Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 262 (2007) 195–202

www.elsevier.com/locate/ijms

Hybrid molecular ions emitted from CO–NH_3 ice bombarded by fission fragments

R. Martinez [a], C.R. Ponciano [a], L.S. Farenzena [a], P. Iza [a], M.G.P. Homem [b], A. Naves de Brito [b], E.F. da Silveira [a,*], K. Wien [1]

[a] *Physics Department, Pontifícia Universidade Católica, 22453-900 Rio de Janeiro, RJ, Brazil*
[b] *Laboratório Nacional de Luz Síncrotron, Box 6192, 13084-971 Campinas, SP, Brazil*

Received 1 October 2006; received in revised form 13 November 2006; accepted 14 November 2006
Available online 22 December 2006

Abstract

CO–NH_3 ice at 25 K is bombarded by 65 MeV fission fragments and the emitted secondary ions are analyzed by time-of-flight mass spectrometry. The yields of the specific ion species (those formed only from CO or from NH_3 molecules) and of the hybrid ion species (formed from both CO and NH_3 molecules) are determined as a function of the ice temperature. The time-temperature dependence of desorption yields has been used for secondary ion identification because its behavior characterizes the ion's origin around the sublimation temperature of CO ice (~30 K). The mass spectrum of positive ions measured before CO sublimation is decomposed into three spectra corresponding to CO specific ions, NH_3 specific ions and hybrid molecular ions, respectively. The observed spectrum after CO sublimation is very similar to that of a pure NH_3 specific spectrum. The total yield of all positive hybrid molecular ions over 600 u mass range is found to be about 2 ions/impact: 20% of this is attributed to N and NH_3 containing ions and 80% are ions having the $C_nO_mH_l^+$ structure. The ions $C_{n\leq3}H_{1,2,3}^+$, COH^+, NO^+, NH_3OH^+ and NH_3CO^+ were identified. At $T = 25$ K, the total yield of negative ions is about 20 times lower than that of positive ions, the most abundant species being the cyanide ion CN^-. Observation of cluster ions based on $(HCN)_n$ indicates the formation of hydrogen cyanide.

Keywords: Secondary ion; Condensed gase; CO–NH_3 ice; TOF SIMS; Hybrid molecular ion; Temperature dependence

1. Introduction

We recently investigated the occurrence of hybrid molecular ions in the flux of particles sputtered by MeV heavy ions from a mixture of CO_2–H_2O ice [1,2]. This search for new molecular ions – in particular organic molecules – is now extended to a mixture of carbon monoxide and ammonia condensed onto a metallic substrate at a temperature of 25 K. The CO–NH_3 ice is bombarded by fission fragments of about 65 MeV, a kinetic energy for which the electronic sputtering dominates. Since CO and NH_3 are constituted by H, C, N and O, the CO–NH_3 mixture provides the basic elements for the genesis of organic molecules. The aim of the present work is to detect, by time-of-flight mass spectrometry, the new molecules which are formed inside the short living nuclear track plasma and ejected into vacuum.

The available data on CO_2–H_2O ice [1,2] reveal that hybrid molecular ions i.e., molecular ions which contain atoms originating from both CO_2 and H_2O molecules, account for about 10% of the total ion yield and that these ions are formed mainly by 1-step reactions between primarily produced ions with CO_2 or H_2O molecules or with their clusters. The major part of the mass spectrum consists of lines of cluster ion series formed by CO_2 and H_2O specific ions. As presented in the following, the ice formed by the mixture CO:NH_3 = 5:1 delivers similar results for the positive ion spectrum; however, the relative yield of hybrid molecular ions is more than a factor of 3 higher than in the case of CO_2–H_2O ice; the majority of these ions stem from multi-step reactions. Secondary ion emission from the ices of pure CO and pure NH_3 has been studied in detail in previous experiments [3–5].

The mass spectrum of the positive ions ejected from CO–NH_3 ice is here studied at ice temperatures between 25

---

[*] Corresponding author. Tel.: +55 21 31141272; fax: +55 21 31141040.
E-mail address: enio@vdg.fis.puc-rio.br (E.F. da Silveira).

[1] Guest of the Institute of Nuclear Physics, Technical University, 64289 Darmstadt, Germany.

