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Theoretical investigation of the collisional dissociation of  
positive cluster ions in balloon borne stratospheric mass  
spectrometry

by

D. FUSSEN, E. ARIJS and D. NEVEJANS

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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## FOREWORD

"Theoretical investigation of the collisional dissociation of positive cluster ions in balloon borne stratospheric mass spectrometry" is the base of a paper to be published in "International Journal of Mass Spectrometry and Ion Processes"

## AVANT-PROPOS

"Theoretical investigation of the collisional dissociation of positive cluster ions in balloon borne stratospheric mass spectrometry" est la base d'un article dont le texte sera publié dans "International Journal of Mass Spectrometry and Ion Processes".

## VOORWOORD

"Theoretical investigation of the collisional dissociation of positive cluster ions in balloon borne stratospheric mass spectrometry" vormt de basis voor een artikel dat zal verschijnen in "International Journal of Mass Spectrometry and Ions Processes".

## VORWORT

"Theoretical investigation of the collisional dissociation of positive cluster ions in balloon borne stratospheric mass spectrometry" ist die Basis für ein Artikel der in "International Journal of Mass Spectrometry and Ion Processes" herausgegeben wird.

THEORETICAL INVESTIGATION OF THE COLLISIONAL DISSOCIATION OF  
POSITIVE CLUSTER IONS IN BALLOON BORNE STRATOSPHERIC MASS  
SPECTROMETRY

by

D. FUSSEN, E. ARIJS and D. NEVEJANS

Abstract

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

This mechanism is investigated by means of an 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 about 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 4 at an altitude of 25 km. The sensitivity of our results to the lacking of experimental data is explored and some criticism is developed about the confidence limits of such a modelling.

## Résumé

Dans la stratosphère, la spectrométrie de masse des ions positifs utilisant une méthode de chimi-ionisation passive est perturbée par la dissociation collisionnelle des agrégats ioniques échantillonnés dans la région au-delà de l'orifice d'entrée du spectromètre. Ce phénomène est étudié dans le cadre d'un modèle uni-dimensionnel pour les agrégats de la famille  $H^+(CH_3CN)_\ell(H_2O)_m$  qui sont impliqués dans la détermination du rapport de mélange de l'acétonitrile dans la stratosphère.

Les trois paramètres physiques dont la dissociation collisionnelle dépend sont dégagés, à savoir : la densité du jet de gaz neutre, la vitesse ou l'énergie centre-de-masse atteinte par les ions dans le champ électrique statique et la section efficace totale du processus de dissociation. Le phénomène est modélisé en utilisant la simple loi d'expansion adiabatique pour le gaz neutre, le concept de mobilité ionique et diverses données expérimentales concernant les sections totales de dissociation. On réalise un calcul macroscopique sans considérer la fonction de distribution des vitesses ioniques ainsi qu'un calcul Monte-Carlo plus réaliste. On montre que la concentration d'acétonitrile est expérimentalement sous-évaluée d'un facteur 4 à 25 km d'altitude. La sensibilité de nos résultats en fonction du manque de paramètres expérimentaux est passée en revue et nous évaluons les limites de confiance de notre modèle.

## Samenvatting

De resultaten van de passieve chemische ionisatiemethode, gebruikt in massaspectrometrie van positieve ionen in de stratosfeer, worden beïnvloed door zogenaamde "collisional induced dissociation" (CID). Dit verschijnsel resulteert in de opbraak van de ionen onmiddellijk na het inlaatgat van de massaspectrometer.

Met behulp van een 1-dimensioneel model, wordt hier het mechanisme van CID onderzocht voor ionen van het type  $H^+(CH_3CN)_l(H_2O)_m$ , waarvan relatieve concentratiemetingen gebruikt worden voor de bepaling van acetonitrile concentraties in de stratosfeer. De 3 fysische parameters, van dewelke CID afhangt, worden belicht : 1) de dichtheid van de neutrale gas jet, 2) de snelheid of de barycentrische kinetische energie van de ionen in het statisch electrisch veld en 3) de totale werkzame doorsnede voor het dissociatieproces. De CID wordt gemodelleerd met behulp van eenvoudige adiabatische gasexpansie wetten, het mobiliteitsconcept voor ionen en verscheidene experimentele gegevens omtrent CID werkzame doorsneden. De berekening wordt enerzijds macroscopisch uitgevoerd, zonder rekening te houden met de snelheidsverdeling der ionen en anderzijds wordt een meer realistische Monte-Carlo behandeling toegepast. Het blijkt dat de uit de ionenmassaspectra afgeleide  $CH_3CN$  mengverhoudingen op 25 km hoogte typisch een factor 4 te klein zijn. De invloed van het gebrek aan experimentele resultaten omtrent bv. dissociatie werkzame doorsneden wordt onderzocht en de betrouwbaarheids-grenzen van het model worden besproken.

## Zusammenfassung

Bei der Messung von stratosphärischen positiven Ionen, welche auf der Methode einer sogenannten passiven chemischen Ionisation beruhen, werden durch stossinduzierte Dissoziation (CID) die gesammelten Clusterionen hinter der Einlassöffnung beeinflusst.

Dieser Mechanismus wird anhand eines eindimensionalen Modells für die Ionenklasse  $H^+(CH_3)CN)_l(H_2O)_m$  geprüft, mit dem sich Acetonitrilkonzentrationen bestimmen lassen. Die drei physikalischen Größen, welche die CID bestimmen, werden beleuchtet : 1) die Dichte des neutralen Gasstrahls, 2) die Geschwindigkeit oder baroklinische kinetische Energie der Ionen nach Durchlaufen des statischen, elektrischen Feldes, und 3) der totale Dissoziationswirkungsquerschnitt. Mit Hilfe einfacher adiabatischer Expansionsgesetze für das Neutralgas, eines Mobilitätskonzepts für Ionen und verschiedener experimenteller CID-Wirkungsquerschnitte wird der CID-Effekt modelliert. Die Rechnung wird einerseits makroskopisch, ohne die Berücksichtigung einer Geschwindigkeitsverteilung der Ionen, durchgeführt. Eine ergänzende, realistischere Rechnung basiert auf der Monte-Carlo-Methode. Die Acetonitrilkonzentration, welche experimentell auf einer Höhe von 25 km bestimmt wurde, liegt dabei um einen Faktor 4 unter dem mit dem Modell bestimmten Wert. Die Empfindlichkeit der Rechnung wurde bezüglich fehlenden experimentellen Größen untersucht, und die Zuverlässigkeitsgrenzen eines solchen Modells geprüft.

