ISSN 0065-3713

INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE

3 - Avenue Circulaire
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AERONOMICA ACTA

A - N° 304 - 1986

Stratospheric positive ion composition measurements between 22 and 45 km - an updated analysis

by

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FOREWORD

This text is part of a paper that will be published in the "Journal of Geophysical Research".

AVANT-PROPOS

Ce texte fait partie d'un travail qui sera publié dans le "Journal of Geophysical Research".

VOORWOORD

Deze tekst vormt een gedeelte van een publikatie die zal verschijnen in het "Journal of Geophysical Research".

VORWORT

Dieser Text ist Teil einer Arbeit der wird herausgegeben werden im "Journal of Geophysical Research".

STRATOSPHERIC POSITIVE ION COMPOSITION MEASUREMENTS BETWEEN 22 AND 45 KM - AN UPDATED ANALYSIS

by

J. INGELS, D. NEVEJANS, P. FREDERICK and E. ARIJS

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. A review of the abundances of proton hydrates and non proton hydrates shows that the latter most probably result from the presence of acetonitrile (CH_3CN) 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).

Résumé

Les résultats de mesures récentes et anciennes de la composition des ions positifs dans la stratosphère, sont présentés et analysés. Ils sont comparés à des calculs théoriques. Un résumé de la quantité de protons hydratés et de "non proton hydrates" montre que ces derniers sont probablement la suite de la présence d'acétonitrile (CH_3CN) dans l'atmosphère. Le profil vertical du rapport de mélange d'acétonitrile a été déduit des mesures des compositions d'ions positifs et correspond à un modèle où l'on suppose avoir une émission d'acétonitrile à la surface terrestre suivie d'une destruction de ce gaz dans l'atmosphère par des réactions chimiques (principalement avec des radicaux OH).

Voorwoord

De resultaten van recente en vroegere metingen van de positieve ionensamenstelling in de stratosfeer, worden voorgesteld en besproken. Ze worden vergeleken met de theoretische berekeningen. Een overzicht van de hoeveelheden protonhydraten en niet-protonhydraten, toont aan dat deze laatste waarschijnlijk het gevolg zijn van de aanwezigheid van acetonitrile (CH_3CN) in de atmosfeer. Het vertikaal profiel van de mengverhouding van acetonitrile werd afgeleid uit de metingen van de positieve ionensamenstellingen en komt overeen met een model waarbij verondersteld wordt dat er acetonitrile geloosd wordt aan het aardoppervlak en dat het daarna in de atmosfeer wordt afgebroken door scheikundige reacties (voornamelijk met OH radicalen).

Zusammenfassung

Die Ergebnisse früheren und neuen Messungen der Massenspektren positiven, stratosphärischen Ionen, werden vorgestellt und analysiert. Sie werden vergleicht mit theoretischen Berechnungen. Ein Ubersicht der Mengen der Protonhydraten und der übrigen Ionen, beweist dass die zweite Gruppe wahrscheinlich eine Folge ist der Anwesenheit des Methanzyanides (CH_3CN) in der Atmosphäre. Die Vertikalverteilung der Mischungsverhältnisse des Methanzyanides wurde bekommen durch Messungen positiven Ionenzusammensetzungen und ist vereinbar mit einem Modell wobei eine Quelle an der Erdoberfläche besteht und eine allmächliche Abnahme in der Atmosphäre auftritt am meistens durch Reaktionen mit Hydroxylradikalen.

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 $H^+(H_2O)_n$ and so-called non proton hydrates (NPH) of the form $H^+X_\ell(H_2O)_m$. X has a mass of 41 amu and is most likely acetonitrile (CH_3CN). 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, 1985). 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 (Böhringer and Arnold, 1981; Smith et al., 1981). Furthermore a combination of a 1-D model of the neutral chemistry of CH_3CN 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 ion composition measurements and to compare them with these model predictions. Previously published data (Arijs et al., 1978, 1980, 1982, 1983a, 1983b) as well as recently obtained results are presented.

2. EXPERIMENTAL TECHNIQUES AND MEASUREMENT CIRCUMSTANCES

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; Nevejans et al., 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 towards 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.

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

TABLE 1.- Characteristics of balloon flights.

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

V means valve controlled balloon.

[1] 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.

