

STRATOSPHERIC POSITIVE ION COMPOSITION MEASUREMENTS AND ACETONITRILE DETECTION: A CONSISTENT PICTURE? *

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ABSTRACT

An overview is given of the positive ion composition measurements performed with balloon-borne ion mass spectrometers in the Earth's atmosphere between 20 and 45 km. In particular, attention is paid to the derivation of the acetonitrile volume mixing ratio profile.

The results are compared with model calculations, data obtained with airplane-borne instruments, and ground-level samplings. The consistency of the present picture is verified.

The comparison with results of recent laboratory experiments show that electric field-induced collisional dissociation occurs in balloon-borne ion mass spectrometers. Probably, this is one of the major causes for the observed discrepancies between the data of airplane- and balloon-borne instruments.

INTRODUCTION

Galactic cosmic radiation, the main ionization source in the Earth's atmosphere between 10 and 50 km altitude [1,2], yields N_2^+ , O_2^+ and electrons as primary charged particles. The electrons are rapidly thermalized and attach to electronegative gases (mainly oxygen). Therefore, the resulting rarified plasma consists of positive and negative ions. Due to the low ionization rate (varying from 0.5 ion pairs $cm^{-3} s^{-1}$ at 50 km to 25 ion pairs $cm^{-3} s^{-1}$ at 10 km altitude) and the value of the ion-ion recombination coefficient ($2 \times 10^{-6} cm^3 s^{-1}$ at 10 km to $10^{-7} cm^3 s^{-1}$ at 50 km), the ion concentration is very low (about $1000 cm^{-3}$) and ion lifetime is very long in the stratosphere (150 s at 10 km to 10^4 s at 50 km). Within this lifetime, ions undergo multiple collisions with neutral gas molecules leading to ion/molecule reactions changing the nature of the ions. With the long lifetimes

* Dedicated to Eldon E. Ferguson in honour of his pioneering work in ion physics and chemistry and his stimulating contributions to aeronomy.

involved and taking typical ion/molecule reaction rates to be of the order of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$, even atmospheric trace gases down to the parts per billion level will still play a role in conversion mechanisms and therefore the identity of terminal stratospheric ions will be determined by the nature and concentration of trace gases.

A measurement of stratospheric positive and negative ion compositions can thus lead to the detection of trace gases not measurable by other methods, if relevant ion/molecule reaction rates or equilibrium constants are known. Furthermore, a knowledge of the ion composition leads to a better insight into atmospheric ion chemistry and can provide a better understanding of some atmospheric electricity phenomena.

Until 1977, no experimental data about stratospheric ion composition were available and our knowledge in this field consisted of predictions [3,4] based upon extensions of theories developed for the D-region of the ionosphere [5,6] and pioneering laboratory work on appropriate ion/molecule reactions [7-9].

Results of mass spectrometric measurements with rocket-borne instruments in the upper stratosphere were reported for the first time by Arnold et al. in 1977 [10].

During the last decade, however, a large number of in situ measurements of the stratospheric ion composition have been performed with balloon-borne quadrupole ion mass spectrometers, mainly by two groups, the Belgian Institute for Space Aeronomy (BISA) and the Max-Planck-Institut für Kernphysik, Heidelberg (MPIH). Reviews on experimental aspects as well as on scientific results have been published previously [11-15]. The major results can be summarized as follows.

(a) The positive ion composition in the altitude range from 20 to 45 km is characterized by the presence of two major ion families; namely $\text{H}^+(\text{H}_2\text{O})_n$ ions or proton hydrates (PH), the formation of which in the stratosphere had previously been predicted [3,4], and non-proton hydrates (NPH) of the form $\text{H}^+\text{X}_l(\text{H}_2\text{O})_n$, where X has been identified as acetonitrile (CH_3CN). The last group of ions results from ion/molecule reactions between PH and CH_3CN , which is present in extremely low concentrations in the atmosphere.

(b) The major negative ions in the same altitude range are cluster ions with NO_3^- or HSO_4^- as cores and HNO_3 and/or H_2SO_4 as ligands. Below 30 km, the $\text{NO}_3^-(\text{HNO}_3)_n$ ions, which were also expected from previous laboratory measurements [9], dominate. Between 30 and 40 km, the $\text{HSO}_4^-(\text{HNO}_3)_n(\text{H}_2\text{SO}_4)_l$ ions, which result from reactions of $\text{NO}_3^-(\text{HNO}_3)_n$ ions with sulphuric acid vapour [16], become more abundant [17].

Studies of the relative abundances of the observed ions have led to the derivation of trace gas concentrations in the stratosphere, such as CH_3CN

profiles from positive ion spectra and H_2SO_4 as well as HNO_3 concentrations from negative ion spectra. Extensive details concerning these results are given in reviews [11–14] and in the references cited therein.