## 1. INTRODUCTION

Since 1978 the results of several ion composition measurements in the stratosphere have been reported in literature [1]. 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 [2].

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  $\text{HNO}_3$  [3], 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 [9-12] 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 concluded earlier [2] 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 would be 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 reactions is given elsewhere [4]. 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

$$[X] = R \propto [n^-]/k \quad (2)$$

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

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

In the stratosphere two major positive ion families have been observed :  $H^+(H_2O)_n$  and  $H^+(CH_3CN)_\ell(H_2O)_m$ .

Taking the mass peak intensities as a measure for the ion number densities, the volume mixing ratio of  $CH_3CN$  has been derived in the region from 20 to 45 km from positive ion mass spectra obtained in different balloon flights [5].

Recently, however, airplane and balloon borne active chemical ionization mass spectrometer (ACIMS) data allowed the derivation of  $CH_3CN$  volume mixing ratios at an altitude range between 17 and 12 km [6]. The data, in good agreement with ground based  $CH_3CN$  measurements [7] suggest an underestimation in those obtained from the balloon experiments. It has been proposed [8] that this systematic underestimation is due to intrinsic errors in the balloon data as a result of collisional 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 [8] and Arijs et al. [9].

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

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

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



The purpose of the present work is to propose a theoretical model for the  $f$  value determination and to evaluate the order of magnitude of the correction factor  $x$ , to be applied to previous acetonitrile abundance derivations.

## 2. GENERAL MODEL PHILOSOPHY

### 2.1. Description of the problem

The experimental set-up of the ion mass spectrometer of the Belgian team, as described in detail previously [10], primarily consists 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 .2mm) in a thin flange, biased a few volt 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 figure 1.

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

- a. the density of the neutral gas jet along the followed path
- b. the barycentric kinetic energy raised within the electric field
- c. the total cross section for the dissociation process.

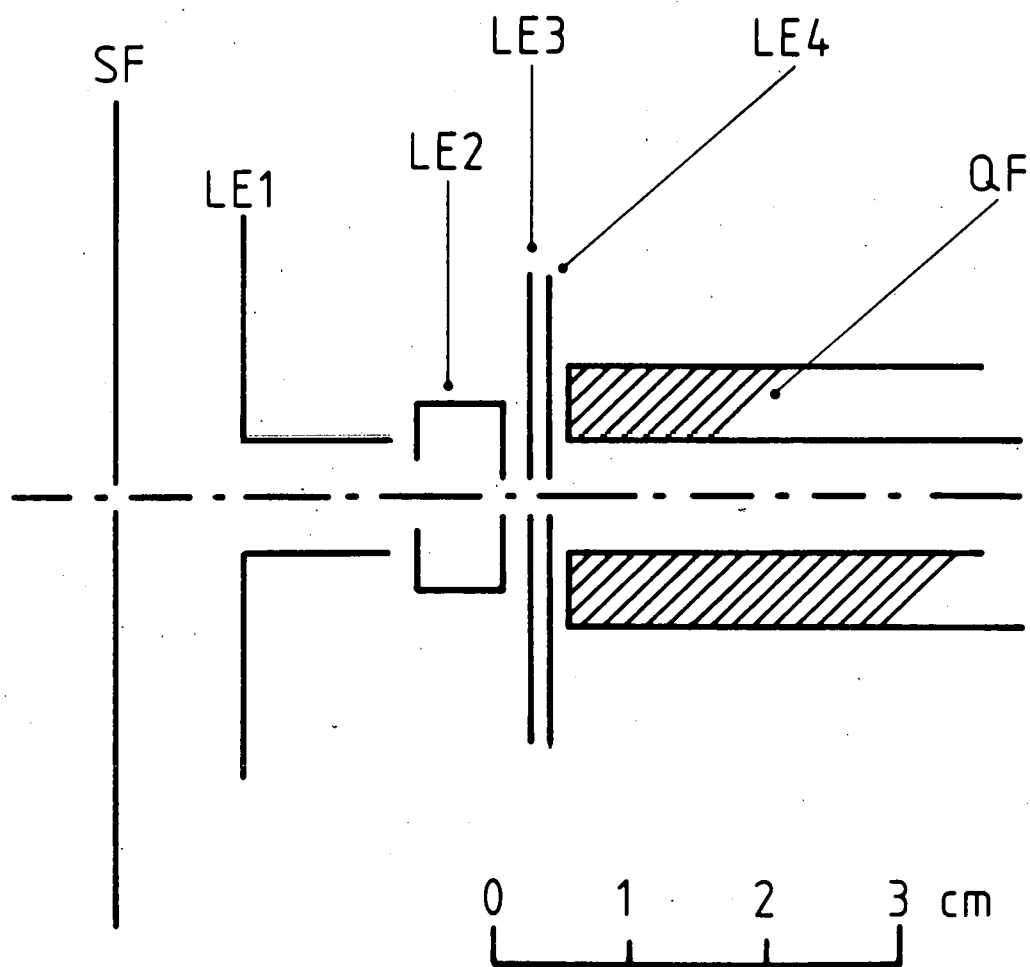


Fig. 1. - Schematic representation of the ion sampling configuration as used by Arijs et al. [9]

SF : sampling flange; LE1, LE2, LE3, LE4 lens elements;

QF : quadrupole filter.