[2] Descending of the balloon due to cooling after sunset.

only at float altitudes to allow an unambiguous identification 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 CH_3CN 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 break-up discussed further on. The mass peaks belonging to the two ion families $H^+(H_2O)_n$ and $H^+X_\ell(H_2O)_m$ can clearly be distinguished in Figure 1. Furthermore it is clear from the presence of the mass peak at 42 amu due to H^+X, that the mass of 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 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 and Brasseur, 1985) calculated for X being CH_3CN 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

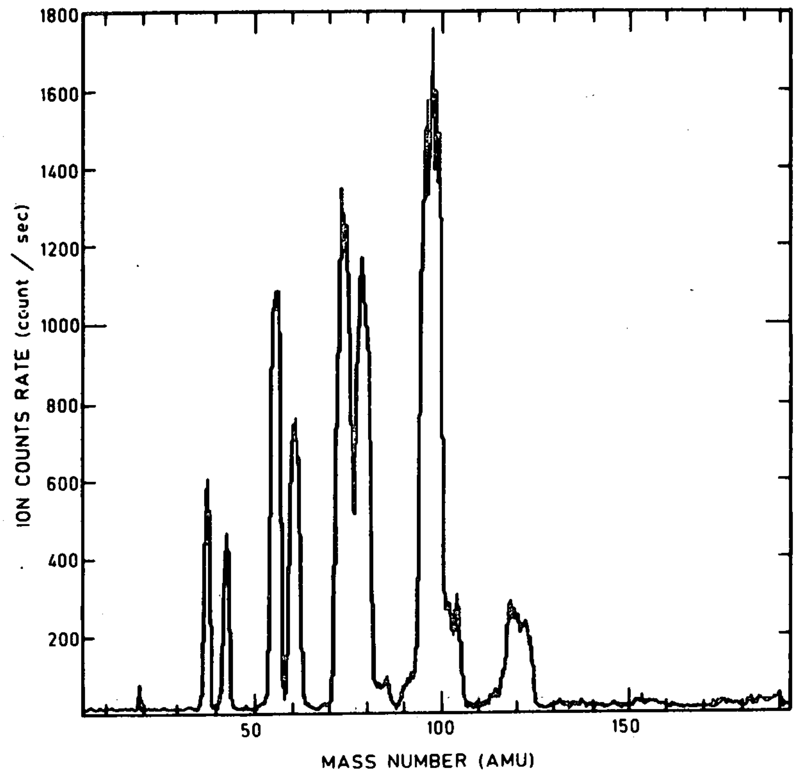

Figure 1.- Typical positive ion spectrum measured with constant resolution ($M/\Delta M = 17$) at 38.6 km altitude on 27 September 1984. The spectrum was obtained after a summation of 4 scans; each scan taking 82 s.

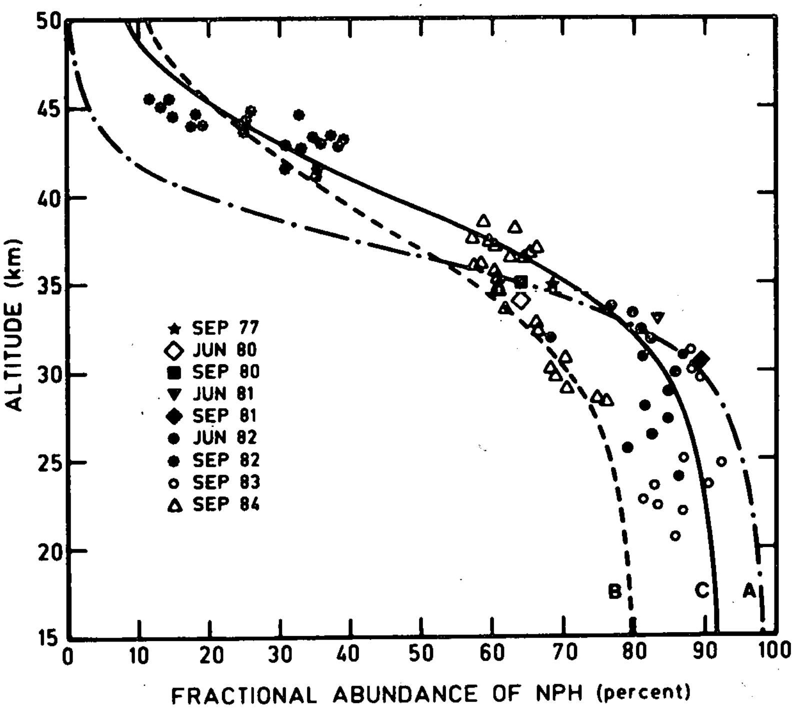

Figure 2.- Fractional abundance (expressed in percent) of NPH ions measured during the different balloon flights realized by the group of the Belgian Institute for Space Aeronomy, compared to model calculations.

