

## THE EFFECT OF COLLISIONALLY INDUCED DISSOCIATION IN BALLOON-BORNE STRATOSPHERIC MASS SPECTROMETRY OF POSITIVE IONS

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### ABSTRACT

Stratospheric mass spectrometry of positive ions using a passive chemical ionization method is biased by collisionally induced dissociation (CID) of the sampled cluster ions behind the inlet hole of the spectrometer.

This mechanism is investigated by means of a one-dimensional model for clusters of the family  $H^+(CH_3CN)_l(H_2O)_m$  which are involved in the volume mixing ratio determination of acetonitrile in the stratosphere. The three physical parameters upon which CID depends are outlined: the density of the neutral gas jet, the velocity or barycentric kinetic energy raised by the ions in the static electric field and the total cross-section for the dissociation process. The CID effect is modelled by using related simple neutral gas adiabatic expansion laws, a mobility concept for the ions and various experimental data for the CID cross-sections. A macroscopic calculation is completed with no allowance for ion velocity distribution, and a more realistic Monte Carlo computation is also performed. The experimental acetonitrile concentration is found to be underestimated by a typical factor of four at an altitude of 25 km. The sensitivity of our results to the lack of experimental data is explored and some criticism is developed of the confidence limits of such a model.

### INTRODUCTION

Since 1978 the results of several ion composition measurements in the stratosphere have been reported in the literature [1–5]. These data obtained with balloon-borne ion mass spectrometers revealed the identity of the major positive and negative natural ions in the altitude region from 20 to 45 km in the Earth's atmosphere. They also confirmed that the nature of these ions, formed by galactic cosmic rays and subsequent ion-molecule reactions, is controlled by trace gases with volume mixing ratios as low as a few ppb or even ppt, as predicted [6,7].

Subsequently ion mass spectra obtained in the stratosphere have been exploited to derive the concentrations of some atmospheric minor constituents such as  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  [8–12], using the stratosphere for a “passive” chemical ionization method (PACIMS), with cosmic radiation as the primary ion source. This method has been extensively discussed in previous papers [8–12] and will therefore only be briefly described here. For the time being we will limit ourselves to the positive ions and the detection of acetonitrile  $\text{CH}_3\text{CN}$ .

It has been shown [6,7] that the terminal positive ions in the stratosphere should be cluster ions of the form  $\text{H}^+(\text{H}_2\text{O})_n$  or proton hydrates (PH). If, however, in the stratosphere a trace gas X is present capable of replacing a water ligand in the proton hydrates, one could expect that these PH ions would partly convert to non-proton hydrates (NPH) of the form  $\text{H}^+\text{X}_l(\text{H}_2\text{O})_m$  through switching ion/molecule reactions



A more detailed description of this kind of reaction is given elsewhere [13–15]. Assuming that the NPH are formed by reaction (1) and that they are subsequently lost by recombination, the concentration of the trace gas X can then be derived from

$$[\text{X}] = R\alpha[n^-]/k \quad (2)$$

where  $k$  is the rate coefficient for reaction (1),  $[n^-]$  is the total number density of negative ions and  $\alpha$  is the ion/ion recombination coefficient.  $R$  is the ratio of the number densities of NPH and PH

$$R = [\text{NPH}]/[\text{PH}] \quad (3)$$

In the stratosphere two major positive ion families have been observed:  $\text{H}^+(\text{H}_2\text{O})_n$  and  $\text{H}^+(\text{CH}_3\text{CN})_l(\text{H}_2\text{O})_m$ .

Taking the mass peak intensities as a measure for the ion number densities, the volume mixing ratio of  $\text{CH}_3\text{CN}$  has been derived in the region from 20 to 45 km from positive ion mass spectra obtained in different balloon flights [16,17].

Recently, however, aircraft- and balloon-borne active chemical ionization mass spectrometer (ACIMS) data allowed the derivation of  $\text{CH}_3\text{CN}$  volume mixing ratios at an altitude range between 17 and 12 km [18,19]. The data, in good agreement with ground-based  $\text{CH}_3\text{CN}$  measurements [20], suggest an underestimation in those obtained from the balloon experiments. It has been proposed [21] that this systematic underestimation is a result of intrinsic errors in the balloon data as a result of collisionally induced dissociation (CID) of the ions in the mass spectrometer itself, just behind the ion inlet hole. Experimental evidence of this process has been given by Schlager and Arnold [21], Arijs et al. [22] and Graul and Squires [23].

If CID reconverts a fraction  $f$  of the NPH ions into PH ions, then the measured ratio  $R_m$  and the true  $R$  are related by

$$R = \frac{R_m}{1 - f(1 + R_m)} = xR_m \quad (4)$$

It can thus easily be seen that the correction factor  $x$  can take large values even in the small  $f$  range.

We propose here a theoretical model for the  $f$  value determination, and we evaluate the order of magnitude of the correction factor  $x$ , to be applied to previous acetonitrile abundance derivations.