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.11.013

and 130 K. As temperature increases, the sublimation of CO precedes that of NH_3. The spectral pattern changes substantially as a function of temperature due not only to the change in the relative concentration of the ice constituents but also to changes in the ice structure. In the present work our attention is focused on the genesis of hybrid molecular ions in the CO–NH_3 mixture around the sublimation point of CO (∼30 K). A second article, in preparation, describes the influence of the ice structure and its composition on the secondary ion formation [6].

The analysis has been performed by ^{252}Cf-plasma desorption mass spectrometry (PDMS [7]), which employs fission fragments as projectiles for sputtering and as trigger for the time-of-flight (TOF) measurement. In Section 2, the experimental methods are shortly described; in Sections 3 and 4, the mass spectra of positive ions obtained during a steady increase of target temperature are analyzed and discussed. Mass spectra of negative ions measured before and after CO sublimation are presented in the Appendix and briefly analyzed.

2. Experimental methods

The whole experimental set-up, including the target temperature controlling system, is the same as that used in the recent studies of CO and NH_3 ices [3,5,8,9]; its sketch is presented in Fig. 1. The time-of-flight (TOF) spectrometer has the target holder connected to the cold finger of a He cryostat. The ^{252}Cf fission fragments, having energies of about 65 MeV (after passing the protection foil of the Cf source), are used for heavy ion bombardment of the ice target. The secondary ions are backward ejected – with respect to the incident projectiles – and accelerated towards the stop detector. The energy loss of α particles passing the target under 45° is used to determine the thickness of the ice layer deposited on the target carrier. For further details see ref. [3].

The substrate for the condensed gases is a thin Au foil (thickness 0.51 μm, diameter 8 mm) stretched over a Cu frame and directly connected to the He-cryostat. To minimize IR radiation exchange with the chamber wall, the target is surrounded by a Cu thermoshield having a temperature of about 50 K. A typical basic residual gas pressure was in the low 10^{-8} mbar. The gases CO and NH_3 were mixed in a separate stainless steel chamber and their relative concentrations were adjusted by means of their partial pressures. For condensation, a weak, steady flow of the mixed gases was directed onto the target foil kept at 25 K, until the ice layer had reached a thickness of about 300 nm. The growth rate was about 20 nm/min.

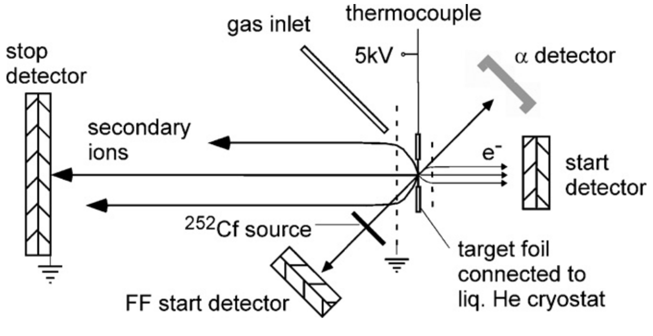

Fig. 1. Sketch of the experimental set-up used to bombard frozen CO–NH_3 by means of ^{252}Cf fission fragment sputtering to produce secondary ions. Details in refs. [3,5].

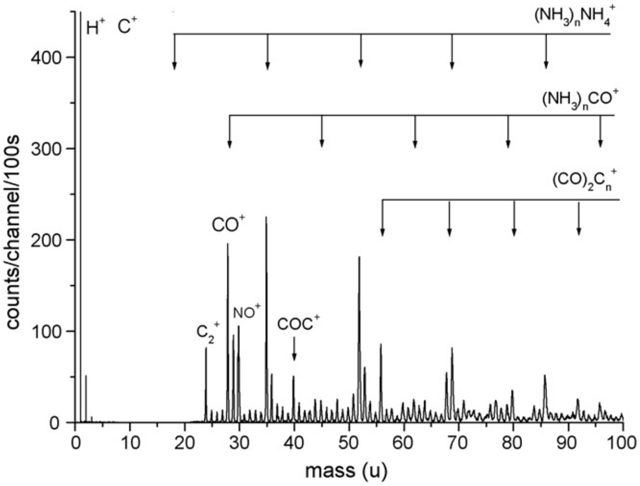

Fig. 2. Mass spectrum of positive ions measured before CO sublimation with CO–NH_3 ice during 30–42 min after interruption of dosing; the target temperature increased from 25 to 29 K in the period.