with a global annual CH_3CN emission of 5×10^{11}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 1.5×10^{10}g. Curve C is derived from an average CH_3CN profile with mean values for the chemical reaction rates and a global CH_3CN emission of 4.7×10^{10}g per year (Arijs and Brasseur 1985).

The uncertainty on the ion abundances derived from ion composition data results from possible experimental errors estimated to be 20 to 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 on the experimental data, it is apparent from Figure 2 that below 35 km, the three model predictions can be brought in 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)

$$k\,[PH]\,[X] = \alpha\,[n_-]\,[NPH] \tag{1}$$

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 α the ion-ion recombination coefficient.

Using for k a value of 3×10^{-9} cm^3 s^{-1}, in agreement with the experiments of Smith et al. (1981) and for α the parameterization

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

where [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_3CN 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 from the same values of α, $[n_-]$ and k are also given in Figure 3.

The three $[CH_3CN]$ 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_3CN mixing ratio of 36 ppt 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_3CN. 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, 1985) seem 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_3CN being emitted from the earth's surface and not produced in-situ.

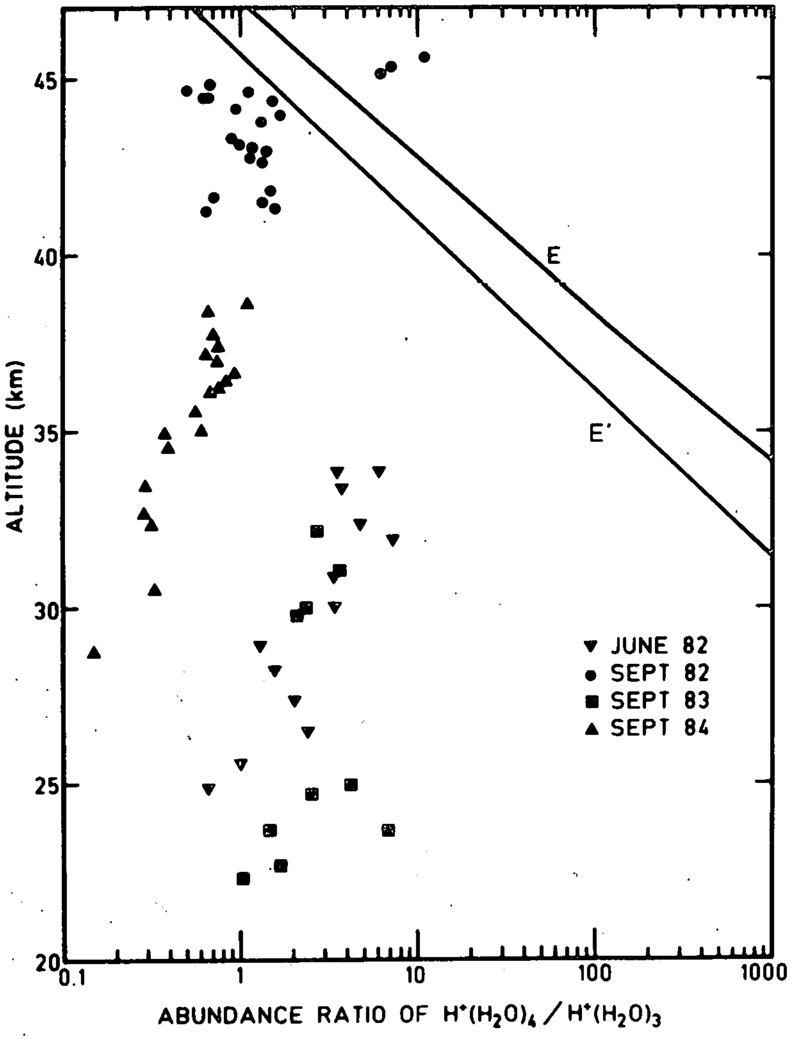

Figure 3.- Comparison of volume mixing ratios of CH_3CN as derived from NPH abundances of Figure 2 with profiles derived from model computations (for details see text).

