

STRATOSPHERIC POSITIVE ION COMPOSITION MEASUREMENTS BETWEEN 22 AND 45 km:  
AN UPDATED ANALYSIS

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**Abstract.** A set of results about the positive ion composition of the stratosphere, consisting of some recently obtained as well as some previously reported data, is presented and analyzed. It is compared with model calculations described in a companion paper. A review of the abundances of proton hydrates and nonproton hydrates shows that the latter most probably result from the presence of acetonitrile ( $\text{CH}_3\text{CN}$ ) in the atmosphere. The vertical mixing ratio profile of this gas deduced from positive ion composition measurements is in good agreement with a model based on the assumption that acetonitrile is released at the earth's surface and subsequently destroyed in the atmosphere by chemical reactions (mainly with hydroxyl radicals). The results of an analysis of the possible isotopic mass peaks of mass 96 ( $\text{H}^+(\text{CH}_3)(\text{H}_2\text{O})_3$ ), is not in contradiction with this conclusion.

ion composition measurements and to compare them with these model predictions. Previously published data [Arijs et al., 1978, 1980, 1982, 1983a,b] as well as recently obtained results are presented. Furthermore, some new measurements of NPH mass peaks, possibly due to isotopes, are included.

2. Experimental Techniques

Most of the results shown and discussed hereafter were obtained with balloon-borne quadrupole ion mass spectrometers described in some detail before [Arijs et al., 1980; Ingels et al., 1978; Nevejans et al., 1982, 1984]. These instruments mainly consist of a quadrupole mass filter and the associated detector (Spiraltron, type 4219) built into a high-speed liquid helium pump. The latter maintains a pressure in the instrument below  $10^{-4}$  torr at ambient stratospheric pressures. Stratospheric ions flow into the mass analyzer through an inlet aperture, the diameter of which is selected from 0.2 to 0.4 mm, depending upon the altitude range covered by the measurements. In all experiments mentioned here a simple ion lens was used to extract ions from the gas beam, except for the most recent flight (September 1984), where ions were attracted toward the quadrupole by its pole bias only. In the latter case the pole bias with respect to the inlet aperture plate could be varied between 35 V and 65 V, depending upon the mass range, in contrast to previous flights where it was fixed at 7 V.

1. Introduction

Continuous progress in the development of balloon-borne ion mass spectrometers and advances in ballooning techniques have allowed regular in situ measurements of the stratospheric ion composition between 20- and 45-km altitude since 1977. Through these experiments, which have been reviewed previously [Arnold, 1980; Arijs, 1983; Arijs et al., 1984], a better understanding of processes and trace gas distributions governing stratospheric ion chemistry was obtained [Ferguson and Arnold, 1981].

Concerning positive ions, two major ion families were detected: proton hydrates (PH), i.e., ions of the form  $\text{H}^+(\text{H}_2\text{O})_n$ , and so-called non-proton hydrates (NPH) of the form  $\text{H}^+\text{X}_m(\text{H}_2\text{O})_n$ . X has a mass of 41 amu and is most likely acetonitrile ( $\text{CH}_3\text{CN}$ ). It has been shown by a recent model calculation that the presence of this gas in the atmosphere can be explained by a budget, taking into account reasonable values of biological and anthropogenic emissions, subsequent diffusion, and several loss processes consisting of established chemical reactions [Arijs and Brasseur, this issue]. It was also deduced from laboratory experiments exploring the ion-molecule reactions of this molecule that NPH similar to those observed in situ can be formed in the stratosphere [Böhlinger and Arnold, 1981; Smith et al., 1981]. Furthermore, a combination of a 1-D model of the neutral chemistry of  $\text{CH}_3\text{CN}$  with an ion model allowed the prediction of the major positive stratospheric ion abundances.

It is the aim of this article to report a more detailed analysis of the results of our in situ

For a more detailed comparison of the experimental results with the model predictions, mainly the data of four balloon flights have been used. These flights were chosen in such a way that the altitude range from 22 to 45 km was covered as completely as possible. The characteristics of these flights are given in Table 1. Occasionally, other flight data are used; the measurement circumstances of those, however, have been reported before [Arijs et al., 1978, 1980, 1982, 1983a, b].

All spectra interpreted here were obtained either during float altitude or during the descent phase to avoid contamination effects as much as possible. The mass range of the instruments used in the J-82, S-82, and S-83 flights was 0 to 330 amu, although for positive ion measurements the mass scanning range was mostly restricted to 150 amu. For the S-84 flight a new spectrometer with an extended mass range up to 400 amu was used, but for positive ions the mass scanning was again stopped at 200 amu.