Presently, the positive ion chemistry seems to be understood more thoroughly, since more laboratory data on the relevant ion/molecule reactions and the neutral atmospheric chemistry of the participating trace gases are available [18].

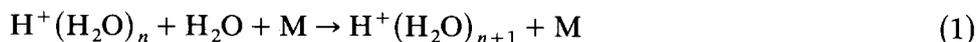
It is the intention of this paper to review critically the results deduced from positive stratospheric ion composition measurements and to investigate whether or not our present set of data leads to a consistent picture.

REVIEW OF PREVIOUS WORK

Results derived from in situ positive ion composition measurements

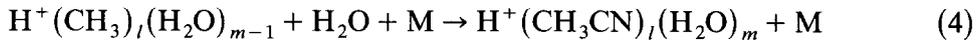
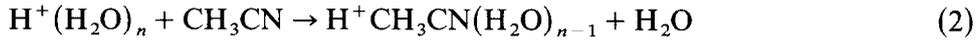
Since 1977, many balloon flights in the altitude range 20–45 km devoted to the measurement of stratospheric positive ion composition and ambient ion spectra have appeared in the literature [19–21]. All balloon launches took place in Southern France at about 44°N (CNES launching bases in Aire-sur-l'Adour and Gap-Tallard). The instruments used consist mainly of a quadrupole mass filter and detector built into a cryopump cooled by liquid helium or neon and the associated electronics [15]. In all the configurations flown so far, the ambient air containing ions leaks into the cryopump through a single hole (0.2–0.4 mm in diameter) in a thin flange biased a few volts with respect to the balloon gondola. Whereas neutral gas molecules are pumped by the cryopump, the ions are focussed into the quadrupole mass filter mounted at a distance of a few cm from the sampling flange in the cryopump. Two methods have been applied to guide the ions into the quadrupole. The first one uses a simple electrostatic lens [15], whereas the second method omits this and takes advantage of the electric field created by the quadrupole bias potential with respect to the sampling flange (10–30 V) [22]. In both cases however, a rather high electric field exists in the gas jet region just behind the sampling aperture. As will be seen later, this can cause ion dissociation, resulting in possible errors in the data interpretations.

As mentioned earlier, two major ion families dominate the stratospheric positive ion composition, namely the PH and NPH. The formation of PH is well understood [5]. The different steps in the mechanism are: charge exchange of N_2^+ with O_2 , clustering of O_2^+ with O_2 , reaction of $\text{O}_2^+ \cdot \text{O}_2$ with water vapour to form $\text{O}_2^+ \cdot \text{H}_2\text{O}$, and further reaction of the latter ion with H_2O leading to $\text{H}^+(\text{H}_2\text{O})$. Three-body reactions of the type



then result in a PH distribution determined by the water vapour mixing ratio in the stratosphere (typically a few ppm) and the temperature (216 K at 20 km to 264 K at 45 km).

The NPHs are subsequently formed by a set of reactions of the type



At first, the presence of CH_3CN in the stratosphere was difficult to explain and some of the earlier experiments were devoted to the unambiguous identification of the NPH. Presently, however, the composition of the NPH is considered to be known and supported by high-resolution spectra [23], in situ electric field collisional activation (ECA) studies [24], laboratory measurements [25,26], ground-level detection of CH_3CN [27], aircraft-borne CH_3CN measurements [28], and model calculations [18].

So far, the major use of positive ion composition data has been the derivation of acetonitrile volume mixing ratios, assuming that reactions of type (2) are the source for NPH and the sink is ion-ion recombination. In that case, we may write

$$k[\text{CH}_3\text{CN}][\text{PH}] = \alpha[\text{n}^-][\text{NPH}] \quad (5)$$

where square brackets denote number densities, k is the reaction rate coefficient for reaction (2), $[\text{n}^-]$ is the total negative ion density, and α the ion-ion recombination coefficient.

The ratio, R , of NPH to PH ion abundances as observed in different balloon flights is shown in Fig. 1, and the acetonitrile volume mixing ratios, derived by applying Eq. (5) to the data of Fig. 1 are shown in Fig. 2. Some remarks concerning the choice of the parameters used should be made here.

The rate coefficient, k , for the switching reactions represented by Eq. (2) was first measured by Smith et al. [25] for $n = 1, 2, 3$ and the measured values vary from $3.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ to $4.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, depending upon the value of n and the temperature. In view of the uncertainty of $\pm 30\%$ reported on these data and the fact that a theoretical calculation of k with the average dipole orientation (ADO) model [29] leads to slightly lower values, we have adopted a value of $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for the practical use of Eq. (5) in previous publications [21].