#### GENERAL MODEL PHILOSOPHY

##### *Description of the problem*

The experimental set-up of the ion mass spectrometer of the Belgian team, as described in detail previously [24], consists primarily of a quadrupole mass filter built into a high-speed liquid helium cryopump. The ambient gas leaks into the instrument through a small hole (with a diameter of the order of 0.2 mm) in a thin flange, biased a few volts with respect to the balloon gondola. The ions are then extracted from the gas jet formed just behind the inlet hole by an electrostatic lens and guided into the quadrupole.

The signals of the ions reaching the detector after mass filtering are subsequently treated by pulse counting techniques to build up the mass spectra. The ion inlet configuration of our instrument is shown in detail in Fig. 1.

The potential difference applied between the ion sampling flange (SF) and the first lens element (LE1) is of the order of 60 V. As a result, the

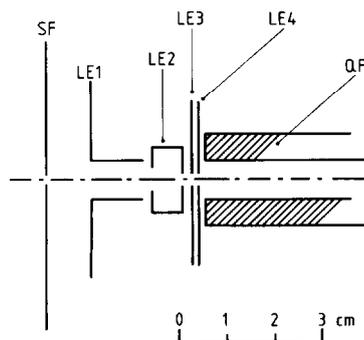


Fig. 1. Schematic representation of the ion sampling configuration as used by Arijs et al. [22]. SF: sampling flange; LE1, LE2, LE3, LE4 lens elements; QF: quadrupole filter.

inflowing ions are accelerated in the gas jet expansion region, thus giving rise to energetic collisions and CID.

The CID depopulation rate of a particular ion family during its transit towards the spectrometer from the inlet hole depends upon the following parameters:

- (1) the density of the neutral gas jet along the path it follows,
- (2) the barycentric kinetic energy raised within the electric field, and
- (3) the total cross-section for the dissociation process.

In the next section we will justify the use of a one-dimensional treatment of the problem by presenting some preliminary considerations on these three parameters.

### *The one-dimensional model*

The numerical computation of a free jet expansion into a vacuum through a small hole is still a difficult problem (see e.g. [25]). As rigorous treatment of this problem is beyond the scope of this first modelling effort, we have followed a derivation by Fite [26].

In this approach it is assumed that the neutral current density can be described along the axis of symmetry ( $z$  axis) by

$$J(z) = J_0 (D/z)^2 \quad (5)$$

where  $D$  is the hole diameter and  $J_0$  the initial neutral current density taken at  $z = D$ . For an adiabatic expansion of the gas starting at zero velocity ( $v_g = 0$ ) from a stagnation temperature  $T_s$ , we respect the enthalpy conservation law:

$$Mv_g^2/2 + C_p T(z) = C_p T_s \quad (6)$$

where  $M$ ,  $C_p$  and  $T(z)$  are molecular mass, specific heat at constant pressure and local gas temperature. At the hole position ( $z = 0$ ) the velocity is set to be equal to the local sound velocity:

$$v_g(0) = \left( \frac{2\gamma}{\gamma+1} \frac{kT_s}{M} \right)^{1/2} \quad (7)$$

$k$  and  $\gamma$  being Boltzmann's constant and the ratio  $C_p/C_v$ , respectively. To a good approximation we obtain from the use of Eqs. 5–7 and  $\gamma = 7/5$

$$v_g(z) \approx v_g(\infty) = \left( \frac{2\gamma}{\gamma-1} \frac{kT_s}{M} \right)^{1/2} \quad (8)$$

and

$$\frac{n(z)}{n_s} \approx \left( \frac{2}{\gamma+1} \right)^{(1/\gamma-1)} \left( \frac{\gamma-1}{\gamma+1} \right)^{1/2} \frac{D^2}{z^2} = 0.259 \frac{D^2}{z^2} = \frac{z_s^2}{z^2} \quad (9)$$

where  $n(z)$  and  $n_s$  stand for the local and stagnation gas number densities.

It is noteworthy [27] that the angular distribution of the gas density is well approximated by a  $\cos^2(0.945\theta)$  function for diatomic molecules, so that the gas jet is mainly contained in a cone of about  $45^\circ$  of semi-aperture.

At an altitude of 30 km ( $T_s = 235$  K), the maximum velocity of the gas is given by (8) to be ca.  $7 \times 10^4$  cm s $^{-1}$ .

The second parameter to be considered is the barycentric kinetic energy  $E_{cm}$  gained by a cluster ion before a collision with an N $_2$  or O $_2$  target molecule of the gas jet:

$$E_{cm} = \frac{\mu}{2} v_d^2 \quad (10)$$

where  $\mu$  is the reduced mass of the projectile/target system and  $v_d$  is the local relative velocity of the ion in the neutral gas jet. We shall assume here that we can relate the drift velocity  $v_d$  to the electric field  $F$  and the neutral gas density  $n$  by the ion mobility concept. It can be shown [28] that, in the high  $F/n$  value range,

$$v_d(z) \approx A\sqrt{F/n} \quad (11)$$

where the constant  $A$  depends upon the ion mass and the elastic collision integral (this approximation will be improved later).