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

## 2.2. The one-dimensional model

The dynamics of a compressible fluid obeys the continuity equation

$$\frac{d\rho}{dt} + \text{div}(\rho \vec{v}) = 0 \quad (4.1)$$

and the Euler equation

$$\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} = - \frac{1}{\rho} \nabla p \quad (4.2)$$

In cylindrical coordinates, the equations (4.1) and (4.2) read

$$\frac{\partial \rho}{\partial t} = - \left[ \frac{\partial}{\partial z} (\rho v_z) + \frac{\partial}{\partial r} (\rho v_r) + \frac{\rho v_r}{r} \right] \quad (4.3)$$

$$\frac{\partial v_z}{\partial t} = - \left[ \frac{1}{\rho} \frac{\partial}{\partial z} p + v_z \frac{\partial}{\partial z} v_z + v_r \frac{\partial}{\partial r} v_z \right] \quad (4.4)$$

$$\frac{\partial v_r}{\partial t} = - \left[ \frac{1}{\rho} \frac{\partial}{\partial r} p + v_z \frac{\partial}{\partial z} v_r + v_r \frac{\partial}{\partial r} v_r \right] \quad (4.5)$$

while the pressure  $p$  is related to  $\rho$ ,  $v_z$  and  $v_r$  by the state equation of the gas.

The numerical computation of a free jet expansion into a vacuum through a small hole is still a difficult problem (see e.g. [11]). A rigorous treatment of this problem being beyond the scope of this first modelling effort we have therefore followed a derivation by Fite [12].

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 Boltzman's constant and the ratio  $C_p/C_v$  respectively. To a good approximation we obtain from the use of (5), (6), (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

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

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

It is worth noting [13] 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 about  $7 \times 10^4$  cm/s.

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 [14] 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 in 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 Volts/cm for the electric field  $F$ , an external stagnation pressure of 10 Torr, and taking a characteristic experiment drift velocity of a system like  $Ar^+$  in  $Ar$ , we find that,

$$v_d(z = 2\text{mm}) \approx 5.10^5 \text{ cm/s} \gg v_g(\infty) \quad (13)$$

Typical ion trajectories for the above mentioned conditions are shown in figure 2. From this figure it can be seen that, except in the very near hole vicinity, ions quickly bend their trajectory parallel to the z-axis, while 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 :

$$\frac{dj_i}{dz} = - Q(z) v_d(z) n(z) n_i(z) \quad (14)$$

with the relation

$$j_i(z) = n_i(z) [v_g(z) + v_d(z)] \approx n_i(z) v_d(z) \quad (15)$$

$n_i$  being the local ion number density.

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

$$z_t = \frac{z_s}{A} \left( \frac{2 E_t n_s}{\mu F} \right)^{1/2} \quad (16)$$

Again an estimation of a typical value for A can be obtained by examining the experimental drift velocity of  $\text{Ar}^+$  in Ar, for which  $\mu$  has a value of 20 amu. Taking a typical value of 1 eV as the bound strength of the ion clusters, we get for  $z_t$  a value of 1.5 mm. Furthermore we can easily integrate the differential equation (14) for  $z > z_t \gg z_s$  to derive the final current density at the end of the gas jet. This leads to

