H <sup>+</sup> CH <sub>3</sub> OH(H <sub>2</sub> O) <sub>2</sub>
73	73	H <sup>+</sup> (H <sub>2</sub> O) <sub>4</sub>
78	78	H <sup>+</sup> CH <sub>3</sub> CN(H <sub>2</sub> O) <sub>2</sub>
82	82±1	H <sup>+</sup> Y(H <sub>2</sub> O) <sub>j</sub>
86	87±2	H <sup>+</sup> CH <sub>3</sub> OH(H <sub>2</sub> O)
91	91	H <sup>+</sup> (H <sub>2</sub> O) <sub>5</sub>
96	96	H <sup>+</sup> CH <sub>3</sub> CN(H <sub>2</sub> O) <sub>3</sub>
99	99±1	H <sup>+</sup> Y(H <sub>2</sub> O) <sub>j+1</sub>

With  $k \cong 1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (FEHSENFELD *et al.*, 1978) and  $\alpha = 6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  (SMITH *et al.*, 1981) and  $[\text{PMH}]/[\text{PH}] < 0.01$  it follows that

$$[\text{CH}_3\text{OH}] < 0.4 \times [n].$$

If reconversion to PH is the dominant loss and assuming in analogy with CH<sub>3</sub>CN that the reverse rate coefficient  $k_r < 10^{-4} k_f$  (forward rate coefficient), which is a safe assumption, it follows as in section 3.3 that

$$[\text{CH}_3\text{OH}] < 10^{-6} [\text{H}_2\text{O}]$$

which results in a safe upper limit of  $3 \times 10^{-12}$  for the mixing ratio of CH<sub>3</sub>OH at 35 km.

In the earlier rocket measurements of the MPI group a mass  $29 \pm 1$  has been observed (ARNOLD *et al.*, 1978), being interpreted as a fragmentation product of CH<sub>3</sub>CN clusters. Such a peak ( $28 \pm 2$  amu) seems to appear also in our September 1977 data. This peak is probably due to cluster break up also, which in that flight was a severe problem, as can be deduced from the PH distribution.

Apart from the previously discussed marginal ion peaks, two more pronounced peaks are seen to exist in Fig. 4b, which are definitely larger than the noise level and therefore real. These peaks are located at mass  $82 \pm 1$  and  $99 \pm 1$ , and can be fitted to a group H<sup>+</sup>Y(H<sub>2</sub>O)<sub>n</sub>, previously deduced from the measurement of mass 117 (ARIJS *et al.*, 1980). Mass  $136 \pm 1$  detected by BÖHRINGER and ARNOLD (1981) probably also belongs to this family.

A possible candidate for Y might be CH<sub>3</sub>COH, a product of the ethane oxydation cycle. Since the proton affinity of acetaldehyde is about

185 kcal mol<sup>-1</sup> (WALDER and FRANKLIN, 1980) and its dipole moment 3.94 debye, it is able to replace H<sub>2</sub>O in the PH. However the chemistry of CH<sub>3</sub>COH formation in the stratosphere should be investigated to a larger extent to decide if its number density can be large enough for an active participation in the stratospheric positive ion chemistry.

An alternative explanation for mass 117 would be H<sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>CO<sub>2</sub> but sufficient information is lacking about its ion chemistry, and laboratory data are needed.

An examination of the high resolution spectra obtained during the June 80 flight, allows us to conclude that the abundances of the masses fitting the formula H<sup>+</sup>(NH<sub>3</sub>)<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub> are lower than 1% of the PH abundance. Accepting a reaction rate coefficient of  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (FEHSENFELD and FERGUSON, 1973) for the reactions of the type



an upper limit can again be deduced for the NH<sub>3</sub> concentration at 35 km altitude, from steady state considerations. Accepting the recombination to be the dominant loss process with a recombination coefficient of  $6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  (SMITH and ADAMS, 1981) the upper limit for the ammonia number density is  $0.3 \times [n]$  (where [n] is the ion density, approximately  $10^3 \text{ cm}^{-3}$ ).

### 3.5. Daytime spectra and possible role of sodium

The main difference between the MPI data and our results, lies in the fact that the MPI data have been obtained from daytime balloon flights, while our measurements reported so far were performed during nighttime. The reason for this was to avoid charging up to the payload due to photoelectron emission during daytime.