The third parameter involved in the depopulation rate of an ion family is the total dissociation cross-section  $Q(E_{cm})$ . If the endothermicity of the CID process is  $E_t$ , we can to a first approximation, consider that

$$Q(E_{cm}) = 0 \quad E_{cm} \leq E_t \quad (12)$$

$$Q(E_{cm}) = Q = \text{constant} \quad E_{cm} > E_t \quad (13)$$

Assuming a 0.2 mm hole diameter and a value of  $100$  V cm $^{-1}$  for the electric field  $F$ , an external stagnation pressure of 10 torr, and taking a characteristic experiment drift velocity of a system such as Ar $^+$  in Ar, we find that

$$v_d(z = 2 \text{ mm}) \approx 5 \times 10^5 \text{ cm s}^{-1} \gg v_g(\infty) \quad (14)$$

Typical ion trajectories for the above-mentioned conditions are shown in Fig. 2. From this figure it can be seen that, except in the immediate vicinity of the hole, ions quickly bend their trajectory parallel to the  $z$  axis, whereas neutrals of the gas jet diverge from the origin. In a first approximation it is therefore justified to treat the problem one-dimensionally and we can write the continuity equation for a particular ion current density  $j_i$  as

$$\frac{dj_i}{dz} = -Q(z)v_d(z)n(z)n_i(z) \quad (15)$$

with the relation

$$j_i(z) = n_i(z)[v_g(z) + v_d(z)] \approx n_i(z)v_d(z) \quad (16)$$

$n_i$  being the local ion number density.

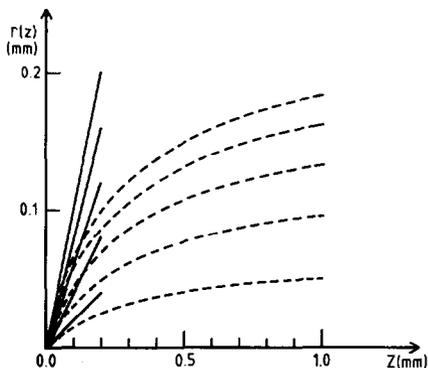


Fig. 2. Typical ion trajectories beginning at the inlet hole and corresponding to different orientations of the neutral gas velocity.

We can also define  $z_t$  as the distance at which the threshold energy  $E_t$  is reached, i.e.

$$z_t = \frac{z_s}{A} \left( \frac{2E_t n_s}{\mu F} \right)^{1/2} \quad (17)$$

Again, an estimation of a typical value for  $A$  can be obtained by examining the experimental drift velocity of  $\text{Ar}^+$  in  $\text{Ar}$ , for which  $\mu$  has a value of 20 u. Taking a typical value of 1 eV as the bound strength of the ion clusters, we obtain a value of 1.5 mm for  $z_t$ . Furthermore, we can easily integrate the differential Eq. 15 for  $z > z_t \gg z_s$  to derive the final current density at the end of the gas jet. This leads to

$$j_\infty = j(z_t) \exp\left(-\frac{Q n_s z_s^2}{z_t}\right) \quad (18)$$

Assuming a total cross-section of the order of  $50 \text{ \AA}^2$ , which is a reasonable approximation in view of the size of the clusters we are dealing with [29], we see that the attenuation factor can easily be as important as  $1/e$ .

#### MULTISPECIES EVOLUTION IN A MACROSCOPIC MODEL

To treat the CID process as it occurs in the ion mass spectrometer, we have applied the current density description of Eq. 15 to the more general case of ions  $\text{H}^+(\text{CH}_3\text{CN})_j(\text{H}_2\text{O})_i$ . The model includes the 22 cluster ions, for which Deakhyne et al. [29] measured the dissociation energies. Those ions are reported in Fig. 3, together with their mass and dissociation energy. As can be seen, the covered mass range extends up to 160 u, which is well