The onboard microprocessor control unit allowed the application of several resolution modes [Nevejans et al., 1982]. As a general policy, however, the high resolution mode with constant peak width was applied only at float altitudes to allow an unambiguous identification

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TABLE 1. Characteristics of Balloon Flights

Flight	Launching Site <sup>1</sup>	Date	Balloon Type	Float Altitude km	Descending Velocity m/s	Minimum Altitude km
J-82	Gap	June 16, 1982	100,000 m <sup>3</sup> Zodiac(V)	33.8	0.9	21
S-82	ASA	September 23, 1982	1,000,000 m <sup>3</sup> Wintzen	45.6	1.3 <sup>2</sup>	41
S-83	ASA	September 18, 1983	100,000 m <sup>3</sup> Zodiac(V)	32.2	1.1	20
S-84	ASA	September 27, 1984	350,000 m <sup>3</sup> Zodiac(V)	38.7	1.2	27

V means valve controlled balloon.

<sup>1</sup> The latitude of the launching sites are Gap, Gap-Tallard (southern France), 44.28°N; ASA, Aire-sur-l'Adour (southern France), 43.42°N.

<sup>2</sup> Descending of the balloon due to cooling after sunset.

of the ions or to investigate fine structure due to isotope peaks. During balloon descent, however, a moderate constant resolution mode was used ( $M/\Delta M = 17$ ). This mode permitted the mass determination of major ion peaks at a more intense signal level, allowing a shorter integration time and a better altitude resolution.

### 3. Results and Discussion

#### 3.1. NPH Abundances and $\text{CH}_3\text{CN}$ Profiles

A typical positive ion mass spectrum as obtained at float altitude during the S-84 flight is displayed in Figure 1. Although similar spectra have been published before, this result is shown intentionally to illustrate effects of cluster breakup discussed further on. The mass peaks belonging to the two ion families  $\text{H}^+(\text{H}_2\text{O})_n$

and  $\text{H}^+\text{X}_2(\text{H}_2\text{O})_m$  can clearly be distinguished in Figure 1. Furthermore, it is clear from the presence of the mass peak at 42 amu, due to  $\text{H}^+\text{X}$ , that the mass of  $\text{X} = 41$  amu, as was already shown by high-resolution spectra reported previously [Arijs et al., 1980]. This was also confirmed in the S-84 flight by high-resolution spectra in the constant peak width mode of the same quality as those reported before [Arijs et al., 1980].

The unambiguous determination of the molecular mass of  $\text{X}$  also excludes the NaOH hypothesis [Ferguson, 1978; Liu and Reid, 1979] and puts some severe constraints on the possible concentrations of sodium compounds in the stratosphere.

The fractional abundances of the NPH ions as derived from positive ion spectra recorded during the different balloon flights realized by our group are shown in Figure 2. For comparison the model predictions in the companion paper [Arijs

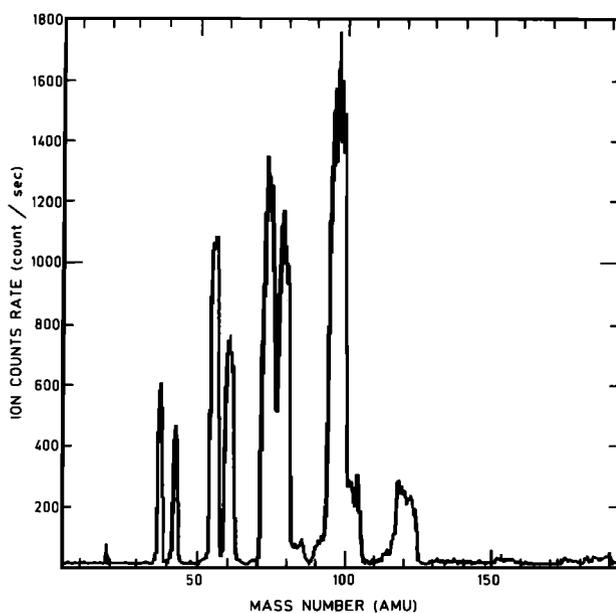


Fig. 1. Typical positive ion spectrum measured with constant resolution ( $M/\Delta M = 17$ ) at 38.6-km altitude on September 27, 1984. The spectrum was obtained after a summation of four scans, each scan taking 82 s.