If the value at 11.3 km reported by Arnold and Hauck (1985) is correct, it seems as if an additional sink for CH_3CN is needed just above the tropopause. However, before speculating on such loss mechanism, which as suggested by Arnold and Hauck (1985) may result from ion-ion recombination, more measurements of CH_3CN below 20 km are needed.

It should also be realized that the CH_3CN 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_3CN, 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 $H^+(H_2O)_n$ ions ($n = 3$ and 4) are in thermodynamical equilibrium. Therefore the abundance ratio of the ions with mass 73 and 55 in the altitude region 20-45 km is given by :

$$[H^+(H_2O)_4]/[H^+(H_2O)_3] = K_{eq}\ [H_2O] \qquad (3)$$

where K_{eq} is the equilibrium constant. This ratio, derived from spectra of the four balloon flights, described in Table 1, is shown in Figure 4, together with the value obtained by equation (3). The latter, represented by curve E in this figure, was calculated using the thermochemical data of Lau et al. (1982) for computation of K_{eq}, a US Standard Atmospheric Temperature profile (spring/fall) and a water vapour mixing ratio derived from a model calculation (Brasseur, private communication) 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 $[H^+(H_2O)_4]/[H^+(H_2O)_3]$ is too large. It was shown before that these deviations are due to collisional induced dissociation of cluster ions in the mass spectrometer (Arnold et al., 1981; Arijs et al., 1982). This cluster break-up 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 break-up 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 break-up effect is very pronounced, as can also be concluded from the spectrum shown in Figure 1, which even contains mass 19 ($H^+(H_2O)$).

In this flight, this is due to the high accelerating fields used to extract the ions from the gas beam just behind the sampling aperture. In principle, it is possible to calibrate the cluster break-up 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 focussing 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.