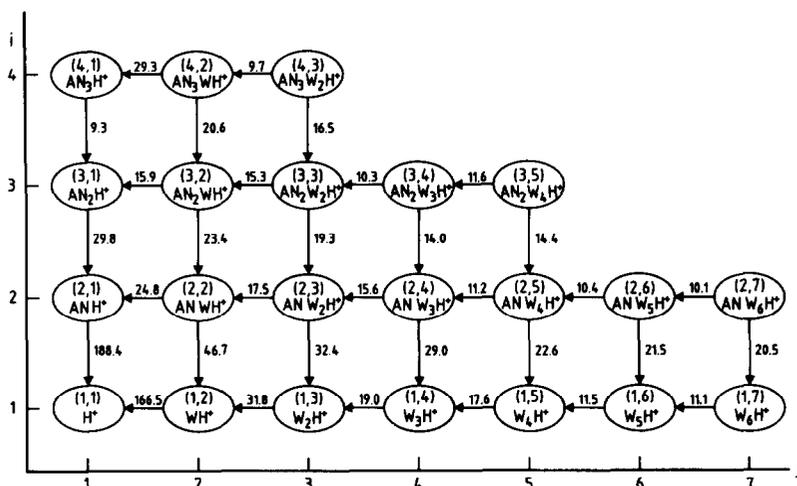


Fig. 3. The 22 ions involved in the calculation. Arrows refer to dissociation paths, with the dissociation energies in  $\text{kcal mol}^{-1}$ . AN and W respectively stand for  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  molecules.

above the range of the experimental spectra obtained in the stratosphere. For the species  $i, j$  we can write the continuity equations

$$\frac{d}{dz} j_{i,j}(z) = -L_{i,j}(z) + G_{i,j}(z) \quad (19)$$

where  $L_{i,j}(z)$  represents the ion current density sink resulting from CID of the species  $i, j$  itself, either by loss of a water or an acetonitrile ligand. This term therefore can be written as

$$L_{i,j}(z) = L_{i,j}^l(z) + L_{i,j}^b(z) \quad (20)$$

The indices  $l$  and  $b$  stand for “left” and “bottom” in Fig. 3 and refer to the loss of a  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{CN}$  molecule respectively. According to Eqs. 15 and 16, these terms can be expressed as

$$L_{i,j}^{l/b} = Q_{i,j}^{l/b}(z) n(z) j_{i,j}(z) \quad (21)$$

the superscripts  $l$  and  $b$  meaning left and bottom respectively and the dissociation cross-section  $Q_{i,j}$  being a function of the species under consideration and of its barycentric energy  $E_{\text{cm}}$ , which in turn is again a function of  $z$ .

The term  $G_{i,j}(z)$  represents the gain resulting from CID of the higher species  $i, j+1$  and  $i+1, j$  which by loss of a water or acetonitrile ligand convert to the  $i, j$  species. Accordingly, this term can be expressed as

$$G_{i,j}(z) = L_{i,j+1}^l(z) + L_{i+1,j}^b(z) \quad (22)$$

Writing down the continuity Eq. 19 for the 22 ions considered here leads to a set of 22 coupled first-order differential equations, which have been integrated using a standard fourth-order Runge–Kutta scheme.

As starting conditions at  $z = 0$ , we have chosen the ion population distribution as calculated in the model by Arijs and Brasseur [30].

#### COMPUTATION OF THE PHYSICAL PARAMETERS

##### *Total CID cross-sections*

The CID cross-sections for PH have been modelled, as shown in Fig. 4, following the experimental results of Dawson [31] and using the linear relation between the cross-section and the number  $n$  of water molecules, as found by him:

$$Q_n = n\sigma_a + \sigma_b \quad (23)$$

with

$$\sigma_a = 12.9 \text{ \AA}^2 \text{ and } \sigma_b = 3.33 \text{ \AA}^2$$

It has been observed by Dawson [31] that the formation of  $\text{H}^+\text{H}_2\text{O}$  is not very dependent upon whether it is formed through a one-step loss of three water molecules or through a three-step loss of one water molecule. This has led us to assume that collision of cluster ions with neutral target molecules can only result in the loss of one ligand for each CID event.

Unfortunately, no data on the CID of acetonitrile cluster ions are available in the literature. We have therefore assumed that the cross-section for the CID of NPH ions can be represented by the same linear relationship (23), which is a rough but probably reasonable approximation.

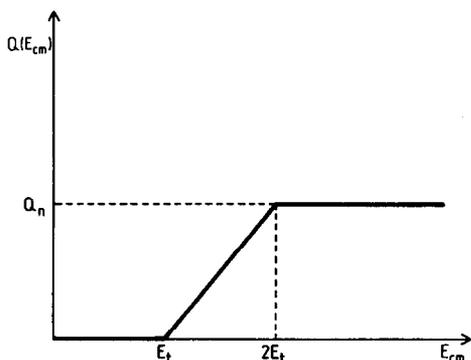


Fig. 4. Total cross-section for CID process vs. barycentric energy  $E_{cm}$ .

### Ion velocities

The velocity distribution of the cluster ions in the accelerating electric field should be solved in the framework of Boltzmann's equation with a good knowledge of the neutral molecule/cluster ion potential interaction. To avoid this difficult theoretical problem, we decided to use the local drift velocity of the clusters, as derived from the mobility concept, assuming that this drift velocity continuously adjusts to the local electric field  $F$  and neutral density  $n$ . This means that the cluster ion should experience sufficient elastic collisions with the neutral gas on a small distance for a drag to appear which stabilizes the velocity. Such an approximation will evidently fail in low-density regions (large  $F/n$  values).