The balloon flight of June 1980 however lasted long enough to enable us to record nighttime as well as daytime spectra. In Fig. 5 the pulse counting rate versus time is shown for different masses at constant draw-in potential during this flight. As can be seen there is a considerable decay of the signal for positive ions after sunrise. Since there is no change in the ionization rate we believe it to be due to the positive charging up of the gondola.

The composition of positive ion spectra obtained before and after sunset are very similar, apart from one point, worth to report and which calls for further investigation. In Fig. 6 a spectrum covering 72 to 82 amu is shown, obtained about 3 hours after sunrise. As can be seen a mass peak appears at 77 amu, which was not observed during nighttime. This mass does not

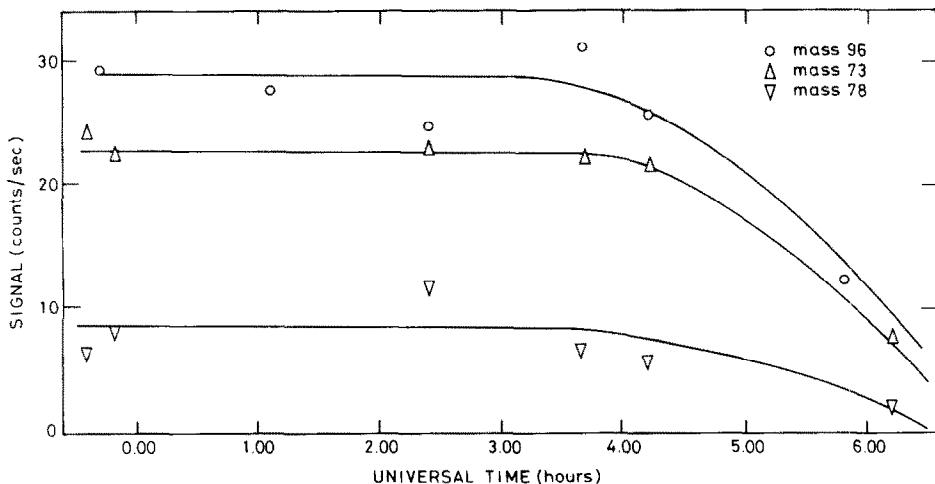


Fig. 5. Ion signal versus time for the June 1980 flight.

fit into the acetonitrile scheme, but can be explained as  $\text{Na}^+(\text{H}_2\text{O})_3$ .

In this context, it is interesting to recall the following points. After the suggestion of FERGUSON (1978) of X being  $\text{NaOH}$ , a model has been made by LIU and REED (1979) to calculate the  $\text{NaOH}$  number density as a function of altitude. This model showed  $\text{NaOH}$  to be present in concentrations high enough to modify the positive ion composition at 35 km. According to MURAD and SWIDER (1979) sodium may be present in other forms than  $\text{NaOH}$ , due to some loss mechanisms not taken into account in the Liu and Reid model. It has been shown by recent laboratory measurements of PERRY *et al.* (1980) that other gaseous sodium forms would also actively participate in the positive ion chemistry and give rise to  $\text{Na}^+(\text{H}_2\text{O})_n$  ions. Since no major mass peaks due to these cluster ions have been observed, the problem remains what happens to sodium originating from meteorite ablation. A possible loss mechanism for meteoric sodium is absorption in atmospheric dust and aerosols, as was suggested by ARNOLD *et al.* (1981). Recent model

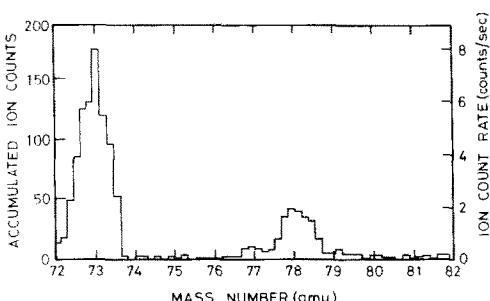
calculations (TURCO *et al.*, 1981) taking into account such removal processes, indicate much lower metal vapor concentrations, than those obtained by LIU and REID (1979). A possible explanation for the origin of mass 77 during daytime, would be the appearance of sodium in a form suitable for participation in the ion chemistry. A mechanism giving rise to such a form, may be photodesorption of sodium from aerosols caused by sunlight or photolysis of sodium containing particles.