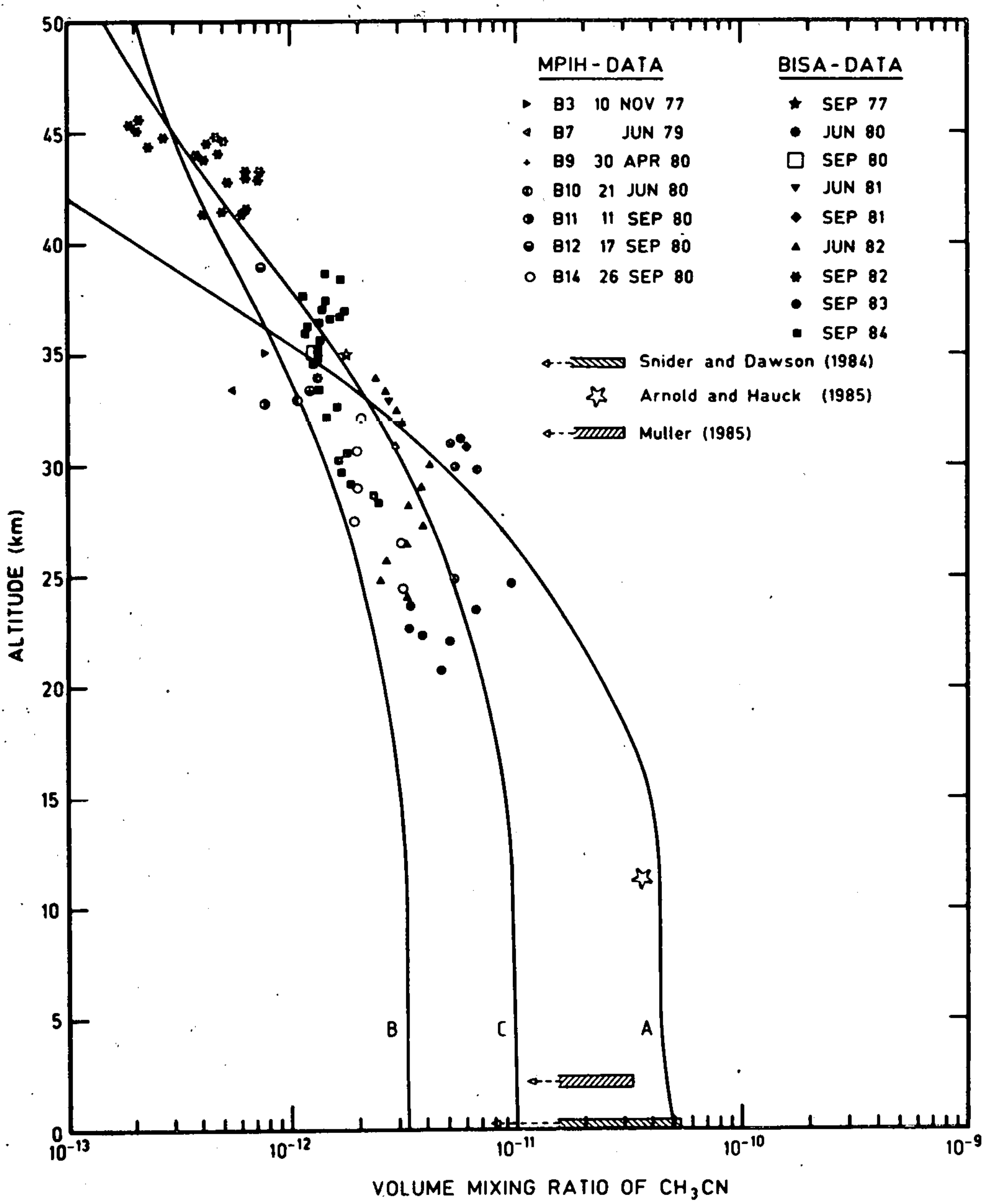

Figure 4.- Ratio of the abundances of $H^+(H_2O)_4$ and $H^+(H_2O)_3$ ions as observed in different balloon flights. Curve E : spring/fall temperature profile, curve E' : summer temperature profile.

The few data points above 45 km, shows a $[H^+(H_2O)_4]/[H^+(H_2O)_3]$ value which 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 $[H_2O]$ 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 break-up products of the $H^+(CH_3CN)(H_2O)_3$ ion at mass 96, formed in the presence of large amounts of water vapour. This explanation is supported by the fact that immediately after the start of the balloon descent, the ratio $[H^+(H_2O)_4]/[H^+(H_2O)_3]$ dropped by a factor of 5.

3.3. NPH distributions

When fractional abundances of the NPH ions are analyzed, similar break-up 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 focussing 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 respectively. 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 $H^+X(H_2O)_m$ (ions containing one CH_3CN molecule) and curve III the abundance profile of all $H^+X_2(H_2O)_\ell$ ions (clusters with two CH_3CN 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 $H^+X(H_2O)_m$ ions and a lower abundance for clusters of the form $H^+X_2(H_2O)_\ell$.