Recently, Viggiano et al. [30] have performed careful measurements to determine the temperature dependence of k for values of n up to 7. According to their results, the temperature dependence of k is larger than the one reported by Smith et al. [25]. For stratospheric temperatures, corrections should be applied to the data shown in Fig. 2, resulting in lower

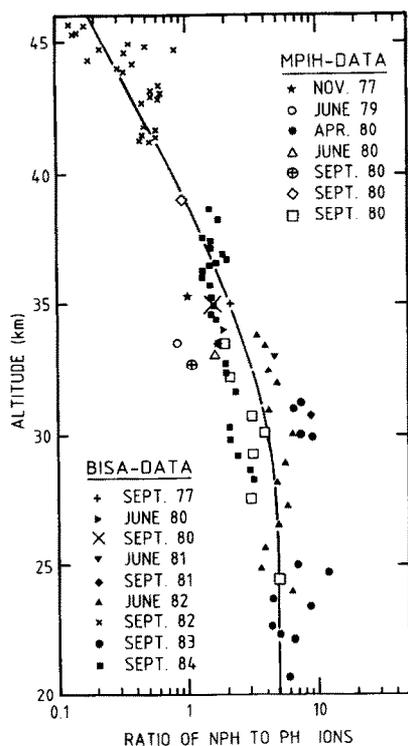


Fig. 1. Ratio of NPH to PH ions derived from positive ion composition measurements with balloon-borne mass spectrometers during different balloon flights. The full line is an estimated average shown to indicate the trend of the data versus altitude.

CH_3CN mixing ratios. This correction is of the order of 30% only and, considering the uncertainties to be discussed later, we have not implemented this correction in Fig. 2.

For the ion-ion recombination coefficient, α , recent results are available from laboratory experiments [25], in situ measurements [31], and theoretical calculations [32]. The value used by the MPIH group is derived from the theory of Bates [32]. In order, however, to be able to use a value in the form of a mathematical expression, we have fitted a formula to different data [25,31,32]. It turns out that

$$\alpha = 6 \times 10^{-8} (300/T)^{0.5} + 1.25 \times 10^{-25} [\text{M}] (300/T)^4 \quad (6)$$

where T is the temperature in K and $[\text{M}]$ the total gas number density, leads to values very close to the average of the different data. Therefore, we have systematically used expression (6) for α for use in Eq. (5) to derive acetonitrile concentrations.

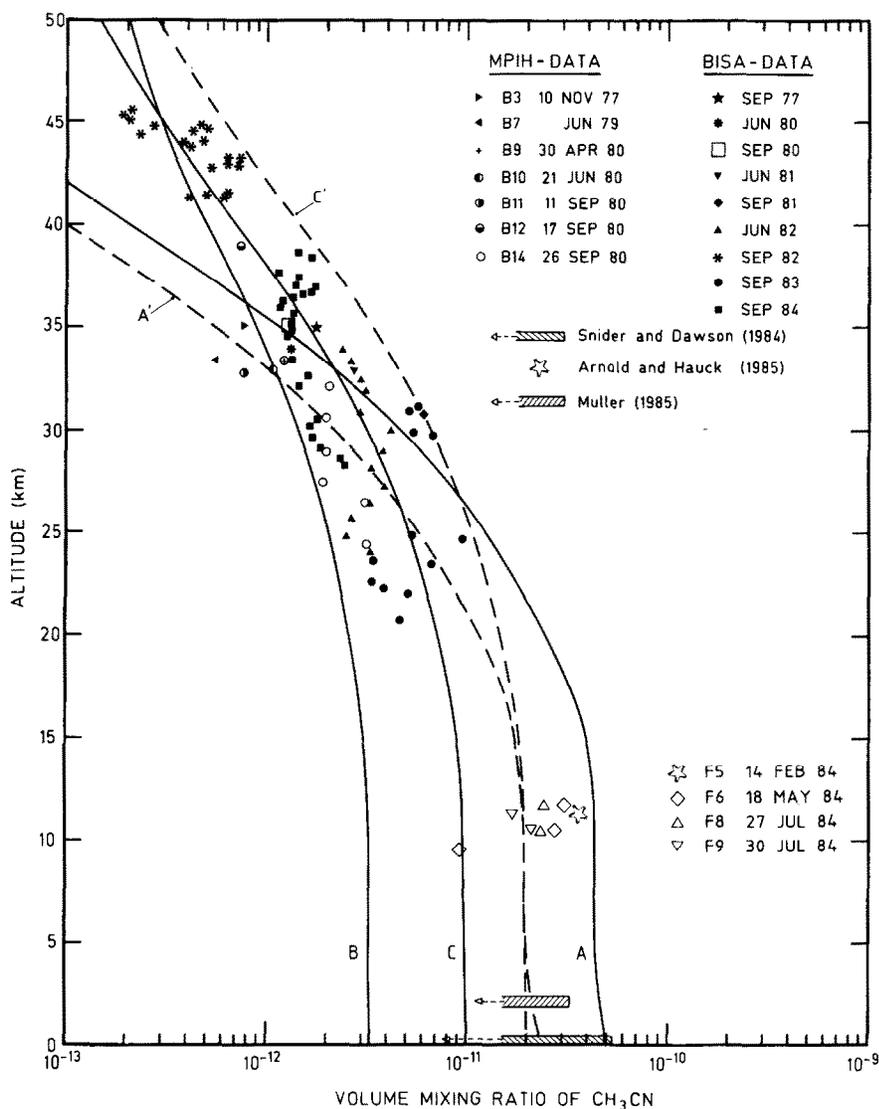


Fig. 2. Acetonitrile mixing ratios inferred from the data of Fig. 1. Also shown are some ACIMS data obtained around the tropopause with an airplane-borne mass spectrometer, ground-level results, and an upper limit estimation at 2000 m derived from infrared spectra. The curves A, A', B, C, and C' are the results of model calculations.