Therefore in the computer code we have constrained ion velocity to be less than or equal to the maximum possible velocity (for a free ion) given by

$$v_d \leq [2 eV(z)/m]^{1/2}$$

where  $e$ ,  $m$  and  $V(z)$  respectively stand for electron charge, cluster ion mass and electric potential on the  $z$  axis [ $V(0) = 0$ ]. The last has been computed for our experimental configuration by means of a standard relaxation method and is almost linear vs.  $z$  in the region of interest ( $0 < z < 10$  mm) where the quasi-constant field is ca.  $70 \text{ V cm}^{-1}$ . Vielhand and Mason [32] have developed a two-temperature theory to calculate the drift velocity of an ion at all  $F/n$  values. Following their theory, we have written the implicit  $v_d$  formula

$$v_d = \frac{3e(2\pi)^{1/2}}{16} \frac{F}{n} \frac{1}{\sqrt{(\mu)}} \frac{1}{\sqrt{(T_e)}} \frac{1}{\Omega(T_e)} \quad (24)$$

$$T_e = T + \frac{M}{3k} v_d^2 \quad (25)$$

where  $M$  is the air molecular mass and  $\Omega(T_e)$  is the elastic collision integral. The evaluation of  $\Omega(T_e)$  has been performed by using the experimental values of the  $\text{H}^+(\text{H}_2\text{O})_n$  ( $n = 1, 2, 3$ ) mobilities obtained by Dotan et al. [33] and the associated  $\Omega$  reported by Ellis et al. [34]. We have chosen to fit  $\Omega(T_e)$  as

$$\Omega(T_e)[\text{\AA}^2] = \frac{a}{(T_e)^{1/2} [b + (T_e)^{1/2}]} + c \quad (26)$$

$$a = 9.457(6), \quad b = 4.914(3), \quad c = 1.171(1)$$

$$\Omega(T_e) \approx \frac{a}{b(T_e)^{1/2}} \quad \text{for } T_e \ll b \quad (27)$$

$$\Omega(T_e) \approx c \quad \text{for } T_e \gg b$$

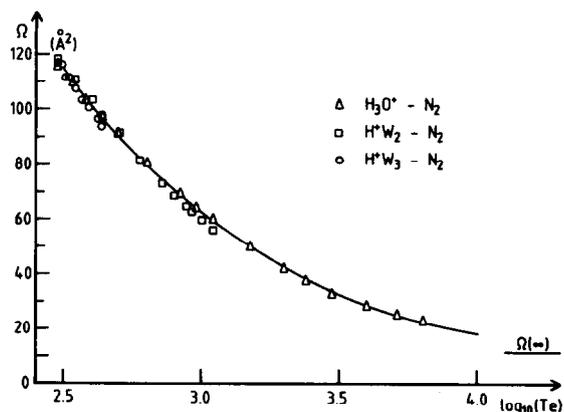


Fig. 5. Elastic collision cross-section  $\Omega$  vs. effective temperature  $T_e$ . Triangles, squares and circles are the experimental values reported by Ellis et al. [34] extracted from mobility measurements of Dotan et al. [33] for  $H^+(H_2O)_n$  in nitrogen.

Such a non-linear fit is hoped to be closely related with an  $(\infty - 4)$ -like potential for the cluster ion/neutral interaction (i.e. hard sphere +  $1/r^4$  polarization attractive potential [35]). In the zero temperature limit expressions, (24) and (26) give for  $H^+H_2O$  a mobility of  $3.22 \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$ , which can be compared with the Langevin value of  $3.14 \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$  and the value of  $2.76 \pm 0.14 \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$  as measured by Dotan et al. [33].

The relation between  $\Omega(T_e)$  and  $T_e$  is shown in Fig. 5. It is noteworthy that all  $\Omega$  values for different ions lie approximately on the same curve (for a discussion of this, see Böhringer et al. [36]). We have then chosen to use the same collision integral for the acetonitrile cluster ions.

## RESULTS OF THE MACROSCOPIC MODEL

Using the approach explained above to calculate the physical parameters of the model, we have computed the solutions of Eq. (19) between 10 and 50 km altitude, with standard atmosphere temperatures and densities as stagnation temperatures and densities respectively. In this way, the ion populations resulting from CID are obtained using the input spectra taken from Arijs and Brasseur [30]. It is then straightforward to calculate the correction factor  $x$ . The result is represented in Fig. 6 by curve A. The factor  $x$ , by which  $R$  has to be multiplied is found to be almost 1 at 50 km, where the density is too low for CID induction, but increases strongly to reach a value of 13 at 15 km.