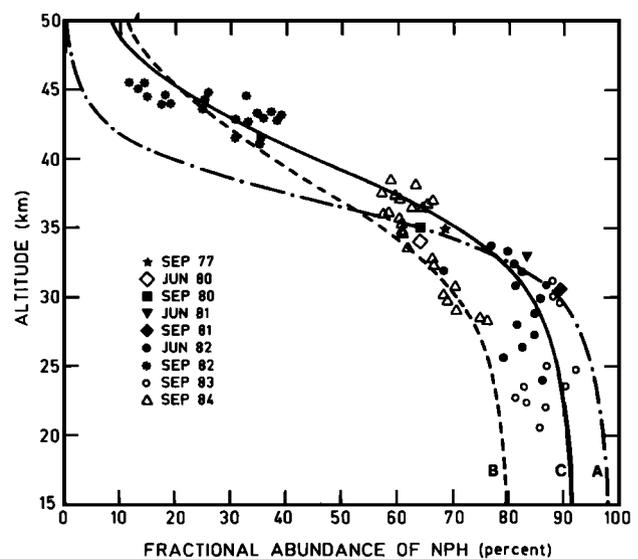


Fig. 2. Fractional abundance (expressed in percent) of NPH ions measured during the different balloon flights realized by the group from the Belgian Institute for Space Aeronomy as compared to model calculations.

and Brasseur, this issue], calculated for X being CH<sub>3</sub>CN, are also represented in Figure 2. The three curves A, B, and C were obtained by applying the same ion chemistry to three different concentration profiles of acetonitrile. Curve A corresponds to a model calculation with a global annual CH<sub>3</sub>CN emission of 5 x 10<sup>11</sup> g, maximum values for the reaction rate coefficients of chemical loss processes, and a small eddy diffusion coefficient. Curve B assumes minimum chemical reaction rates, a larger diffusion, and a global annual acetonitrile emission of 1.5 x 10<sup>10</sup> g. Curve C is derived from an average CH<sub>3</sub>CN profile with mean values for the chemical reaction rates and a global CH<sub>3</sub>CN emission of 4.7 x 10<sup>10</sup> g per year [for more details, see Arijs and Brasseur, this issue].

The uncertainty on the ion abundances derived from ion composition data results from possible experimental errors, estimated to be 20%-30%, and possible mass discrimination effects in the quadrupole mass filter, for which no correction was applied. Laboratory measurements show, however, that these mass discrimination effects are small in the mass domain 0 to 150 amu with the resolution used in most of the flights. In view of these uncertainties of the experimental data, it is apparent from Figure 2 that below 35 km the three model predictions can be brought into agreement with the experimental results. Above this altitude, however the prediction of curve A is clearly too low. This could be expected in view of the unlikely high values adopted for the chemical loss coefficients in this case. Nevertheless it should be kept in mind that the high-altitude measurements of the S-82 flight have not been repeated so far and may have been influenced by contamination problems [Arijs et al., 1983]. Therefore to confirm these results, a repetition of such a flight is strongly recommended.

The knowledge of fractional abundances of the NPH ions allows a derivation of the concentration of trace gas X, responsible for the conversion of PH to NPH, through the steady state equation [Arnold et al., 1978]

$$k [\text{PH}] [\text{X}] = \alpha [n_-] [\text{NPH}] \quad (1)$$

where square brackets denote number densities,  $[n_-]$  represents the total negative ion concentration,  $k$  the reaction rate coefficient for the conversion of PH to NPH, and  $\alpha$  the ion-ion recombination coefficient. Using for  $k$  a value of  $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , in agreement with the experiments of Smith et al. [1981], and for  $\alpha$  the parameterization

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

where  $[\text{M}]$  is the total neutral number density and  $T$  the temperature [Arijs et al., 1983], the NPH abundances of Figure 2 can be converted to CH<sub>3</sub>CN mixing ratios shown in Figure 3. The negative ion concentration used in formula (1) was calculated with the parameterization of Heaps [1978]. The

results obtained by the group of the Max-Planck-Institut für Kernphysik [Arnold et al., 1977, 1978, 1981; Henschen and Arnold, 1981] reduced with the same values of  $\alpha$ ,  $[n_-]$  and  $k$  are also given in Figure 3.

The three [CH<sub>3</sub>CN] profiles A, B, and C, derived from the model calculations as described before, are also shown in Figure 3 for comparison. Furthermore, the recent CH<sub>3</sub>CN mixing ratio of 36 pptv obtained by Arnold and Hauck [1985] at 11.3 km through the "active chemical ionization" method with an airplane-borne instrument is also indicated, as well as the surface measurements of Snider and Dawson [1984] and the upper limit deduced by Muller [1985].

When comparing model calculations with experimental data it appears that the balloon data fit within curves B or C, whereas aircraft and surface measurements are more in favour of profile A for CH<sub>3</sub>CN. Since the three model curves were obtained with different emissions and different values for the reaction rates of the chemical loss of acetonitrile, it is excluded that at lower altitude one model case should be representative of reality and another one at high altitudes. The value deduced by Muller [1985] from infrared spectra (32 pptv at 2 km) is an absolute upper limit and does not seem to help in solving the dilemma. Although the estimation of the emission source strength given in the companion paper [Arijs and Brasseur, this issue] seems to support a profile similar to curve A below 20 km, it should be noted that this estimation is very approximate and was merely given as a support for the basic idea of CH<sub>3</sub>CN being emitted from the earth's surface and not produced in situ.