The total negative ion concentration, $[n^-]$, can again be derived from different sources. The MPIH group [33] adopted the values measured by Rosen and Hofmann [34] with a balloon-borne ion probe above Wyoming (U.S.A.) in 1978 and 1979. The ion concentration being a function of

latitude [1] and time through the solar cycle [35], we have chosen to derive $[n^-]$ from

$$[n^+] = [n^-] = \left(\frac{Q}{\alpha}\right)^{1/2} \quad (7)$$

where Q is the ionization rate calculated with a parametrization formula of Heaps [19,36]. For α , we again adopt Eq. (6). It turns out that the values thus obtained are in good agreement with the data of Rosen and Hofman [34] if appropriate values for date and geomagnetic latitude are used.

We have applied Eqs. (6) and (7) to calculate the values of α and $[n^-]$ for all data shown in Fig. 2. The results of the MPIH group as shown in Fig. 2 are therefore slightly different from their data as reported in the literature [20,22].

Recently, acetonitrile has been measured by the MPIH group in the tropopause region using aircraft-borne active chemical ionization mass spectrometry (ACIMS) [28]. In this method, the CH_3CN mixing ratio is derived from measurements of the flux ratio for product and precursor ions in a flow tube with an active ion source. Apart from the measured NPH to PH ion abundance ratio, the only parameters used to calculate acetonitrile number densities from these data are the reaction rate coefficient, k , and the residence time of ions in the flow tube, measured in situ. The values in Fig. 2 around the tropopause (9–10 km) have therefore been adopted as reported in the literature [28]. However, in this altitude range, the influence of the temperature dependence of k becomes most pronounced and applying the appropriate correction would shift the CH_3CN mixing ratios to values which are 30–40% lower.

Also shown in Fig. 2 are the range of ground-level mixing ratios as measured by Snider and Dawson [27] as well as the upper limit estimation deduced from infrared spectra by Muller [37].

Modelling efforts

Recently, some modelling efforts have been made to explain the observed positive ion composition and derived acetonitrile mixing ratios [18,38–40]. The most recent 1-dimensional model [18] describes the CH_3CN budget assuming that this gas is released at the Earth's surface and that it is destroyed on its way up into the atmosphere mainly by reactions with hydroxyl radicals and atomic oxygen. An assessment of acetonitrile destruction by scavenging due to precipitation (wash out) shows that this process, efficient only below 10 km, is negligible compared with gas-phase reactions. It was shown that the CH_3CN profiles deduced from balloon-borne ion mass spectrometry data can be reproduced satisfactorily in different ways by

TABLE 1

Conditions for model cases of Fig. 2

Case	Reaction rate constants ^a		Eddy diffusion coefficient ^b	Yearly global emission ($\times 10^{10}$ g)
	CH ₃ CN + OH	CH ₃ CN + O(³ P)		
A	Bonanno max	Harris max	MH	50
B	min	Kurylo	B	1.5
C	mean	Kurylo	MH	4.7
A'	max	Harris max	MH	24.4
C'	mean	Kurylo	MH	9.4

^a Bonanno min, mean and max represent the minimum, mean and maximum values of k_8 obtained by using the appropriate values of the experimental uncertainties in Eq. (11) in text. Applying the same method to Eq. (9) gives Harris min, mean and max. Kurylo indicates the use of Eq. (10).

^b B and MH stand for eddy diffusion coefficients proposed by Brasseur, and Massey and Hunten, respectively. The eddy diffusion coefficients are shown in detail in ref. 18.

using different sets of eddy diffusion constants and reaction rates for the loss processes in the model.

Three typical calculated profiles are shown in Fig. 2 by the full lines A, B, and C and the characteristics of these are shown in Table 1. The global annual emission of CH₃CN as estimated from three possible major sources (direct release by industry, car exhaust gases and biomass burning) is of the order of $1.6\text{--}3.1 \times 10^{11}$ g. This rough estimate is within the emission range set by the two extreme curves A and B.