After dosing, in order to determine the temperature dependence of positive secondary ion yields, the target temperature was slowly increased (0.36 K/min) and acquisition of a series of 40 TOF spectra was started. Among these, 32 spectra were taken for positive ions and used for studying the temperature dependence of positive ion yields. During data acquisition the temperature of the Cu frame was measured continuously by means of a Cooper–Constantan thermocouple, which has a sensitivity of ≤0.008 mV/K close to 25 K. Because of this low sensitivity of the thermocouple at low temperatures and on account of instabilities of the reference temperature, the absolute ice temperature values given in the following are uncertain within ±4° around $T = 30$ K. The sublimation point of CO ice around $T = 30$ K was reached 45.5 min after the interruption of dosing and the start of measurements.

3. Results

The TOF measurements started at a target temperature of 25 K and ended at 130 K, when the ice layer had already disappeared by complete sublimation of the ice deposited on the Au foil. Fig. 2 represents the sum of 6 single spectra, each of them acquired for 100 s, while the target temperature has increased from 25 to 29 K. The mass lines with intensities above 25 counts/channel/100 s are easily attributed to ions observed in measurements with pure CO and NH_3 ices [3,5]. For instance, the $C_n(CO)_2^+$ cluster series is typical for CO ice

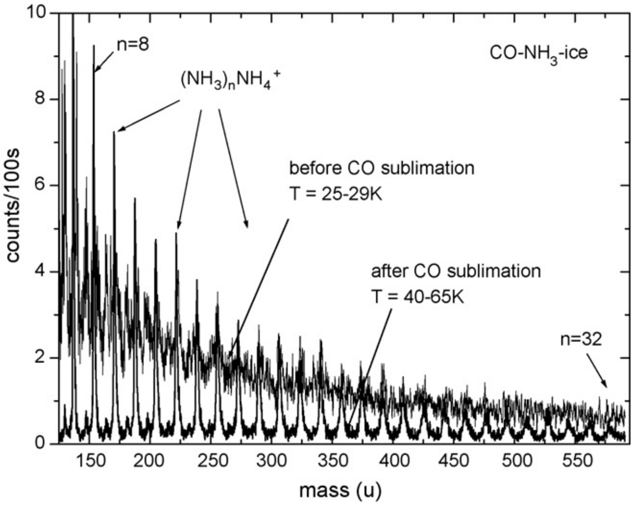

Fig. 3. High mass region of the CO–NH_3 ice spectrum. Upper and lower lines correspond to measurement before and after CO sublimation, respectively.

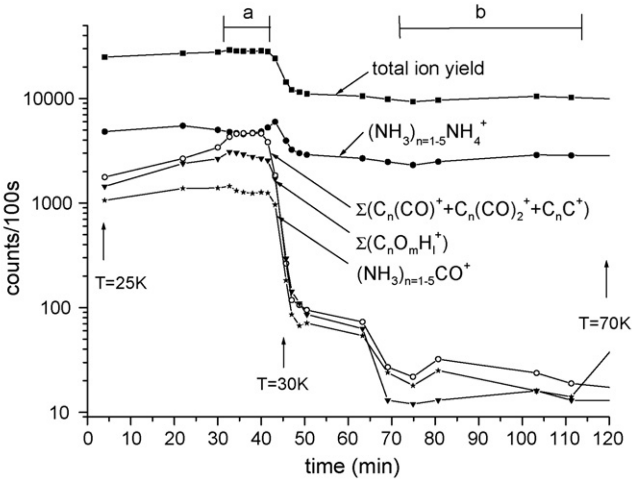

Fig. 4. TTY curves: cluster ion yields as a function of time/temperature. The "total ion yield" (squares); $(NH_3)_nNH_4^+$ yields, summed from $n = 1$–5 (circles); $C_n(CO)^+$, $C_n(CO)_2^+$ and C_nC^+ yields, summed from $n = 1$–6 (open circles); sum of 22 species of $C_nO_mH_l^+$ hybrid molecular ion yields (triangle data), Section 3.3. The intervals a and b mark the time/temperature range before (Fig. 1) and after CO sublimation.

and the $(NH_3)_nNH_4^+$ one for NH_3 ice. Since CO sublimates around $T = 30$ K, the CO specific mass lines disappear from the mass spectra obtained at higher temperatures. This is demonstrated in Fig. 3, where the high mass region of the spectrum shown in Fig. 2 is compared with the spectrum measured after CO sublimation from the same target. The presence of CO in the ice causes an enhancement of ion yields over the whole mass range presented in Fig. 3 by a factor of 3.