If the value at 11.3 km reported by Arnold and Hauck [1985] is correct, it seems as if an additional sink for CH<sub>3</sub>CN is needed just above the tropopause. However, before speculating on such loss mechanism, which as suggested by Arnold and Hauck may result from ion-ion recombination, more measurements of CH<sub>3</sub>CN below 20 km are needed.

It should also be realized that the CH<sub>3</sub>CN mixing ratio may be influenced strongly by temporary variations due to changes in emissions or transport, which have not been included in the simple 1-D model. That such variations are real is illustrated by the scatter of the experimental balloon data and by the form of the profiles, which differ strongly from flight to flight. In general it can be concluded that within our present understanding of the chemistry of CH<sub>3</sub>CN, the data are in good agreement with the model predictions.

More in situ measurements, especially below 20 km, as well as a detailed study of acetonitrile emission sources, are required to make the model more complete and consistent.

### 3.2. PH Distributions

From the reasonable agreement of the total NPH abundance with the model calculations it follows automatically that the total PH abundance is also in agreement with the model.

For the internal distribution of the PH it is shown by the model calculations that the most abundant H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> ions ( $n = 3$  and  $4$ ) are in

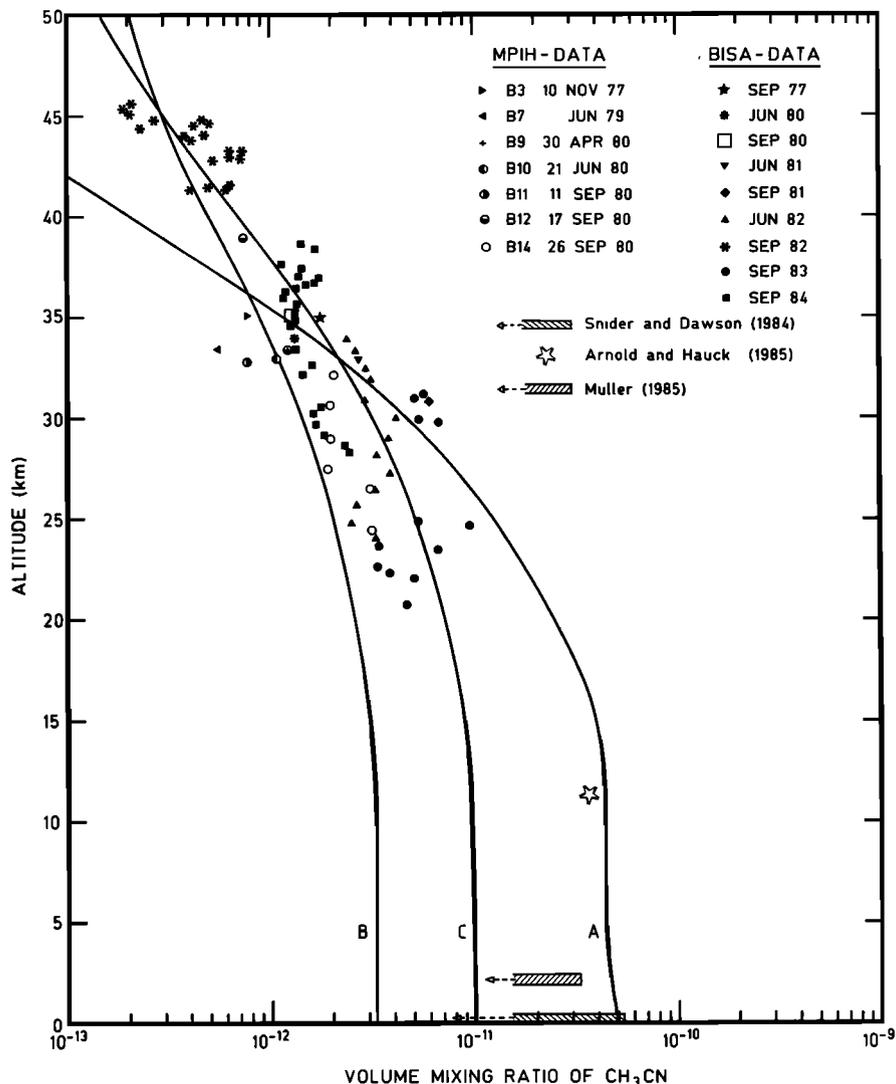


Fig. 3. Comparison of volume mixing ratios of  $\text{CH}_3\text{CN}$  as derived from NPH abundances of Figure 2 with profiles derived from model computations (for details see text).