The most critical parameter in the model seems to be the reaction rate, k_8 , for the process



For this reaction, Harris et al. [41] measured

$$k_8 = 5.86 \times 10^{-13} \exp[(-750 \pm 125)/T] \text{ cm}^3 \text{ s}^{-1} \quad (9)$$

whereas Kurylo and Knable [42] report

$$k_8 = 6.28 \times 10^{-13} \exp(-1030/T) \text{ cm}^3 \text{ s}^{-1} \quad (10)$$

Atmospheric loss of acetonitrile by reaction with O(³P) was studied by Bonanno et al. [43] who found the rate constant

$$k_9 = (7.27 \pm 1.75) \times 10^{-13} \exp[(-2385 \pm 100)/T] \text{ cm}^3 \text{ s}^{-1} \quad (11)$$

The rate constant for the reaction of CH₃CN with O(¹D) was assumed to be $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in the model.

As can be seen in Fig. 2, the best fit to the data above 20 km (curve C) is obtained by using the reaction rate k_8 as reported by Kurylo and Knable [42]. At room temperature, Eq. (10) yields a value in good agreement with those measured by other authors [44,45] but three times smaller than the one observed by Harris et al. [Eq. (9)] [41]. Very recently, a simple model was made by the MPIH group [22] in which the OH concentration was considered as a variable parameter. Their results indicate a rough agreement with the data if a low concentration profile of OH and the value of Harris et al. [41] for k_8 is used. It should be kept in mind, however, that the OH profile used in the BISA model [18] to derive curves A, B, and C of Fig. 2, was calculated in a consistent way in the model itself using the appropriate photochemical reactions and constants. Actually, the applied 1-dimensional neutral model takes into account 108 reactions and computes the number density of 51 atmospheric species from 0 to 100 km altitude. In spite of this, the resulting OH profile still contains some uncertainty due to the uncertainties in the reaction rate constants used.

Finally, the acetonitrile profiles derived from this neutral model have also been introduced in a 1-dimensional ion model [18], taking into account an updated reaction scheme and the most recent available data on the implied ion/molecule reactions. This model is based on the assumption that all ions are in a steady state and considers the formation of 29 different ion species through 58 reactions. It has been shown that the results obtained are in reasonable agreement with the observed ion distribution [21] of the NPH and PH containing one and two CH_3CN molecules. A detailed comparison between the model results and the measured relative abundances of all positive ion species is not possible at present due to the fact that the observed ion distribution is strongly disturbed by cluster break-up just behind the sampling aperture of the mass spectrometer.

So far, it has been assumed that this cluster break-up only results in a loss of water molecule ligands through the process



where M is the collision partner in the jet-formation region of the instrument. The loss of CH_3CN ligands leading to reconversion of NPH was assumed to be very unlikely since the proton affinity of acetonitrile is much larger than that of water ($186 \text{ kcal mol}^{-1}$). However, we will see in the next paragraphs that such a process should not be excluded.

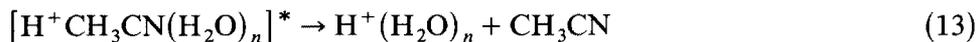
RECENT LABORATORY WORK

A comparison of the model curves shown in Fig. 2 with the experimental points shows that, within the errors in the in situ data and the uncertainty of

the model, there is reasonable agreement above 30 km. In particular, curve C (average model conditions) seems to reproduce quite well the CH₃CN mixing ratio profile as derived from ion composition measurements performed between 30 and 45 km. If, however, we consider the ground-level measurements [27] and the data obtained by the airplane-borne ACIMS instrument [28], there appears to be a factor of 2 discrepancy between the latter and the values predicted by model curve C. The fact that Knop and Arnold [28] report an error in the ACIMS data of only 50% and that the average of the inferred acetonitrile abundances (23 pptv) is in good agreement with the lower limit derived ground level measurements [27], seems to confirm those data.

If we manipulate curves A and C in Fig. 2 so as to fit both the ground-level and ACIMS data, we obtain curves A' and C', the characteristics of which are also given in Table 1. It is obvious that, by taking other model conditions (in between those of curves A' and C'), we can find a theoretical profile which would still fit reasonably to the ambient ion mass spectrometry data above 30 km. It is interesting to note that the required global annual emission of CH₃CN for such a curve (between 9.4×10^{10} and 24.4×10^{10} g) comes closer to the estimated emission value of possible acetonitrile sources ($16.4\text{--}31.4 \times 10^{10}$ g according to ref. 18).

However, as can be seen in Fig. 2, it still remains difficult to explain the low values of the CH₃CN mixing ratios inferred from ambient ion measurements below 30 km. The MPIH group, who first drew the attention to this discrepancy [28], suggested that this is due to errors in the balloon data induced by electric field-induced collisional activation (ECA), resulting in conversion of NPH to PH in the mass spectrometer. Briefly, such a re-conversion would be caused by the decomposition of NPH ions excited by energetic collisions in the gas jet, just behind the sampling hole



As mentioned above, sampled ions are accelerated in this region of the instrument by focussing electric fields. Since pressure is still rather high, these ions undergo energetic collisions which can excite them to energies well above the bond strength of a CH₃CN ligand in the NPH.