$$j_\infty = j(z_t) \exp \left( - \frac{Q n_s z_s^2}{z_t} \right) \quad (17)$$

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

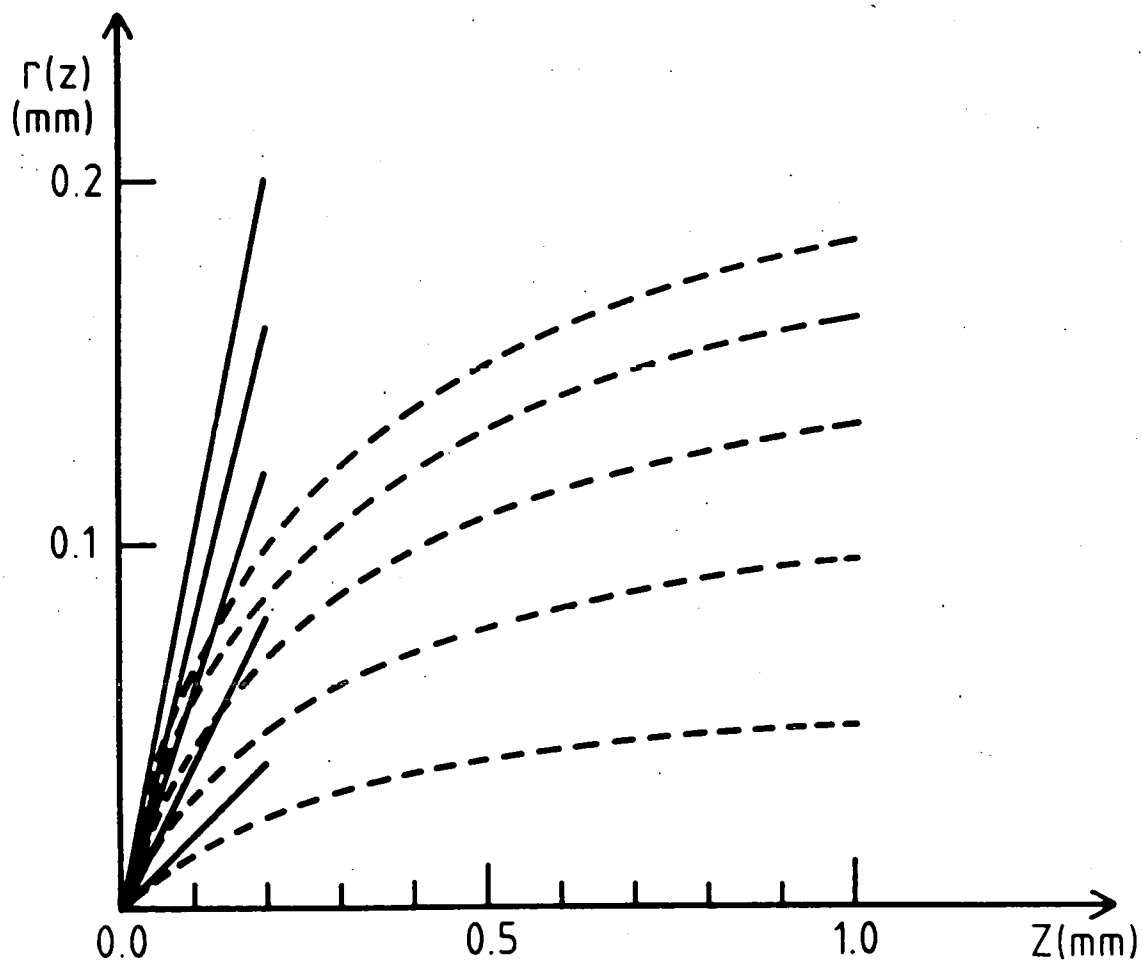


Fig. 2. - Typical ion trajectories beginning at the inlet hole and corresponding to different orientations of the neutral gas velocity.

dealing with [15], we see that the attenuation factor can easily be as important as  $1/e$ .

### 3. 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 (14) to the more general case of ions  $H^+(CH_3CN)_j(H_2O)_i$ . The model includes the 22 cluster ions, for which Deakhyne et al. [15] 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 amu, which is well above the range of the experimental spectra obtained in the stratosphere. For the species  $i,j$  we can write the continuity equations

$$\frac{d}{dz} j_{i,j}(z) = -L_{i,j}(z) + G_{i,j}(z) \quad (18)$$

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

$$L_{i,j}(z) = L_{i,j}^{\ell}(z) + L_{i,j}^b(z) \quad (19a)$$

The indices  $\ell$  and  $b$  stand for "left" and "bottom" in Fig. 3 and refer to the loss of a  $H_2O$  or  $CH_3CN$  molecule respectively. According to equations (14) and (15) these terms can be expressed as

$$L_{i,j}^{\ell/b} = Q_{i,j}^{\ell/b}(z) n(z) j_{i,j}(z) \quad (20)$$

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

The term  $G_{ij}(z)$  represents the gain due to 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 :

$$G_{i,j}(z) = L_{i,j+1}^{\ell}(z) + L_{i+1,j}^b(z) \quad (19b)$$



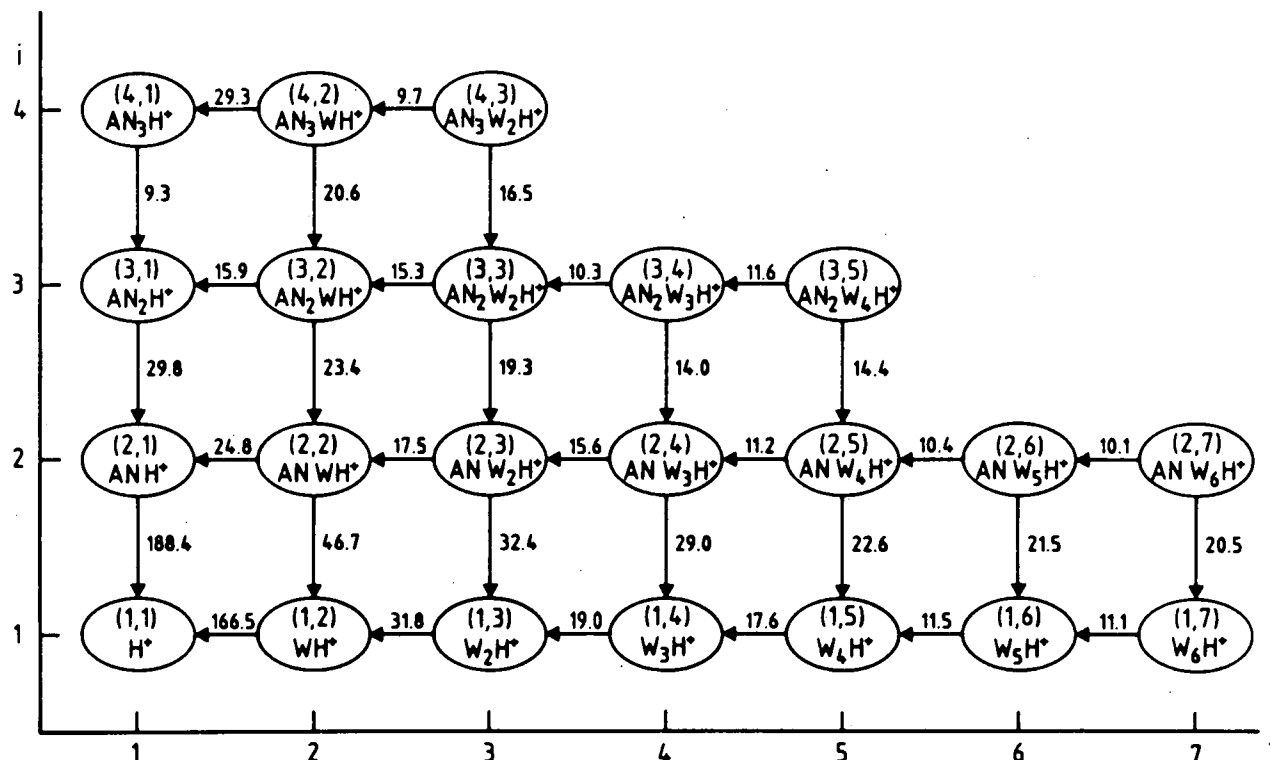


Fig. 3.- The 22 ions involved in the calculation. Arrows refer to dissociation paths with the dissociation energies in kcal/mole. AN and W respectively stand for CH<sub>3</sub>CN and H<sub>2</sub>O molecules.