The ion yields measured as a function of time (i.e., of the target temperature) are quite characteristic of the ion species. One can distinguish mass lines of ions being specific for (i) pure CO ice, (ii) pure NH_3 ice and (iii) hybrid molecular ions. Most mass lines are a superposition of different ion species, thus, the derived chemical assignment given in the figures concerns the dominant contribution to one mass line. The time–temperature dependence of ion yields, expressed by the so called TTY curves, was determined for more than 80 different ions by setting channel windows over the corresponding mass lines and integrating the counts throughout these windows. In the high mass range, background counts were subtracted.

Fig. 4 depicts the TTY curve of the "total ion yield", i.e. the sum over all ions with masses between 1 and 175 u, of three cluster series always summed over the first five or six members of the series and of the integrated yield of 22 hybrid molecular ions (see also Fig. 8). Two of the cluster curves correspond to CO and NH_3 specific ions, the third one to the hybrid ions $(NH_3)_nCO^+$, which overlap with the very weak series $(NH_3)_nN_2^+$(see Section 3.3). Note that, at around $T = 30$ K, the yields of molecular ions which contain C or CO decrease by 1–2 orders of magnitude, indicating that the CO sublimation is practically finished. The "total ion yield" is almost constant between $T = 25$ and 29 K and drops just above 30 K by a factor 3. It continues on this level until the disappearance of the NH_3 ice layer from the target by sublimation, after which the yields decrease. The last part of the TTY curves shown in Fig. 4 (120–315 min, $T = 70$–130 K) will be analyzed in ref. [6]. TTY curves of various single ions will be presented in the next sections, generally around the sublimation point of CO for temperatures from 25 to 38 K.

3.1. CO specific ions

As seen in Fig. 4, after $T = 30$ K has been reached, the yields of the CO specific cluster ions fall down dramatically. They remain on this low level for about 60 min and then increase steadily, probably as a result of the continuous condensation of rest gas being evaporated from parts of the He cryostat-in particular from the thermoshielding-which had warmed up faster than the target [6].

A comparison between the patterns of the mass spectrum observed with pure CO ice [3] and of the spectrum measured with the CO–NH_3 ice mixture reveals a high similarity. This can be expected because of the relatively high concentration (83%) of CO in the CO–NH_3 mixture. The $C_n(CO)_2^+$ series, the most pronounced cluster series desorbed from pure CO ice, is also seen in Fig. 2. The ion yields of this series have been normalized to the pure CO ice spectrum and compared to the ice mixture. Results are shown in Fig. 7, where the adjusted reference spectrum (dark bars) is superposed on the spectrum of the ice mixture (thin bars). The primarily produced ions C^+ and CO^+ and the cluster series C_nC^+, $C_n(CO)^+$, $C_n(CO)_2^+$ can be recognized. The $(CO)_m^+$ series, well established in the pure CO ice spectrum, is not observable, even above $m = 8$, where the overlap with the C_n series is low (see Fig. 5 of ref. [3]). As seen also in Fig. 4, the TTY curve representing the sum of the C_nX^+ series yields possesses a characteristic shape, which is also reproduced by pure carbon cluster ions, as demonstrated in Fig. 5 for six members of the C_nC^+ series. Regarding the yield distributions of the C_n^+ ion clusters, the periodic intensity alteration with relative maxima at odd n recently reported for pure CO ice [3] was not so well defined for the ice mixture.