In order to demonstrate this NPH to PH conversion mechanism, the MPIH group performed a series of experiments in the laboratory as well as during balloon flights [22]. It has been shown [22] in the laboratory that the conversion of NPH to PH can be realized by accelerating NPH ions in a collision chamber filled with 0.02 torr of argon gas and the occurrence of reaction (13) in balloon experiments was shown by applying a supplementary high electric field (400 V cm^{-1}) in the gas jet formation region. Also, a comparison of spectra of different balloon flights where different diameters

of sampling holes were used led the MPIH group to the conclusion that quite different ratios of $R = [\text{NPH}]/[\text{PH}]$ were obtained. As was pointed out [22], the efficiency of the NPH–PH reversion is strongly dependent on the experimental conditions and mass spectrometer configuration (especially sampling hole diameter and applied focussing fields). Nevertheless, it can easily be shown that even small reversion efficiencies can lead to quite large errors in the CH_3CN derivations. If f is the fraction of NPH ions which reconvert to PH in the sampling process, a straightforward calculation shows that the real ratio, R , of NPH to PH ions is related to the measured ratio, R_m , by

$$R = \frac{R_m}{1 - f(1 + R_m)} \quad (14)$$

If, for example, only 10% of the ions reconvert ($f = 0.1$), then the measurements would lead to an underestimation of R by a factor of 2.5 ($R = 2.5 R_m$) for the value of $R_m \approx 5$ as shown in Fig. 1

In order to check whether or not the ECA reversion can lead to such errors with our balloon-borne instrument, we have also recently performed a series of laboratory tests. For this reason, we have built a simple flow tube on one of our mass spectrometers which allows us to simulate the stratospheric positive ion composition. The mass spectrometer used was a QMS 2 equipped with a quadrupole of 12 cm long and 0.6 cm rod diameter. The ion lens and its dimensions are shown in detail in Fig. 3. A sampling hole of 0.2 mm was used to simulate most of our flight conditions. The voltages applied in the flight configuration and low-field configuration are shown in Table 2. For all laboratory work, exactly the same electronics and software was used as in the balloon flights [15].

The flow tube is shown schematically in Fig. 3. It consists of a glass tube of 3 cm diameter and 55 cm long. At one end is an ion source which can operate in two modes. In the first mode, a gas mixture consisting of N_2 , NO (typically 1%), and water vapour is injected through the inlet BG and the ionization is created by illuminating with a xenon discharge lamp. The 129.6 nm line of this source results in a very efficient photoionization of NO and the NO^+ ions are quickly converted to PH by a well-known series of ion/molecule reactions [46]. In the second mode of operation, a hot filament ion source, F, is used in a gas mixture of N_2 and H_2O and again the primary N_2^+ ions are quickly converted to PH [47]. At a distance of 35 cm from the ion source, a $\text{CH}_3\text{CN}/\text{N}_2$ gas mixture (typically a few torr of acetonitrile vapour in 1 to 2 atmospheres of N_2) can be injected through the inlet port RG. The resulting terminal ion compositions (consisting mainly of PH and NPH containing CH_3CN) can be controlled by varying the gas flow of the

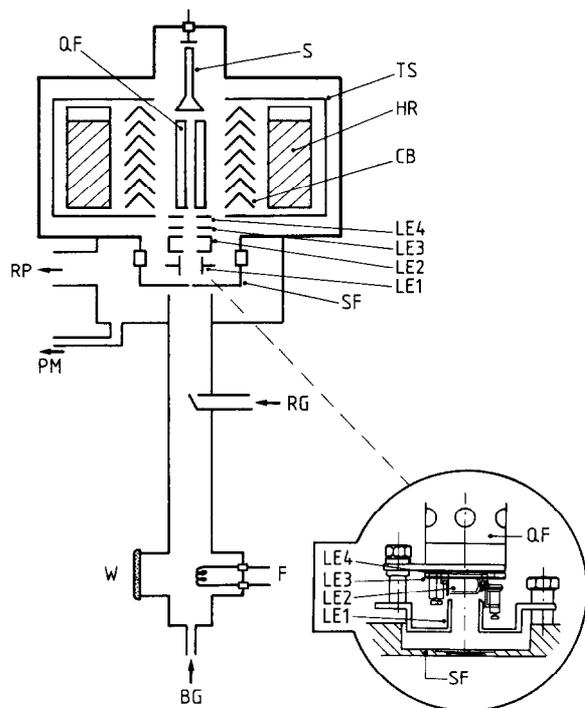


Fig. 3. Flow tube coupled to flight mass spectrometer. S, Spiraltron electron multiplier; QF, quadrupole filter; TS, thermal shield; HR, helium reservoir; CB, Chevron baffle; LE1–LE4, lens elements to focus ions in QF; SF, sampling flange with hole of 0.2 mm diameter; RP, to Roots pump; PM, pressure measurement (Baratron); RG, reactant gas ($\text{N}_2 + \text{CH}_3\text{CN}$) inlet; F, filament; W, MgF_2 window; BG, source gas ($\text{N}_2 + \text{H}_2\text{O}$ or $\text{NO} + \text{N}_2 + \text{H}_2\text{O}$) inlet. Also shown is a detail of the ion lens, which consists of 1 cylindrical lens element, LE1, added to the commercial ion source of the quadrupole (Finnigan), the elements of which are used as lens elements (LE2 and LE3). An extra diaphragm (LE4) was put between this ion source and the quadrupole.