Writing down the continuity equation (18) 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 [16].

#### 4. COMPUTATION OF THE PHYSICAL PARAMETERS

##### 4.1. Total CID cross sections

The CID cross sections for PH have been modelled, as shown in Fig. 4, following the experimental results of Dawson [17] and using the linear relation between the cross section and the number  $n$  of water molecules, as found by this author :

$$Q_n = n\sigma_a + \sigma_b \quad (21)$$

with

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

It has been observed by Dawson [17] that the formation of  $\text{H}^+\text{H}_2\text{O}$  is not very dependent upon whether the latter is formed through a one-step three water molecules loss or through a three-step one water molecule loss. 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 of (21), which is a rough but probably reasonable approximation.

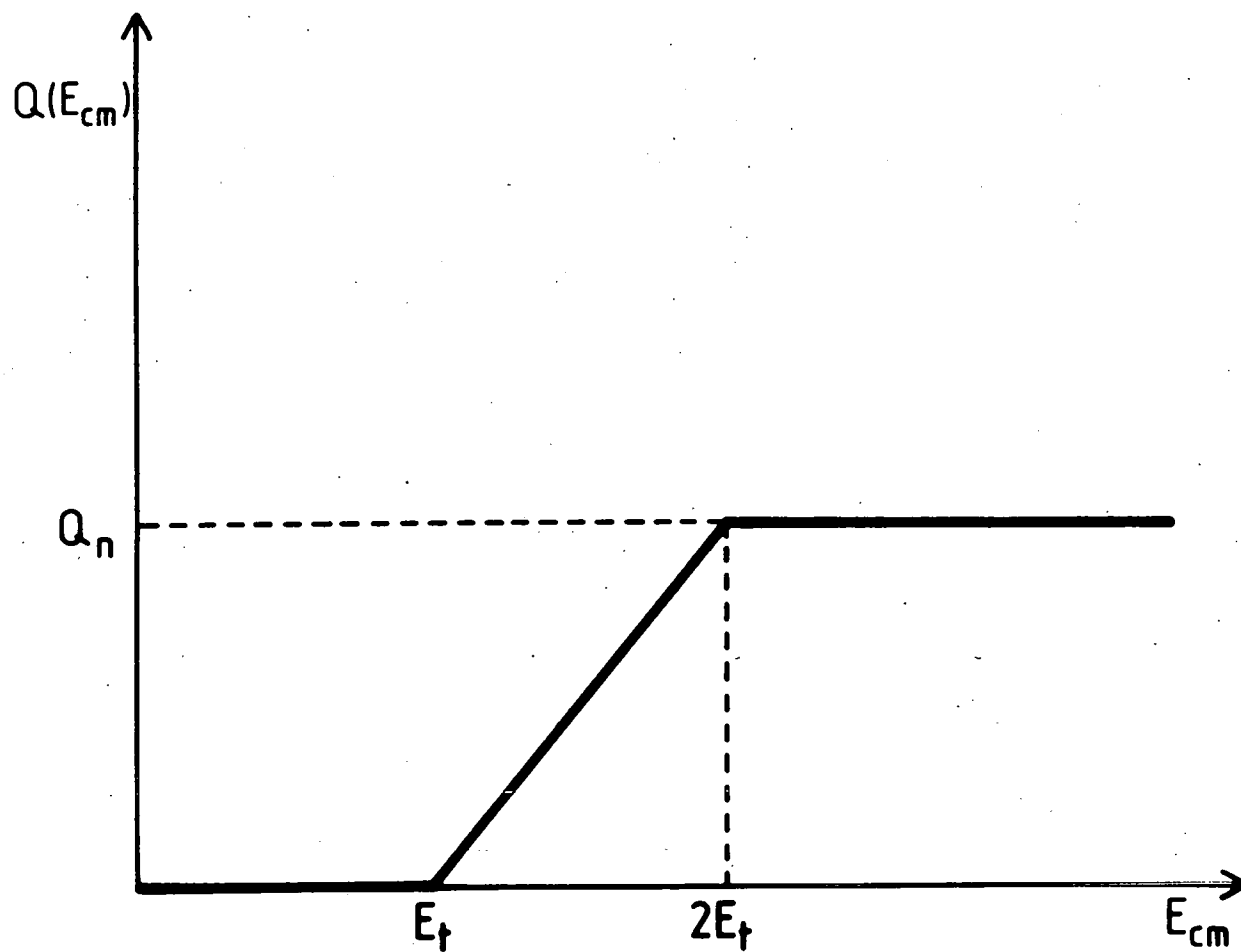


Fig. 4. - Total cross section for CID process versus barycentric energy  $E_{cm}$ .

#### 4.2. Ion velocities

The velocity distribution of the cluster ions in the accelerating electric field should be solved in the Boltzmann's equation frame with a good knowledge of the neutral molecule-cluster ion potential interaction. In order 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 enough elastic collisions with the neutral gas on a small distance so that a drag appears which stabilises 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 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 latter has been computed for our experimental configuration by means of a standard relaxation method and is almost linear versus  $z$  in the region of interest ( $0 < z < 10$  mm) where the quasi-constant field is about 70 volts/cm. Vielhand and Mason [18] have developed a two-temperature theory to calculate the drift velocity of an ion at all  $F/n$  values. According to them we have written the implicit  $v_d$  formula

$$v_d = \frac{3e\sqrt{2\pi}}{16} \frac{F}{n} \frac{1}{\sqrt{\mu}} \frac{1}{\sqrt{T_e}} \frac{1}{\Omega(T_e)} \quad (22)$$

$$T_e = T + \frac{M}{3k} v_d^2 \quad (23)$$

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  $H^+(H_2O)_n$  ( $n = 1, 2, 3$ ) mobilities obtained by Dottan et al. [19] and the associated  $\Omega$  reported by Ellis et al. [20]. We have chosen to fit  $\Omega(T_e)$  as :

$$\Omega(T_e) [A^2] = \frac{a}{\sqrt{T_e}(b+\sqrt{T_e})} + c$$

$$\begin{aligned} a &= 9.457(6) \\ b &= 4.914(3) \\ c &= 1.171(1) \end{aligned} \quad (24)$$

$$\Omega(T_e) \sim \frac{a}{b\sqrt{T_e}} \quad T_e \ll b \quad \Omega(T_e) \sim c \quad T_e \gg b \quad (25)$$