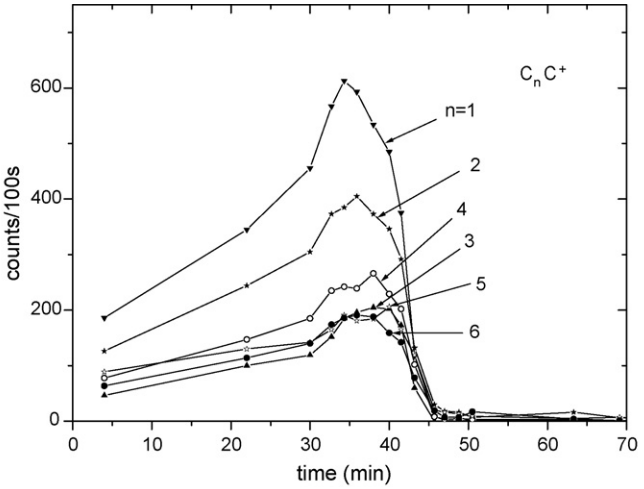

Fig. 5. Time/temperature dependence of yields of the C_nC^+ cluster ions.

3.2. NH_3 specific ions

During the sample temperature interval of 40–65 K (corresponding to the time period from 72 to 115 min (interval b in Fig. 4), the obtained mass spectrum is very clean, meaning that the NH_3 layer left on the target carrier foil after CO sublimation was free of contaminants. It is presented as a bar spectrum in Fig. 6. This spectrum has also been superposed (but not normalized) on the spectrum which has been measured before CO sublimation (see Section 3.3). The spectrum shape is almost identical to that known from our previous work with pure NH_3 ice [5]. An exception is a mass line at $m = 71$ u, being probably $(NH_3)_3H_2NH_4^+$, a reaction product of $(NH_3)_3NH_4^+$ with H_2. Note that the dominant cluster series, $(NH_3)_nNH_4^+$, is always accompanied by the $(NH_3)_nHNH_4^+$ series and that, at higher cluster masses ($n > 8$), even more attached H atoms are observed. Contrary to the $(NH_3)_nNH_4^+$ series, the yields of $(NH_3)_nHNH_4^+$ ions increase with n, the number of ammonia molecules per cluster. At $m = 154$ u (i.e., $n = 8$) the cluster ion and its H-satellite have the same yield (see Fig. 6). The H_n-satellite yields have been always included in the yields of the ammonia cluster ion data.

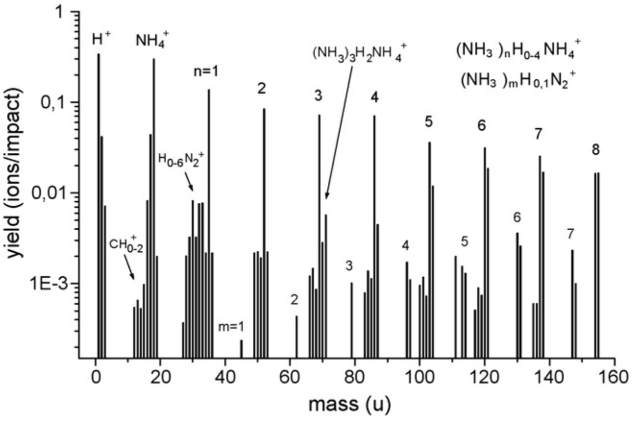

Fig. 6. Bar spectrum of ions ejected from the CO–NH_3 ice target in a temperature interval from 40 to 65 K after CO sublimation. The chemical designation of the mass line at $m = 111$ u is not known.

Table 1
Integral ion yields (ions/impact) of positive ions measured for CO–NH_3 ice before and after CO sublimation

Ions	CO–NH_3 ice	Ions	NH_3 ice
NH_3 specific	1.80	NH_3 specific (total)	1.58
$(NH_3)_{n=0–32}NH_4^+$	1.5	$(NH_3)_{n=0–32}NH_4^+$	1.07
H_1^+, H_2^+, H_3^+	0.24	H_1^+, H_2^+, H_3^+	0.39
CO specific	1.5	Satellite ions	0.054
Hybrid	1.85	N^+, NH^+, NH_2^+, NH_3^+	0.053
Total	5.2	$NH_3)_{n=1–7}N_2^+$	0.017

Satellite ions are $(NH_{0–2})(NH_3)_{n-1}NH_4^+$ and $H_{0–6}$ N_2^+. The yield of "NH_3 specific" includes the yield of the hydrogen ions.