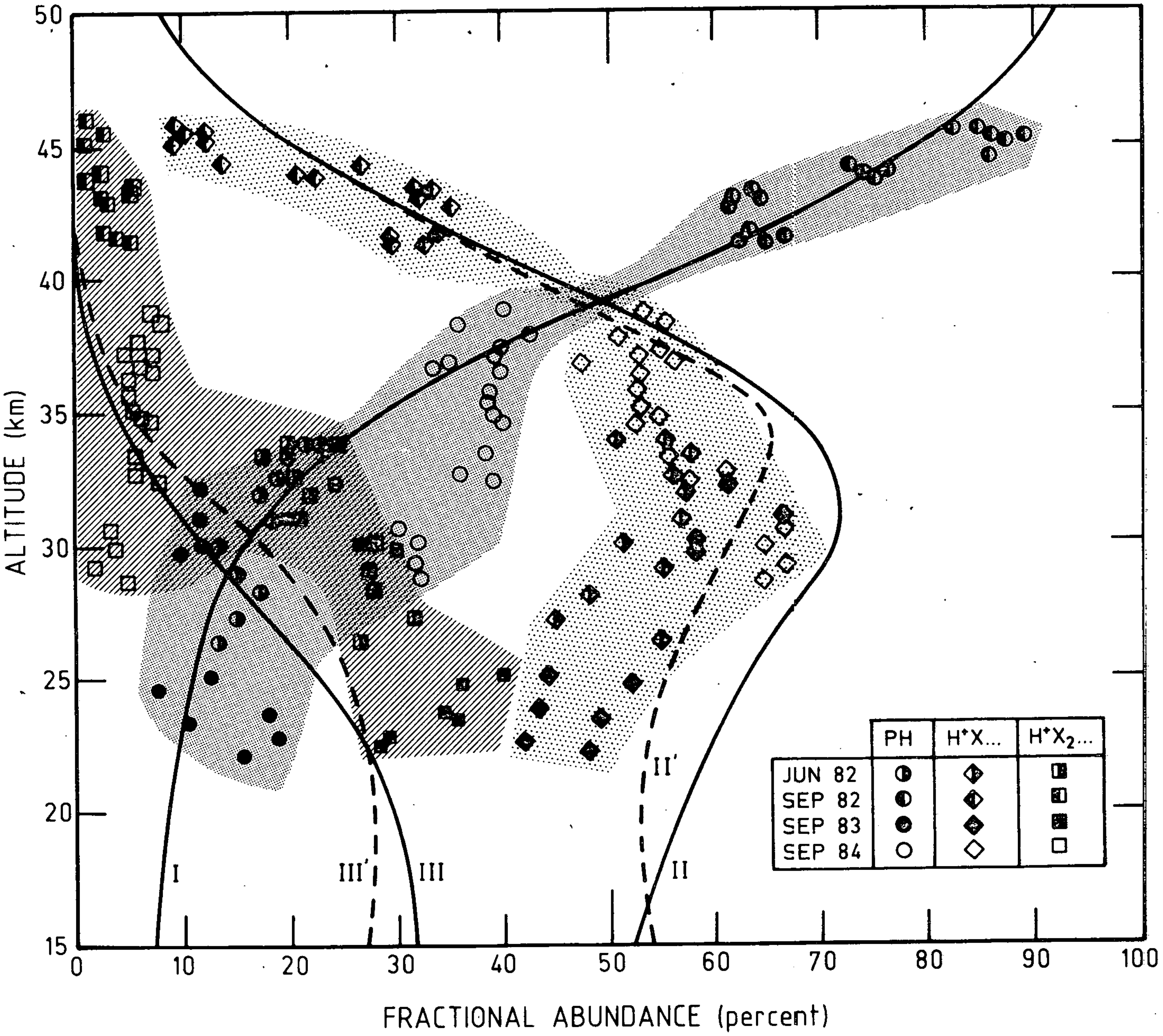

Figure 5.- Fractional abundance ratio of $H^+(H_2O)_n$, $H^+X(H_2O)_m$ and $H^+X_2(H_2O)_m$ ions derived from different balloon experiments, compared to model predictions.

Several reasons can be envisaged to explain these discrepancies. The first one is that the conversion of $H^+X(H_2O)_\ell$ to $H^+X_2(H_2O)_m$ 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. The first one is a switching reaction

$$H^+X(H_2O)_\ell + X \rightarrow H^+X_2(H_2O)_{\ell-1} + H_2O \qquad (4)$$

and the second one, a three body association, of the type

$$H^+X(H_2O)_\ell + X + M \rightarrow H^+X_2(H_2O)_\ell + M \qquad (5)$$

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, 1985). The reverse k_r reaction rate for 2 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

$$- RT \ell n\, K_{eq} = \Delta H^\circ - T\Delta S^\circ \qquad (6)$$

where for ΔH° and ΔS° only a limited number of measurements were available, namely for $\ell = 0$ and $\ell = 1$ (Meot-Ner, 1978, 1984, private communication). The missing values of ΔH° and ΔS° were computed from a thermodynamic cycle. Such a computation can induce large errors taking into account the experimental uncertainties on the values of ΔH° and ΔS° 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 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 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 degrees.

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.

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 $H^+X_\ell(H_2O)_m$ is acetonitrile.

A comparison of the NPH distribution with the model results, discussed in the companion paper (Brasseur and Arijs, 1985) 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 CH_3CN 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 CH_3CN;
- 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.

ACKNOWLEDGEMENTS

We would like to thank the technical staff of the Belgian Institute for Space Aeronomy, especially E. Van Ransbeeck, J. Neven and G. Van den Wyngaert for their valuable help in constructing the balloon payloads used in the experiments described here.

We also appreciate the help of the personel of the C.N.E.S. balloon launching base in Aire-sur-l'Adour (France), who made these measurements possible.

One of the balloon flights (S-83) discussed in this article took place within the framework of the MAP-Globus 1983 campaign, organized and coordinated by Dr. D. Offermann (University of Wuppertal, G.F.R.).

This work has been partly financed by N.F.W.O contracts (Belgian National Science Foundation) nrs. 2.009.79 and 2.0095.83.

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