Such a non-linear fit is hoped to be closely related with a  $(\infty-4)$ -like potential for the cluster ion-neutral interaction (i.e. hard sphere +  $1/r^4$  polarisation attractive potential [21]). In the zero temperature limit expressions (22) and (24) give for  $H^+H_2O$  a mobility of  $3.22 \text{ V}^{-1} \text{ cm}^2 \text{ s}^{-1}$  to be compared to 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. [19].

The relation between  $\Omega(T_e)$  and  $T_e$  is shown in figure 5. It is worth noticing that all  $\Omega$  values for different ions lie approximately on the same curve (for a discussion of this see Böhringer et al. [22]). We have then chosen to use the same collision integral for the acetonitrile cluster ions.

## 5. RESULTS OF THE MACROSCOPIC MODEL

Using the approach explained in the previous paragraphs to calculate the physical parameters of the model, we have computed the solution of the equations (18) between 10 and 50 km altitude, with

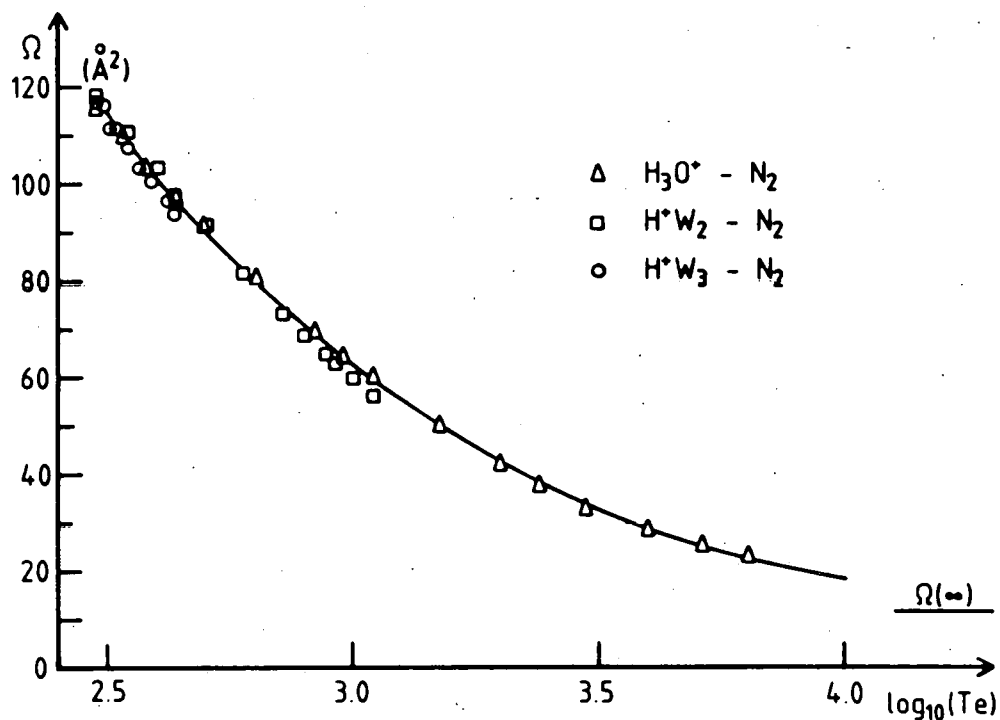


Fig. 5. - Elastic collision cross section  $\Omega$  versus the effective temperature  $T_e$ . Triangles, squares and circles are the experimental values reported by Ellis et al. [34] extracted from mobility measurements of Dottan et al. [33] for  $H^+(H_2O)_n$  in nitrogen.

standard atmosphere temperatures and densities as stagnation temperatures and densities respectively. In this way the ion populations resulting from CID is obtained using the input spectra taken from Arijs and Brasseur [16]. It is then straightforward to calculate the correction factor  $x$ . The result is represented in figure 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 inducing CID, but increases strongly to reach a value of 13 at 15 km.

In fig. 7A the input mass spectrum at 25 km is represented and the final spectrum calculated in the present model is shown in fig. 7B. It is clear that the latter is strongly perturbed by CID. The dominant mass peak at 96 amu -  $H^+CH_3CN(H_2O)_3$  - is replaced by mass 60 -  $H^+(CH_3CN)H_2O$ . Furthermore light proton hydrates begin to appear and the whole spectrum is shifted to lower masses.

## 6. MONTÉ-CARLO SIMULATION

In the macroscopic model we have assumed that the drift velocity of an 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 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] a reasonable assumption, justified for laboratory energies  $\frac{mv^2}{2} \gg E_t$ . 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 by expressing the total energy conservation as

$$\frac{mv^2}{2} = \frac{mv'^2}{2} + \frac{MV'^2}{2} + E_t \quad (25.1)$$

and the total momentum conservation as

$$mv = mv' + MV' \quad (25.2)$$

$$v' = \frac{v}{1+\xi} \left[ \xi - \left( 1 - (1+\xi) \frac{E_t}{E} \right)^{\frac{1}{2}} \right] \quad (26)$$

with  $\xi = \frac{m}{M}$

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 meet 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  $p_\ell$  and  $p_b$ , the probabilities of loosing a water or an acetonitrile molecule respectively, after a step  $\Delta z$ , as :

$$p_\ell = Q_{i,j}^\ell n \Delta z \quad (27)$$

$$p_b = Q_{i,j}^b n \Delta z \quad (28)$$

Such a probabilistic approach can easily be shown to be equivalent to the macroscopic result.