thermodynamical equilibrium. Therefore the abundance ratio of the ions with mass 73 and 55 in the altitude region 20–45 km is given by

$$[\text{H}^+(\text{H}_2\text{O})_4]/[\text{H}^+(\text{H}_2\text{O})_3] = K_{\text{eq}} [\text{H}_2\text{O}] \quad (3)$$

where  $K_{\text{eq}}$  is the equilibrium constant. This ratio, derived from spectra of the four balloon flights and described in Table 1, is shown in Figure 4, together with the value obtained by using equation (3). The latter, represented by curve E in this figure, was calculated by using the thermochemical data of Lau et al. [1982] for computation of  $K_{\text{eq}}$ , a U.S. Standard Atmosphere temperature profile (spring/fall), and a water vapor mixing ratio derived from a model calculation [G. Brasseur, private communication, 1985] which corresponds to about 5 ppmv. To illustrate the effect of temperature, the same ratio has also been calculated with a temperature profile for summer conditions (curve E').

As can be seen in Figure 4 the measured values are always smaller than the one expected from equilibrium, apart from the data above 45 km

where the ratio  $[\text{H}^+(\text{H}_2\text{O})_4]/[\text{H}^+(\text{H}_2\text{O})_3]$  is too large. It was shown before that these deviations are due to collisionally induced dissociation of cluster ions in the mass spectrometer [Arnold et al., 1981; Arijs et al., 1982]. This cluster breakup probably occurs just behind the inlet hole, where the pressure is still considerably high and where the ions are accelerated by electric fields used to focus them into the mass filter. As observed in Figure 4 this cluster breakup is strongly dependent on the flight conditions, such as altitude range covered, dimension of the sampling hole, and strength of the internal focussing electric field. For the J-82 and S-83 flights, where a similar flight configuration (same ion lens, same sampling hole diameter, i.e., 0.2 mm) was used, the effects are comparable. For the S-84 flight the cluster breakup effect is very pronounced, as can also be concluded from the spectrum shown in Figure 1, which even contains mass 19 ( $\text{H}^+(\text{H}_2\text{O})$ ).

In this flight it is due to the high accelerating fields used to extract the ions from the gas beam just behind the sampling aperture. In

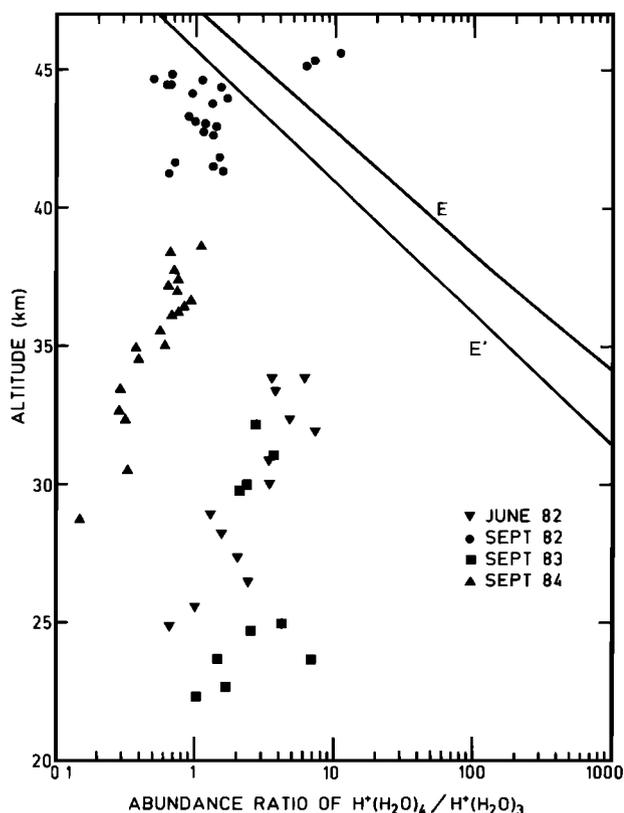


Fig. 4. Ratio of the abundances of  $\text{H}^+(\text{H}_2\text{O})_4$  and  $\text{H}^+(\text{H}_2\text{O})_3$  ions as observed in different balloon flights: curve E, spring/fall temperature profile; curve E', summer temperature profile.

principle it is possible to calibrate the cluster breakup effects in the laboratory and to correct for them. In cases where this was done [Arnold et al., 1981; Arijs et al., 1982], good agreement was found with equilibrium distributions. It is evident, however, that this collisional dissociation should be avoided in future. This implies the use of low ion focusing fields and therefore much more sensitive instruments. The solution of this problem may lie in the use of magnetic mass spectrometers combined with simultaneous ion detection techniques.