Above $n = 1$, each cluster mass line M_n is accompanied by triple weak lines at $m = M_n$ −1, −2, −3. These lines correspond to reactions between $(NH_3)_n$ and N, NH, NH_2, the dissociation products of NH_3, and can be assigned as $(NH_{0–2})(NH_3)_{n-1}NH_4^+$. The ions N^+, NH^+, $NH_2^+$and NH_3^+, a group having masses between 14 and 17 u, also react with NH_3 and the fragments of NH_3, the resulting ion group in Fig. 6 is $H_{0–6}$ N_2^+. The integral yield of all these satellite lines accounts for 0.054 ions/impact. The yields of the $(NH_3)_nNH_4^+$ series ($n = 0$–32), the hydrogen ions H_1^+, H_2^+, H_3^+ and other relevant ions of the bar spectrum shown in Fig. 6 are listed in Table 1. It is also seen in Fig. 6 that the $(NH_3)_mN_2^+$ series has a relatively low yield and exhibits an opposite behavior with respect to all other cluster series: its ion yield increases with m, the number of cluster constituents. Such clusters are probably formed by the reaction between an ionized N_2 (a surface contaminant) and neutral ammonia clusters. Their yields increase with time due to a persistent rest gas condensation [6].

3.3. Hybrid molecular ions

Secondary molecular ions containing C and O, or N and H form the CO or the NH_3 specific ions; on the other hand the groups C/N, C/H, N/O, O/H, C/N/O, N/O/H and C/N/O/H form the hybrid molecular ions. The large number of possible hybrid species and the frequent coincidence in their masses makes this study quite complex. The TTY diagram, representing the desorption yield dependence on the target temperature, is a practical method for the elucidation of the hybrid species genesis. The sublimation of one of the ice constituents has a relatively small influence on the desorption yield of the other constituents, but, on the other hand, it has a strong influence on that of the hybrid molecular ions and a dramatic effect on that of the corresponding specific ions.

The low mass region, defined by $10 < m < 98$ u, is displayed in Fig. 7. The mass spectrum measured before CO sublimation (thin bars) is compared with that measured after CO sublimation (thick bars). In addition, the CO ice reference spectrum (dark bars) is superposed after being normalized to the strong $C_n(CO)_2^+$ series. The CO specific ions can appear only at masses multiple of 4. All the thin mass lines which do not overlap

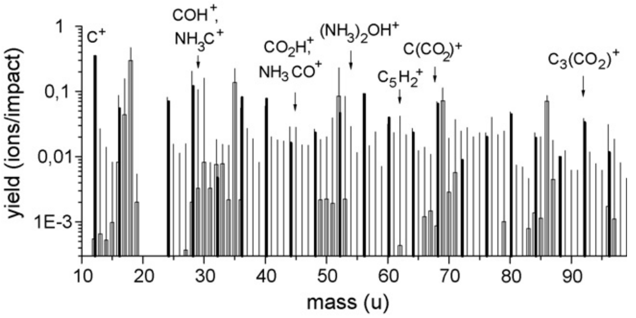

Fig. 7. Low mass region of the bar spectrum obtained for CO–NH$_3$ ice at $T = 25$–29 K (thin bars). The dark bars is the same CO reference spectrum: the four strongest $C_n(CO)_2^+$ lines are normalized (0.65) to those of the spectrum measured with the same CO–NH$_3$ ice target but after CO sublimation (thick bars).

with black or thick mass lines are attributed to hybrid molecular ions, but those which have a height distinctly above the black or/and thick bars indicate the position of hybrid molecular ions.

The TTY curves of nine ions having masses between 25 and 45 u are shown in Fig. 8. In this mass range, four groups of ions can be identified by their TTY behavior at around 29 K:

(i) the NH$_3$ specific cluster ions, represented by the $NH_3NH_4^+$, $NH_3NH_2^+$ and NH_3N^+ ions. Their TTY curves have a pronounced peak (or at least a shoulder) at $T = 29.5$ K and drop a factor of 2 to 3 after that;
(ii) the NH$_3$- or N-containing hybrid ions, represented by the NO^+, NH_3OH^+ and NH_3CO^+ ions. Their TTY curves drop one order of magnitude at 29 K;
(iii) the C-, O- or H-containing hybrid ions, such as COH^+ and C_2H^+. Their yields drop by more than one order of magnitude;
(iv) the CO specific ions, represented by the CO^+ ion. Its TTY curve drops almost two orders of magnitude when the CO sublimation temperature is reached (see also Figs. 3 and 4).