Let us suppose an attenuation process with constant cross section  $Q$  and density  $n$ . After a distance  $z^*$  the attenuation factor is



$$\frac{j(z^*)}{j_0} = e^{-z^* nQ} \quad (28.1)$$

The survival probability for a step  $\Delta z$  is

$$1 + \frac{\Delta j}{j} = 1 - Qn\Delta z = 1 - p \quad (28.2)$$

The final survival probability for  $z^* = m\Delta z$  is

$$P = (1 - p)^m \quad (28.3)$$

If  $\Delta z$  is small ( $p \ll 1$ ) then  $m$  is large and we get

$$\lim_{\substack{\Delta z \rightarrow 0 \\ m \rightarrow \infty}} P = \lim_{\Delta z \rightarrow 0} e^{\frac{z^*}{\Delta z} \ln(1 - Qn\Delta z)} = e^{-z^* Qn} \quad (28.4)$$

which is the same as the macroscopic result given by (28.1).

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

$$\lambda_{\ell/b} = \frac{1}{Q_{i,j}^{\ell/b} \cdot n} \quad (29)$$

with  $\lambda = \min(\lambda_\ell, \lambda_b)$  and

$$\Delta z = \epsilon \lambda \quad (30)$$

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

In case of an event the following parameters are updated :

- (i,j) is transformed in (i-1,j) or (i,j-1)
- the velocity  $v'$  of the daughter cluster ion is calculated and recorded together with the electric potential  $V^*$  at which it has been created.
- 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 :

$$v(z) = \min \left( (v')^2 + \frac{2e}{p} (V(z) - V^*(z))^{1/2}, v_d(z) \right) \quad (31)$$

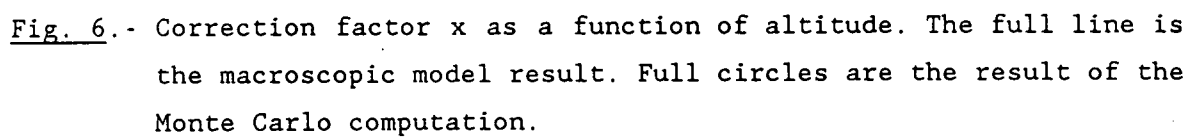
where  $v_d$  is computed and also limited to a maximum value in the same way as in the macroscopic model.

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 (about 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 figure 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 figure 7a as input is shown in figure 7c. The left shift of the latter is, as can be seen, somewhat decreased.

## 7. 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 with this factor since the  $\text{CH}_3\text{CN}$  mixing ratio is directly proportioned to  $R$  [see formula (3)].



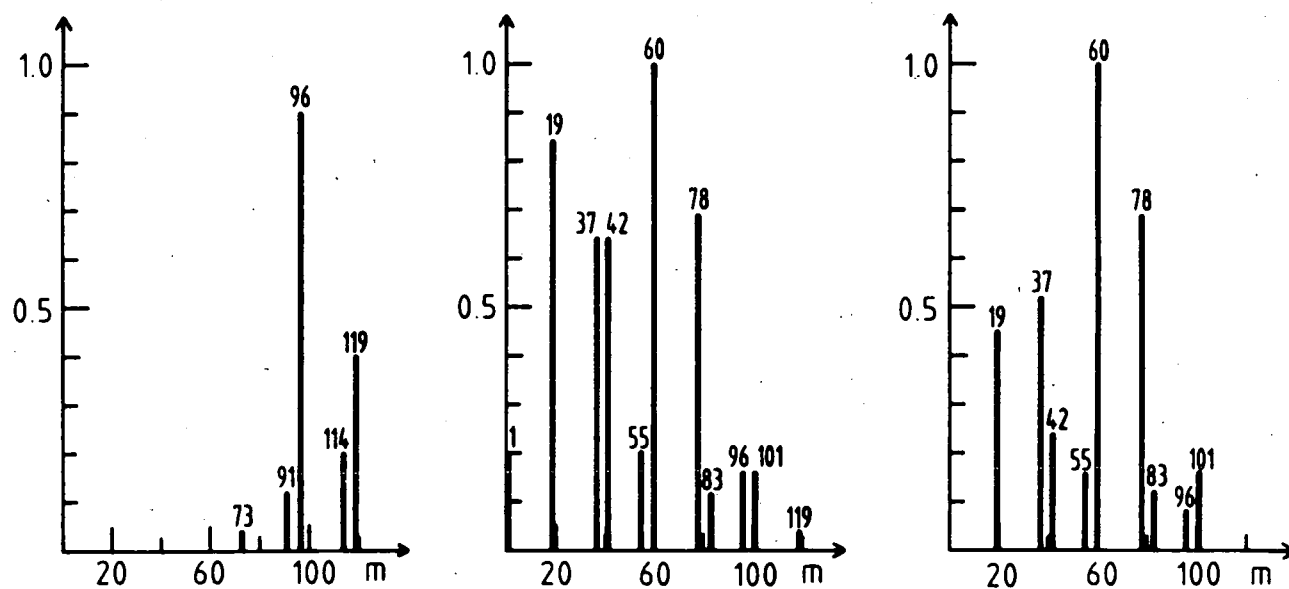


Fig. 7.- From left to right, at the same altitude of 25 km  
a : input spectrum as computed by Arijs and Brasseur  
b : output spectrum of the macroscopic model  
c : output spectrum of the Monte Carlo model.