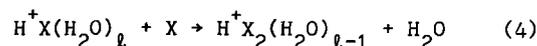
The few data points above 45 km show a  $[\text{H}^+(\text{H}_2\text{O})_4]/[\text{H}^+(\text{H}_2\text{O})_3]$  value that is too large compared to the equilibrium ratio. This is most likely due to contamination. It is believed that during the high-altitude balloon flight (S-82), a considerable amount of water vapour, as well as some other gases [Arijs et al., 1983a, b], were desorbed from balloon and gondola at float altitude and that the high value of  $[\text{H}_2\text{O}]$  entered into equation (3) gives rise to an excessive abundance ratio for the PH. In fact the observed signal at mass 73 in this flight is probably due to cluster breakup products of the  $\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_3$  ion at mass 96 formed in the presence of large amounts of water vapor. This explanation is supported by the fact that immediately after the start of the balloon descent, the ratio  $[\text{H}^+(\text{H}_2\text{O})_4]/[\text{H}^+(\text{H}_2\text{O})_3]$  dropped by a factor of 5.

### 3.3. NPH Distributions

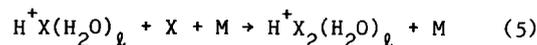
When fractional abundances of the NPH ions are analyzed, similar breakup effects as for PH ions are observed. Apparently, the loosely bound water molecules are easily detached during collisions with neutrals in the mass spectrometer, when ions are accelerated in the focusing fields. For this reason we have plotted in Figure 5 the sum of the concentrations of all ions containing no, one, and two molecules of acetonitrile. At the same time the model predictions for these groups of ions (case C) are shown in Figure 5. Curve I represents the PH abundance versus altitude of ions containing no acetonitrile, curve II the abundance of all ions of type  $\text{H}^+\text{X}(\text{H}_2\text{O})_l$  (ions containing one  $\text{CH}_3\text{CN}$  molecule), and curve III the abundance profile of all  $\text{H}^+\text{X}_2(\text{H}_2\text{O})_m$  ions (clusters with two  $\text{CH}_3\text{CN}$  molecules).

As can be seen the general trend is that there exists a reasonable agreement between the experimental data presented in this form and the model results, although the latter predicts a somewhat higher concentration of  $\text{H}^+\text{X}(\text{H}_2\text{O})_l$  ions and a lower abundance for clusters of the form  $\text{H}^+\text{X}_2(\text{H}_2\text{O})_m$ .

Several reasons can be imagined to explain these discrepancies. The first is that the conversion of  $\text{H}^+\text{X}(\text{H}_2\text{O})_l$  to  $\text{H}^+\text{X}_2(\text{H}_2\text{O})_m$  ions is more effective than assumed in the model. This cannot be excluded, since in the model this conversion was assumed to happen through two processes: a switching reaction



and a three body association of the type



The reaction rate coefficient of conversions given by (4) were calculated through the ADO theory of Su and Bowers [1975] and may in fact be higher, as shown by measurements of Smith et al. [1981].

Forward reaction rate constants for the three-body associations were obtained as explained in detail in the companion paper [Arijs and Brasseur, this issue]. The reverse  $k_r$  reaction rate for two-body as well as three-body reactions was obtained through

$$k_r = k_f/K_{eq}$$

where  $k_f$  is the forward reaction rate coefficient. The equilibrium constant was obtained by

$$-RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

where for  $\Delta H^\circ$  and  $\Delta S^\circ$  only a limited number of measurements were available, namely, for  $l = 0$  and  $l = 1$  [Meot-Ner, 1978, 1984; M. Meot-Ner, private communication, 1985]. The missing values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were computed from a thermodynamic cycle. Such a computation can induce large errors, taking into account the experimental uncertainties on the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for those steps in the cycle where measured values are available.

A second possible explanation for the deviations between measured values and model results in Figure 5 can be found in the temperature