A calculation of the hydrate distribution of  $\text{Na}^+(\text{H}_2\text{O})_n$  with the thermochemical data of KEBARLE (1977) shows that at 35 km altitude, with a temperature of 239 K and water vapor mixing ratio of 3 ppm, mass 77 [ $\text{Na}^+(\text{H}_2\text{O})_3$ ] would be the most abundant ion (73%). The next abundant ion would be mass 95 [ $\text{Na}^+(\text{H}_2\text{O})_4$ ] with a relative abundance of 26%. For mass 77 a count rate of 0.5 counts/s was observed; thus for mass 95 a count rate of 0.18 counts/s is expected if the assumption about sodium liberation is right. Unfortunately such low mass peaks could not be detected, due to the presence of the neighboring important peak at mass 96.

Therefore the question calls for more detailed investigations and a critical consideration of daytime positive ion mass spectra, preferably with high resolution and high sensitivity.

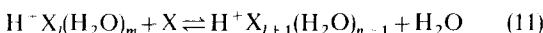
#### SUMMARY AND CONCLUSIONS

The dissociation of ions during the sampling process in the stratospheric ion mass spectrometer has been studied in the laboratory. It was found that PH as well as NPH cluster ions are breaking up under the influence of the focussing electric fields and collisions

Fig. 6. Daytime spectrum in the mass region 72–82 amu obtained in the constant peak width mode ( $\Delta m = 0.8$  amu).

with neutrals in the region just behind the sampling hole. A correction factor, taking into account cluster break up, was determined for the PH. This correction factor was applied to the measured abundances for two balloon flights. From the corrected PH distributions and the known thermochemical data, a temperature was derived for the two balloon flights. These two experiments (June 80 and September 80) together with the results of one MPI-flight (November 77) constitute a set of data at three different stratospheric temperatures, allowing a check of some hypotheses.

The NPH abundances for these three flights are compared and discussed in view of some recent laboratory measurements (BÖHRINGER and ARNOLD, 1981; SMITH and ADAM, 1981). A detailed inspection of the data indicate that reactions of the type



are also operative in the reverse direction, confirming previous suggestions (ARNOLD *et al.*, 1981; BÖHRINGER and ARNOLD, 1981). Such reactions having been observed in the laboratory (BÖHRINGER and ARNOLD, 1981) for  $\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_n$  ions,  $\text{CH}_3\text{CN}$  remains a viable candidate for the unknown trace gas X. A laboratory study of these reverse reactions (especially for  $l = 0$  or reconversion from NPH to PH) would be very useful and would enable a better estimation of the number density of X. If such an estimation is known with a greater certainty, other methods for the detection of X (such as IR absorption) might be considered helping in the definite identification of X.

The abundance ratios of NPH obtained from *in situ* measurements are compared with those measured in the laboratory (BÖHRINGER and ARNOLD, 1981) for mixed  $\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_m$  clusters. Within the experimental errors, a reasonable agreement is found, supporting the hypothesis of X being acetonitrile.

An investigation of the abundances of mass peaks due to heavy isotopes for the NPH ions, measured in the stratosphere, gives additional support for this hypothesis.

From an investigation of minor peaks in positive ion spectra, an upper limit for the  $\text{CH}_3\text{OH}$  mixing ratio in the stratosphere of  $3 \times 10^{-11}$  is given. The presence of ammonia at significant concentrations, can also be excluded from such spectra.

Apart from the NPH series due to  $\text{CH}_3\text{CN}$ , another family of NPH ions has been detected, which is called  $\text{H}^+\text{Y}(\text{H}_2\text{O})_n$ . As possible candidate for Y,  $\text{CH}_3\text{COH}$  (acetaldehyde) is suggested, although due to the lack of laboratory data and, *in situ* measurements, this suggestion remains speculative.

Finally, it is suggested that sodium, which cannot participate in nighttime ion chemistry (being adsorbed on or absorbed in aerosol particles), is liberated by sunlight in daytime and becomes available for ion chemistry in daytime.

This last suggestion certainly merits further research, helping our understanding of aerosol photochemistry.

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*Note added in proof*—Our attention was drawn by the referee to a recent article (HENSCHEIN and ARNOLD, 1981, *Nature* **291**, 211) which was published after the submission of this paper. In this work a number of minor mass peaks observed in stratospheric ion composition measurements are reported. Some of the observed masses as well as their tentative identifications are confirming our results.

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