In Fig. 7(a) the input mass spectrum at 25 km is represented and the final spectrum calculated in the present model is shown in Fig. 7(b). It is clear

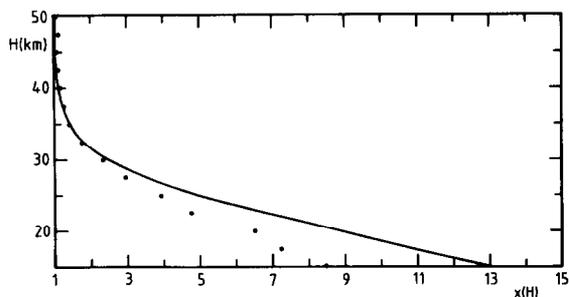


Fig. 6. Correction factor  $x$  as a function of altitude. The full line is the macroscopic model result. Full circles are the result of the Monte Carlo computation.

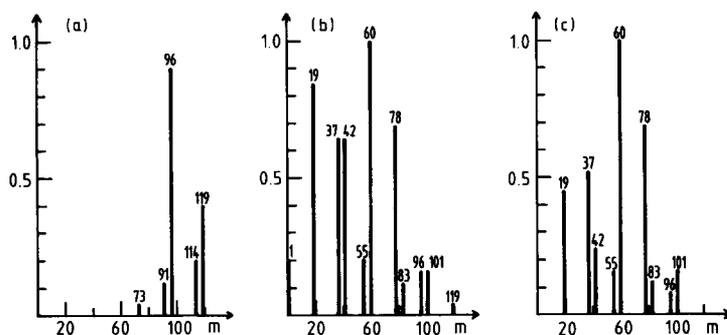


Fig. 7. From left to right, at the same altitude of 25 km, (a) input spectrum as computed by Arijis and Brasseur, (b) output spectrum of the macroscopic model, (c) output spectrum of the Monte Carlo model.

that the latter is strongly perturbed by CID. The dominant mass peak at 96 u  $\text{H}^+\text{CH}_3\text{CN}(\text{H}_2\text{O})_3$  is replaced by mass 60  $\text{H}^+(\text{CH}_3\text{CN})\text{H}_2\text{O}$ . Furthermore, light proton hydrates begin to appear and the whole spectrum is shifted to lower masses.

#### MONTE CARLO SIMULATION

In the macroscopic model we have assumed that the drift velocity of a cluster ion adjusts instantaneously to the local electric field and density. This can be incorrect just after a CID fragmentation. Let us consider a molecular ion of mass  $m$  moving with a velocity  $v$  and colliding with a neutral target of mass  $M$ , at rest in the laboratory. We consider the break-up of  $m$  into masses  $l$  and  $p$ , with  $m = l + p$  and  $l$  standing for the mass of an acetonitrile or water ligand.

We assume that the dissociation has occurred in a glancing collision with a negligible scattering angle. This is according to the experimental results of Dawson [31], and is a reasonable assumption, justified for laboratory energies  $mv^2/2 \gg E_t$ . Considering that the fraction of translational energy converted into internal energy is almost equal to the dissociation energy  $E_t$ , we can easily derive the velocity  $v'$  of the molecular complex ( $l+p$ ) after the collision:

$$v' = \frac{v}{1+\xi} \left\{ \xi - \left[ 1 - (1+\xi) \frac{E_t}{E} \right]^{1/2} \right\} \quad (28)$$

with  $\xi = m/M$ .

The velocity  $v'$  is also the velocity of the fragment  $p$  after the dissociation of the complex. For instance, at large laboratory energies  $E$ , we find  $v' = 0.54v$  for  $m = 96$  and  $M = 29$ .

Although the local drift velocity hypothesis can be conserved for a parent ion  $m$ , it cannot be accepted for a daughter ion  $p$  created in a CID event, which should accelerate to reach its own drift velocity. Unfortunately, the ions  $p$  are born everywhere along the  $z$  axis so that again we are led to a Boltzmann's transport equation to determine the velocity distribution for  $p$  and all its grand-children!

This is the reason why we have also considered a Monte Carlo simulation of our problem. A Monte Carlo run consists of following a cluster ion from the inlet hole during a multistep evolution. We define  $p_l$  and  $p_b$ , the probabilities of losing a water or an acetonitrile molecule respectively, after a step  $\Delta z$ , as

$$p_l = Q_{i,j}^l n \Delta z \quad (29)$$

$$p_b = Q_{i,j}^b n \Delta z \quad (30)$$

To simulate correctly a macroscopic evolution,  $p_l$  and  $p_b$  must be small. For this purpose, we can compute the related mean free paths at each step

$$\lambda_{l/b} = \frac{1}{Q_{i,j}^{l/b} n} \quad (31)$$

with  $\lambda = \min(\lambda_l, \lambda_b)$  and

$$\Delta z = \epsilon \lambda \quad (32)$$

with  $\epsilon \ll 1$  (correct results have already been obtained with  $\epsilon = 0.1$ ). After each step a random number  $r$  between zero and one is generated. If  $0 < r \leq p_l$ , then a water ligand is lost. If  $p_l < r \leq p_l + p_b$ , an acetonitrile is broken from the ion, and if  $r > p_l + p_b$  no CID occurs.