TABLE 2

Voltages applied in the two-lens configurations

Lens element ^a	Flight configuration	Low-field case
SF	– 5 V	– 5 V
LE 1	– 65 V	– 6.4 V
LE 2	– 9.7 V	– 6.6 V
LE 3	– 65 V	– 6.4 V
LE 4	– 9.7 V	– 6.6 V

^a The lens configuration and explanation are given in Fig. 3.

reactant gas ($\text{CH}_3\text{CN} + \text{N}_2$) or the ion residence time in the flow tube by changing the flow of the source gas ($\text{N}_2 + \text{H}_2\text{O}$ or $\text{N}_2 + \text{NO} + \text{H}_2\text{O}$).

The total gas flow, gas composition, and total pressure in the flow tube are controlled and stabilized by a MKS Instruments type 254 gas flow-pressure controller. Experiments were performed in the pressure range from 5 to 30 torr.

To measure the NPH–PH reversion for a given ion composition in the flow tube, the following procedure was used. After stabilization of the primary ion production and gas flows, a spectrum was taken with the mass spectrometer in flight condition. Immediately thereafter, a spectrum was recorded using the low-field configuration of Table 2. It is assumed that, with those low lens voltages yielding a still workable signal, the cluster break-up and NPH–PH reversion is minimized. The observed ratio of NPH to PH in the flight configuration and low-field configuration are then R_m and R , respectively. Subsequently, a spectrum was recorded in the flight configuration to verify whether the original ion composition had changed or not. To avoid such composition fluctuations, a moderate mass resolution (~ 17) was used in order to enhance the signal and thus limit the integration time. After this series of 3 spectra, an unambiguous mass identification was performed in the high-resolution mode. In fact, the spectra used to determine NPH–PH reversion were recorded in exactly the same mode as most of the flight spectra used to infer the BISA data of Fig. 2.

One of the major problems encountered in the experiments was caused by residual acetone vapour in the flow tube (or gas containers?), which gave rise, in many cases, to mixed clusters of the form $\text{H}^+(\text{CH}_3\text{CN})_l(\text{CH}_3\text{COCH}_3)_m(\text{H}_2\text{O})_n$. To avoid these mixed clusters, rather high N_2 flows were used (10 000 sccm) and therefore a ratio of NPH to PH ions, R , as observed in the lower stratosphere could not be simulated. Typical values for R as obtained at high pressures were of the order of 0.5. As expected, the NPH–PH reversion was strongly dependent on the terminal ion composition and therefore no real calibration of this mechanism, leading to a correction of in situ data of Fig. 2, was possible in the first series of measurements.

A typical spectrum obtained in flight configuration and low-field configuration is shown in Fig. 4. From these spectra obtained at 32.3 torr, values of $R_m \approx 0.5$ and $R \approx 0.6$ are deduced, corresponding to an efficiency of $f \approx 0.11$. With a value of $R_m \approx 5$, as observed around 21 km (corresponding to an ambient pressure of about 34 torr), this would lead to a real value of $R = 3 R_m$, shifting the appropriate CH_3CN mixing ratio to a value three times higher in Fig. 2. It is clear that, in view of the low resolution used, this value of f can only be considered as a rough estimate. In fact, we evaluate the error to be of the order of 50% and it is clear that more elaborate