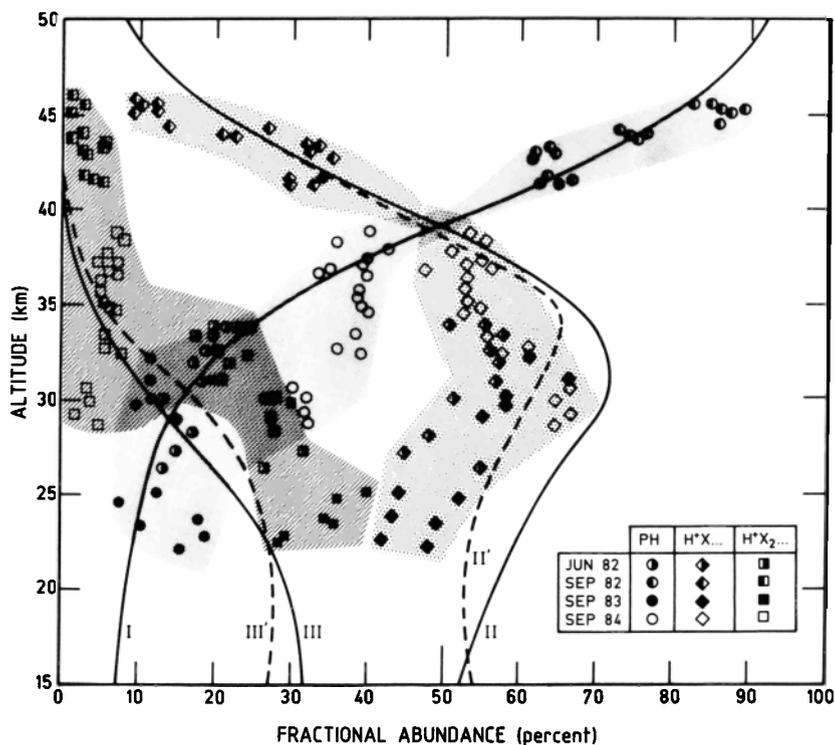


Fig. 5. Fractional abundance ratio of  $H^+(H_2O)_n$ ,  $H^+X(H_2O)_l$  and  $H^+X_2(H_2O)_m$  ions derived from different balloon experiments as compared to model predictions.

profile used in this model. As is noticed from equation (6), small temperature differences can give rise to large variations in the equilibrium constant. The full lines II and III are obtained by using the U.S. Standard Atmosphere (1966) profile. The effect of temperature is illustrated by the dotted lines (II' and III') obtained by lowering the temperature in the model by  $10^\circ$ .

Finally, it should again be noted that a 1-D model cannot explain temporary and local variations in the acetonitrile profile caused, e.g., by transport phenomena and that curves I to III' of Figure 5 are only representative for an average smoothed profile, such as case C in Figure 3.

In view of these remarks it can be concluded that the agreement between model calculations and experimental results is very satisfactory.

#### 3.4. Measurements of Mass Peaks Due to Isotopes

So far, all evidence given to demonstrate that the molecule X in  $H^+X_l(H_2O)_m$  is indeed acetonitrile is of an indirect nature. It can be summarized as follows:

$CH_3CN$  has a molecular mass of 41 amu, as required for X,

The proton affinity of acetonitrile is substantially larger than that of water [Walder and Franklin, 1980],

$CH_3CN$  reacts rapidly with PH to form NPH of the nature observed in the stratosphere [Smith et al., 1980],

The presence of acetonitrile in the stratosphere in concentrations compatible with the ion observations can be explained by a model based on

reasonable values of surface emissions and a chemistry previously confirmed in the laboratory [Arijs and Brasseur, 1985],

The presence in the troposphere has been confirmed through independent measurements at ground level [Becker and Ionescu, 1982; Snider and Dawson, 1984, 1985], although the results of Becker and Ionescu are probably only representative for polluted areas.

The arguments cited above seem to be rather persuasive, since it is very difficult to imagine another molecule having all these properties. Nevertheless a more direct proof would be very welcome. Such additional evidence may be obtained by measuring the peak intensity at mass  $(m + 1)$  and  $(m + 2)$  due to the presence of isotopes for an ion with mass  $m$ . Since these peak intensities will be small, it is evident to choose for  $m$  the mass of the most abundant ion. For this reason a series of high-resolution scans has been performed in the S-84 flight around mass 96 and has been integrated during a long time. The expected abundance of mass 97 and 98, if X were acetonitrile, can be calculated [Beynon and Williams, 1963], and it turns out to be 2.82% and 0.63% of the abundance of mass 96. Figure 6 shows the result of a summation of 48 scans performed in a mass range from 93 to 101 amu. Two neighboring mass peaks located at 97 and 98 amu can be seen in addition to mass 96. The measured relative abundances of these peaks are