In the case of an event the following parameters are updated:

- (1)  $(i, j)$  is transformed in  $(i - 1, j)$  or  $(i, j - 1)$ ;
- (2) the velocity  $v'$  of the daughter cluster ion is calculated and recorded, together with the electric potential  $V^*$  at which it has been created;
- (3) the new ion is then allowed to reaccelerate as a free ion from  $v'$  until it reaches its own drift velocity. This is done simply by using

$$v(z) = \min\left(v'^2 + \frac{2e}{p} [V(z) - V^*(z)]^{1/2}, v_d(z)\right) \quad (33)$$

where  $v_d$  is computed and also limited to a maximum value in the same way as in the macroscopic model.

This step procedure is repeated along the  $z$  axis up to the negligible density region and the final state of the cluster ion is stored (typically 1000 steps are performed in a run for  $\epsilon = 0.01$ ). The full calculation is then completed by starting a great number of runs (ca. 1000) with initial conditions sampled to fit the initial ion population distribution.

The correction factor  $x$  obtained by the Monte Carlo method is represented in Fig. 6 by full dots. A significant departure from the macroscopic model result is observed for altitudes below 25 km. The corresponding resulting spectrum for the altitude of 20 km with the spectrum of Fig. 7(a) as input is shown in Fig. 7(c). The left shift of the latter is, as can be seen, somewhat reduced.

## DISCUSSION OF THE RESULTS

As is shown in Fig. 6, a correction factor  $x$  as high as 8.5 is found at an altitude of 15 km. Once the correction factor is known the true acetonitrile mixing ratio profile can be derived by multiplying the measured profile by this factor, as the  $\text{CH}_3\text{CN}$  mixing ratio is directly proportional to  $R$  (see Eq. 3).

At this point, however, we should underline some delicate aspects of the previous model calculations. First, it must be emphasized that the value of the correction factor  $x$  depends upon the value of  $f$  and  $R$  themselves (see Eq. 4). The previous model allows us to derive  $x$  from a known  $R$  and derive  $R_m$ ; however, the inverse i.e. starting from the measured spectrum and finding the input spectrum, is not possible. If our computation itself would be strictly exact, the only way to find the correction factor and the true  $R$  values corresponding to the measured  $R_m$  would be to apply a trial and error method which calculates  $R_m$  from several guessed  $R$  values until the resulting  $R_m$  profile corresponds to the measured one.

This procedure, however, would consume much computer time and require many calculations, especially as the correction factor  $x$  depends not

only on the value of  $R$  but also on the details of the input mass spectrum. These details, i.e. the ion distributions, are coupled to the acetonitrile concentrations through the ion/molecule chemistry as described in the model of Arijs and Brasseur [30] and therefore the ion distribution at each altitude should be calculated for each guess of  $R$ . In the computations above, the input ion distribution was taken from case C of the model of Arijs and Brasseur [20], for which the acetonitrile mixing ratio profile was constrained to fit the experimental values, which were already perturbed by CID! Therefore the input  $R$  value is clearly too low and should be increased towards the value corresponding to the inaccessible true acetonitrile concentration.

By increasing  $R$  or the acetonitrile concentration, the input ion spectrum is shifted to higher masses, which results in a somewhat delayed CID reconversion of NPH in PH and thus lowering of  $f$ .

From Eq. 4 itself it is clear that for the same  $R_m$  and lower  $f$  values the correction factor  $x$  will be smaller. The value of  $x$  obtained with the input spectra of the previous paragraphs can thus be considered as an upper limit. Therefore the direct application of the obtained  $x$  values to  $R_m$  (i.e. multiplication of the experimental  $R_m$  values with these  $x$  values) can only result in an upper limit estimation of  $R$ . A crude check of this conclusion was made as follows. A model acetonitrile concentration has been constructed by matching with the high-altitude experimental data ( $z > 40$  km) and the ACIMS low-altitude data, on which it is believed that CID has little influence. With this concentration profile, we ran the code of Arijs and Brasseur and injected the resulting spectrum, input in the present model. The correction factor  $x$  has been found to change less than 50% in the altitude range between 15 and 50 km. It is noteworthy that the  $f$  values obtained in this test decrease with increasing  $R$  at a particular altitude.

Although the previous considerations clearly show that our calculations lead to an uncertainty of about 50% in the estimation of the correction factor  $x$ , we feel that at present it is irrelevant to estimate this undetermination by a trial and error method as described above, because of other uncertainties, described below.

It is clear that our derivation of the neutral density in the gas jet region is only a first approximation and that a more refined model will require a numerical solution of the equations describing the fluid dynamics of the gas expansion.