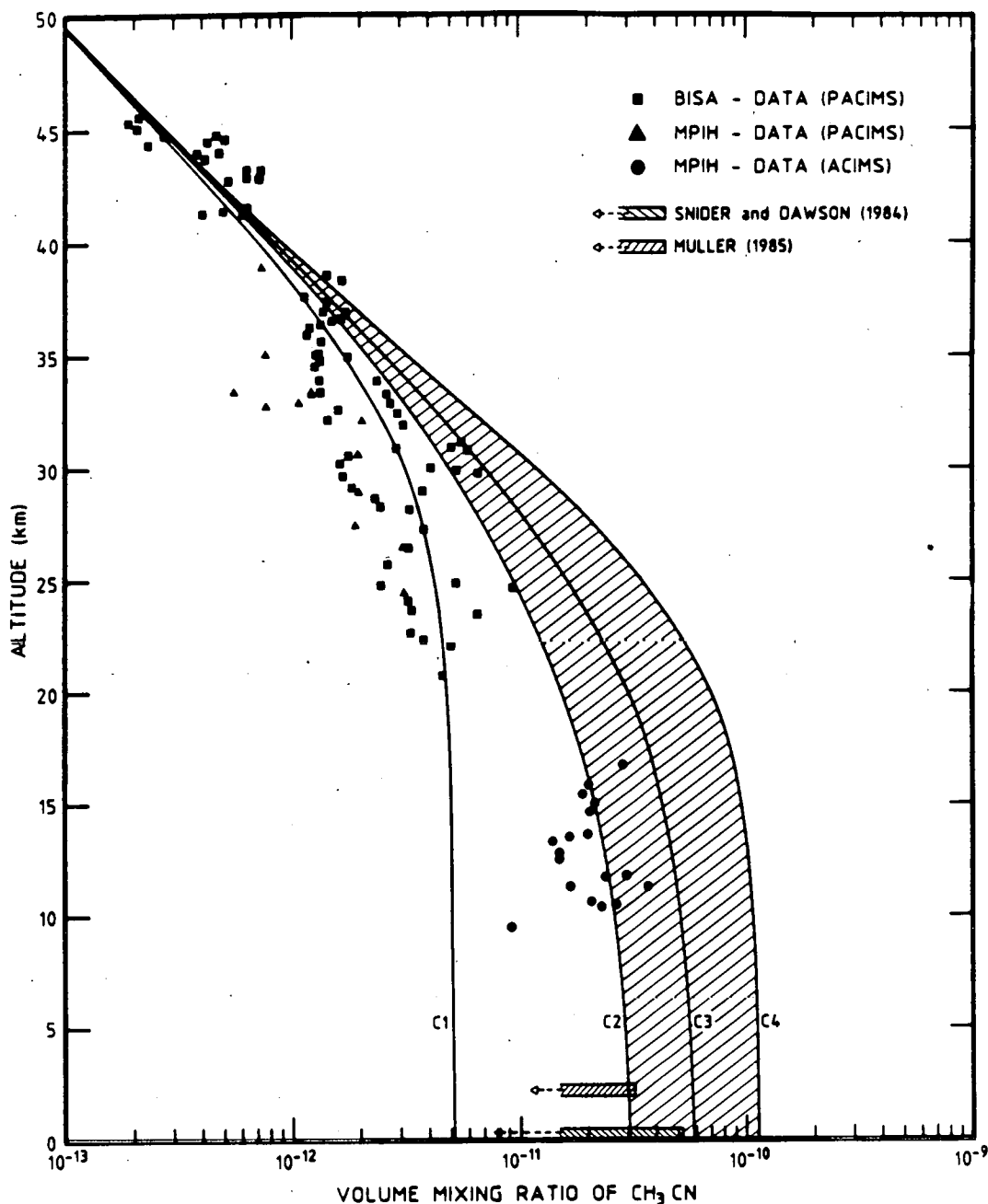


Fig. 8.- Volume mixing ratio for acetonitrile versus altitude.

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 [25] and by Snider and Dawson [26].

Curve c1 is a least-square fit through the experimental values.

Curve c2, c3 and c4 are the present Monte-Carlo results with  $\sigma_{AN} = \frac{1}{2} \sigma_W$ ,  $\sigma_{AN} = \sigma_W$ ,  $\sigma_{AN} = 2\sigma_W$ .

At this point however we should underline some delicate aspects of the previous model calculations. Firstly it must be emphasized that the value of the correction factor  $x$  depends upon the value of  $f$  and  $R$  themselves [see formula (4)]. The previous model allows us to derive  $x$  from a known  $R$  and derive  $R_m$ , the inverse however, namely starting from the measured spectrum and find 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 be very computer time-consuming and require many calculations, especially since the correction factor  $x$  depends not only on the value of  $R$  but also on the details of the input mass spectrum. These details, namely the ion distributions are coupled to the acetonitrile concentrations through the ion-molecule chemistry as described in the model of Arijs and Brasseur [16] and therefore the ion distribution at each altitude should be calculated for each guess of  $R$ . In the computations of the previous paragraphs the input ion distribution was taken from case C of the model of Arijs and Brasseur [16] 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 formula (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 for which it is believed that CID is of 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 worth noticing that the  $f$  values obtained in this test are decreasing with increasing  $R$  at the same 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 before, because of other uncertainties described hereafter.

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 one could imagine a sophisticated Monte-Carlo code including ion-neutral elastic collisions, scattering angles, internal energy (in rotational and vibrational degrees of freedom) conversions ...

One crucial point is evidently the total cross section for CID about which experimental information is scarce (see the review paper of Märk and Castleman [23]). 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 [24]) whatever the physical mechanism of CID. We present in fig. 7 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 air-plane and ground-level results should be attributed to apparatus induced CID occurring between the inlet sampling hole and the spectrometer itself.

## 8. 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 4 is obtained at an altitude of 25 km. Confidence in such calculation is strongly related with 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 would draw attention to the possible interest of studying spectrometer configurations allowing non-axial gas injection and ion extraction out of the neutral gas jet.



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