$$[97]/[96] = 3.8 \times 10^{-2}$$

and

$$[98]/[96] = 1.3 \times 10^{-2}$$

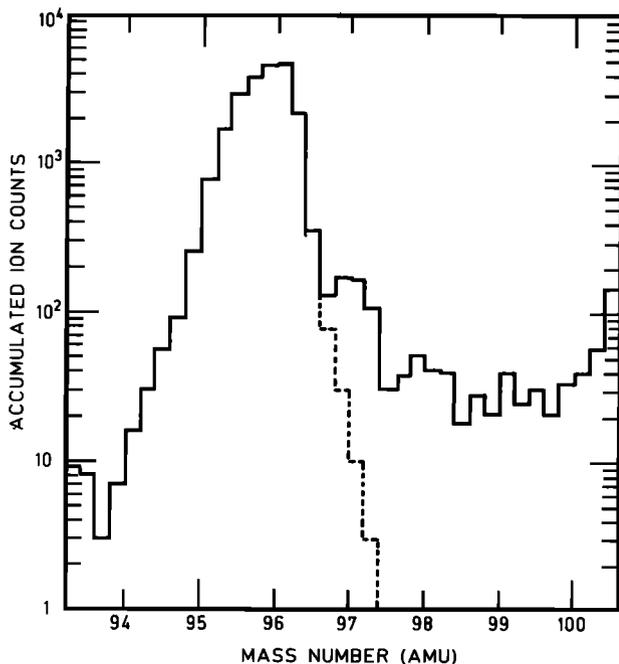


Fig. 6. High-resolution spectrum in the mass range 93 to 101 amu obtained at 38-km altitude during the S-84 balloon experiment. This spectrum is the sum of 48 scans, each of 7.4-s duration.

This is somewhat higher than the expected values which, however, is not necessarily in contradiction with X being  $\text{CH}_3\text{CN}$ . It should indeed be noticed that, although a constant peak width of 0.8 amu (FWHM) has been adopted for this measurement, the tail of a peak at mass  $m$  can still significantly contribute to a peak at  $m + 1$ . This is illustrated in Figure 6 by the dotted line, which is an extrapolation of the descending edge of the mass peak at 96 amu.

Estimating the contribution of the tail of the mass peak 96 to the peak at 97 amu to be 20 counts and the contribution of the tail of mass 97 to the peak at 98 amu to be 10 counts and subtracting from both peaks (97 and 98) a background of about 0.3 c s<sup>-1</sup>, the abundance distribution expressed in accumulated ion counts (Figure 6) becomes 4598, 152, and 39 counts at masses 96, 97, and 98, respectively. It also cannot be excluded that besides the isotopic neighbors of  $\text{H}^+(\text{CH}_3\text{CN})(\text{H}_2\text{O})_3$  there exist minor stratospheric ions, having the same mass numbers. Such ions can either be natural ions or be due to contamination.

Finally, apart from these error sources, the dispersion due to the statistical nature of the counting event should also be investigated.

We can now consider the total number of counts (4789) collected for masses 96, 97, and 98 as the result of counts corresponding to mass 96 and of counts that originate from mass 97 and 98. In this case the probability  $P$  of having  $i$  counts due to mass 97 or 98 during  $n$  observations is given by a binomial distribution. The mean value  $\mu$  for this distribution is given by

$$\mu = n\theta \quad (7)$$

and the dispersion  $\sigma$  by

$$\sigma^2 = n\theta(1 - \theta) \quad (8)$$

where  $\theta$  is the probability of finding for one measurement an ion due to masses 97 or 98. With the theoretically expected abundances 0.0282 and 0.0063 the value found for  $\theta$  is 0.033. For the total number of events  $n = 4789$  we then obtain  $\mu = 158$  and  $\sigma = 12$ . If we now take a  $2\sigma$  value as a confidence level, the number of counts  $n_c$  belonging to masses 97 and 98 should be

$$134 < n_c < 182$$

Experimentally, we find  $n_c = 152 + 39 = 191$ . Taking into account the possible contribution of "contaminant" ions to  $n_c$ , the agreement is quite acceptable.

It can therefore be concluded that the measurement of the abundances of ions due to isotopes does not lead to the conclusion that  $\text{CH}_3\text{CN}$  can be ruled out as a candidate for X.

#### 4. Conclusions

The analysis of experimental data (presented in the previous sections) as well as the new data about ion mass peaks due to isotopes support the hypothesis that the molecule X of the NPH of the form  $\text{H}^+\text{X}_l(\text{H}_2\text{O})_m$  is acetonitrile.

A comparison of the NPH distribution with the model results, discussed in the companion paper [Brasseur and Arijs, this issue], leads to the conclusion that this model is most probably a good representation of reality.

The present set of data, however, does not allow a definite choice of the mean profile of  $\text{CH}_3\text{CN}$  in the atmosphere.

Some additional experimental research will be necessary to elucidate this problem. Among the remaining questions to be resolved, we cite: a detailed analysis of the emission sources of  $\text{CH}_3\text{CN}$ ; more in situ measurements, especially below 20 km and above 40 km; and laboratory experiments, needed to investigate the detailed neutral and ion chemistry of acetonitrile.

The absence of sodium clusters as major ions in the altitude region 20 to 45 km, suggest that sodium is probably removed by processes bringing it in a form unsuitable for participation in the ion chemistry [Arnold and Henschen, 1982]. In situ composition measurements in the altitude region above 40 km may shed some new light on this problem.

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