We believe that the drift velocity approach is a reasonable representation of the energetics, although we could imagine a sophisticated Monte Carlo code including ion/neutral elastic collisions, scattering angles, internal energy (in rotational and vibrational degrees of freedom) conversions, etc.

One crucial point is evidently the total cross-section for CID; experimen-

tal information on this is scarce (see the review paper of Märk and Castleman [37]). The result we present is, of course, sensitive to the  $Q_{\max}$  value we took for the acetonitrile cluster ions. This can be seen in Fig. 7, which shows the corrected  $\text{CH}_3\text{CN}$  profile obtained by doubling or halving the value of  $Q$  for acetonitrile CID. Furthermore, nothing is known about the high-energy behaviour of  $Q$ , but it seems to be very smooth (see Douglas

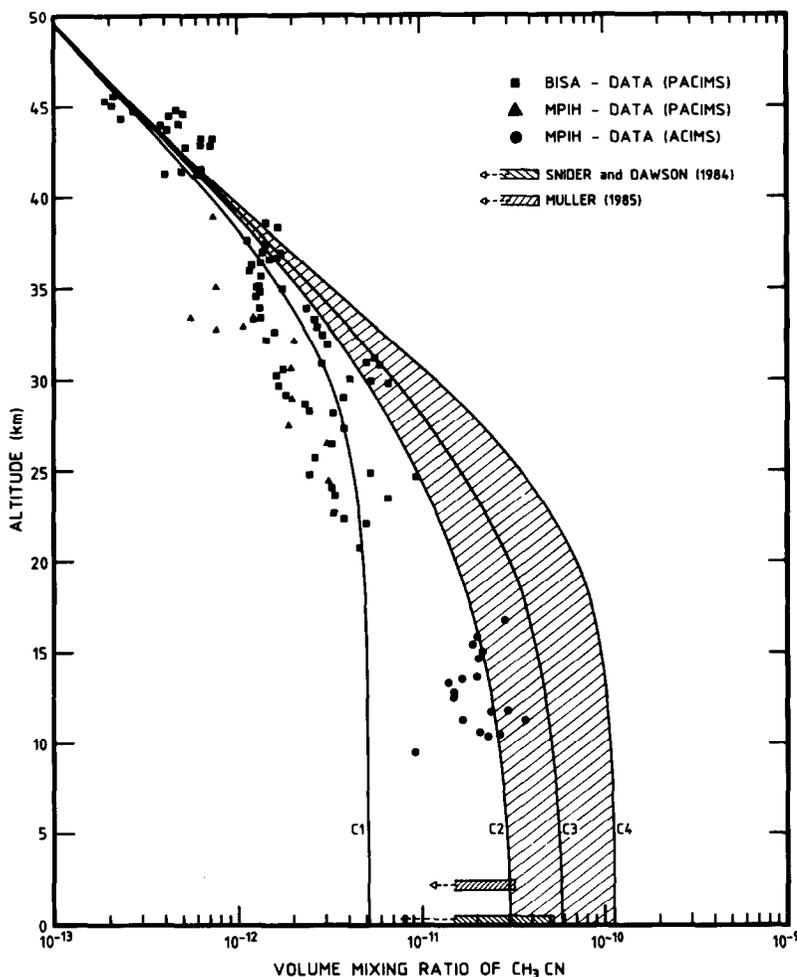


Fig. 8. Volume mixing ratio for acetonitrile vs. altitude. BISA stands for experimental results obtained by the Belgian Institute for Space Aeronomy team. MPIH stands for experimental results obtained by the Max-Planck-Institut für Kernphysik, Heidelberg, team. Also shown are upper limit estimations by Muller [39] and by Snider and Dawson [20]. Curve C1 is a least-squares fit through the experimental values. Curves C2, C3 and C4 are the present Monte Carlo results with  $\sigma_{\text{AN}} = (1/2)\sigma_{\text{W}}$ ,  $\sigma_{\text{AN}} = \sigma_{\text{W}}$ ,  $\sigma_{\text{AN}} = 2\sigma_{\text{W}}$ .

[38]) whatever the physical mechanism of CID. We present in Fig. 8 the experimental value compilation of Arijs et al. for the acetonitrile mixing ratio in the stratosphere, together with the corrected values given by the present calculation. It is well confirmed that the disagreement observed between balloon-borne results and aircraft and ground-level results should be attributed to the occurrence of apparatus-induced CID between the inlet sampling hole and the spectrometer itself.

## CONCLUSIONS

We have presented a calculation of the CID influence on the ratio of non-proton hydrates to proton hydrates in stratospheric positive ion mass spectrometry. A typical correction factor of four is obtained at an altitude of 25 km. Confidence in such calculation is strongly related to precise total cross-section measurements for acetonitrile cluster ion CID, which are, to our knowledge, still lacking. In view of the importance of the CID perturbation in stratospheric measurements we draw attention to the possible interest of studying spectrometer configurations that allow non-axial gas injection and ion extraction out of the neutral gas jet.

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