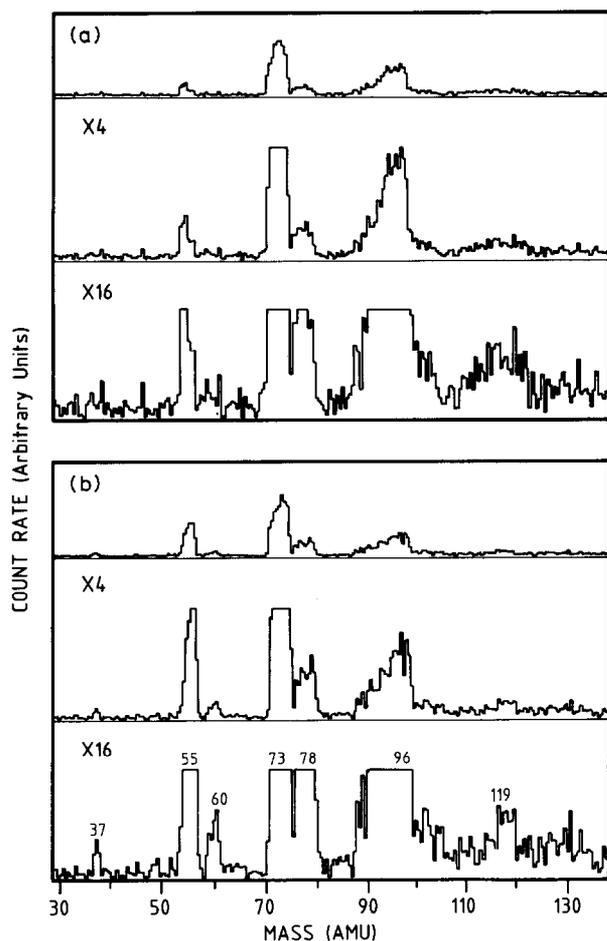


Fig. 4. Typical spectra obtained from sampling positive ions from a gas mixture at 32.3 torr, with (a) the flight configuration of the lens (Table 2) and (b) the low-field lens voltages (Table 2). The resolution used ($m/\Delta m$) was about 17, similar to that used in the balloon flights.

measurements are needed to determine the exact correction factor. As was explained above, however, it is very difficult to realize this with the equipment used in the present experiment.

Our results, as obtained at different pressures, indicate that, in agreement with the conclusions of Schlager and Arnold [22], the NPH-PH reconversion is probably negligible above 35 km but becomes effective at lower altitudes. The obtained results as a function of pressure (or altitude) show no pronounced consistency but at present this is probably due to the difficulty in simulating stratospheric conditions. It is clear, however, that the reconversion of NPH to PH is a factor to be taken into account and from

the example shown and the recent experiments of the MPIH group [22], it follows that this mechanism is probably the main cause of the discrepancy found between the balloon and airplane data (ACIMS). As was pointed out by Schlager and Arnold [22], these ACIMS data are much less sensitive to possible NPH–PH reversion because of the low values of R_m in these experiments and consequently, according to Eq. (14), R_m should not differ too much from R .

SUMMARY AND CONCLUDING REMARKS

The primary ions formed by cosmic rays in the stratosphere are converted to proton hydrates or ions of the form $H^+(H_2O)_n$ by a number of well-understood ion/molecule reactions. These PH react with a trace gas with higher proton affinity than that of water to form NPH of the form $H^+X,(H_2O)_m$. The molecule X has been identified with a good confidence level as acetonitrile. Model calculations of the positive ion distribution in the altitude range 10–50 km using the most recent laboratory data, lead to results which are in good agreement with the observed ion composition [18,21].

Although, originally, the presence of acetonitrile in the stratosphere was difficult to explain, evidence has been given that this gas is produced at the Earth's surface by human activities and biomass burning and reaches the stratosphere through eddy diffusion where it is destroyed by chemical reaction with hydroxyl radicals, atomic oxygen, and photodissociation.

However, to make the picture 100% consistent and to enable us to exploit the positive ion mass spectrometry data to the full extent, some questions remain to be answered. The points where clarification is needed or additional information is required are now briefly discussed.

In the field of ion composition measurements, an effort must be made to understand the ion sampling process in the mass spectrometer. In particular, cluster break-up effects and NPH–PH reversion mechanisms should be studied in more detail in order to correct future measurements and, if possible, existing data. Furthermore, measurements should be performed at altitudes between 25 and 15 km and more data should be obtained above 40 km. New, more sensitive instruments are required to enable measurements of the major ion signals with lower focussing fields or to detect the minor ion mass peaks. Measurements of total ion densities and ionization rates should be performed in situ simultaneously with ion composition measurements. In this way, $[n^-]$ and Q (and consequently α) can be measured independently and used for the interpretation of the ambient ion data.

To understand completely the neutral chemistry of CH_3CN and to permit the perfection of the models we need

(a) accurate measurements of rate constants for the atmospheric reactions of CH_3CN , in particular with OH;

(b) a detailed study of the emission sources of acetonitrile; and

(c) a better knowledge of the eddy diffusion process.

Finally, more information should be obtained on the products of ion-ion recombination to verify whether or not acetonitrile can be lost through ion/molecule reactions with PH and subsequent recombination.

It should be kept in mind that, although acetonitrile is an exotic trace gas not playing a major role in neutral atmospheric chemistry, a full understanding of its budget is required to understand the stratospheric positive ion chemistry in detail.

In obtaining a 100% consistent picture, a great deal of confidence may be gained in the method of atmospheric trace gas detection (and inferring their mixing ratios) through ion composition measurements. The acquired experience can be utilized to understand negative ion chemistry, which can lead to the derivation of concentrations of more important gases such as nitric acid and sulphuric acid vapours which rely upon the same principles [33,48].

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