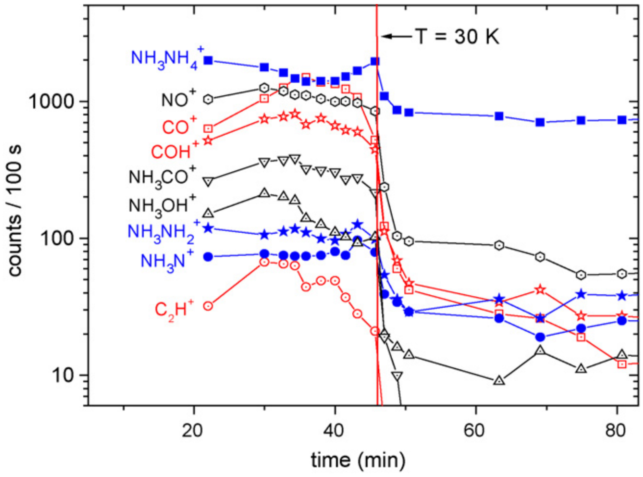

Fig. 8. TTY curves (ion yield dependence on time and temperature) of several positive ions between $m = 25$ and 45 u. The solid symbols belong to NH$_3$ specific ions. The open symbols correspond to CO ions or to hybrid molecular ions.

Table 2
Yields (ions/impact) of positive hybrid molecular ions

Ions	CO–NH$_3$ ice
$CH_{1,2,3}^+$	0.047
$C_2H_{1,2,3}^+$	0.043
$C_3H_{1,2,3}^+$	0.054
COH^+	≅0.1
NO^+	0.15
$(NH_3)_nCO^+$	≅0.15
$(NH_3)_{n=1,2}OH^+$	0.02
Total hybrid (%)	1.85 (35)

Some of the mass lines can be composed by ions of different types. For instance, the line at $m = 30$ u is probably a superposition of NO^+, $N_2H_2^+$ and COH_2^+ (formaldehyde) as learned from Fig. 7. The existence of the $N_2H_2^+$ ion is a reasonable explanation for the fact that the TTY curve-in Fig. 8 assigned as NO^+ curve-does not fall after CO sublimation as low as those of the other ions.

Above mass 50 u, the possible combinations of carbon, oxygen and hydrogen atoms become too manifold to specify the chemical designation of the hybrid ions. In fact, at higher masses, the thin bars build a continuous pattern of lines in which the lines of CO and NH$_3$ specific ions are embedded. The yields of positive hybrid ions are given in Table 2.

The C_nH_m groups

The series of hydrocarbon ions $CH_{1,2,3}^+$, $C_2H_{1,2,3}^+$, $C_3H_{1,2,3}^+$ are easily recognized at masses 13–15, 25–27 and 37–39 u in Fig. 7. It should be noted that only the mass line of C_2H^+ at $m = 25$ u is free of possible contributions of other ions. Regarding the general spectral pattern over the whole mass range, some periodic features are recognized. In particular, the gaps between the thick and dark mass lines are filled with lines of C_nH_m containing compounds, such as the lines corresponding to $m = 41$, 42 and 43 u and which are probably a superposition of $C_3H_{5,6,7}^+$ and $C_2OH_{1,2,3}^+$. This means that, above $m = 40$ u, the C_nH_m groups can also be groups of type $C_nO_mH_l$.

The $C_nO_mH_l^+$ ions

In Fig. 9, the TTY analysis is extended to 22 ions having the $C_nO_mH_l^+$ structure and whose mass lines are probably not superposed by contributions from CO and NH$_3$ specific ions. Their TTY curves are sorted according to the ion's mass and normalized to a mean curve for each group. The shape of the TTY curve (dashed line) relative to the C_2H^+ ion is typical for most of these ions, which correspond to the thin mass lines represented in Fig. 7. Their common behavior is the yield decreasing at about 28.5 K, distinctly below the sublimation temperature of CO (30 K). Note that the behavior of the integral yield of these 22 hybrid molecular ions, shown in Fig. 4, has a shape quite different from the other curves shown. Above the mass range

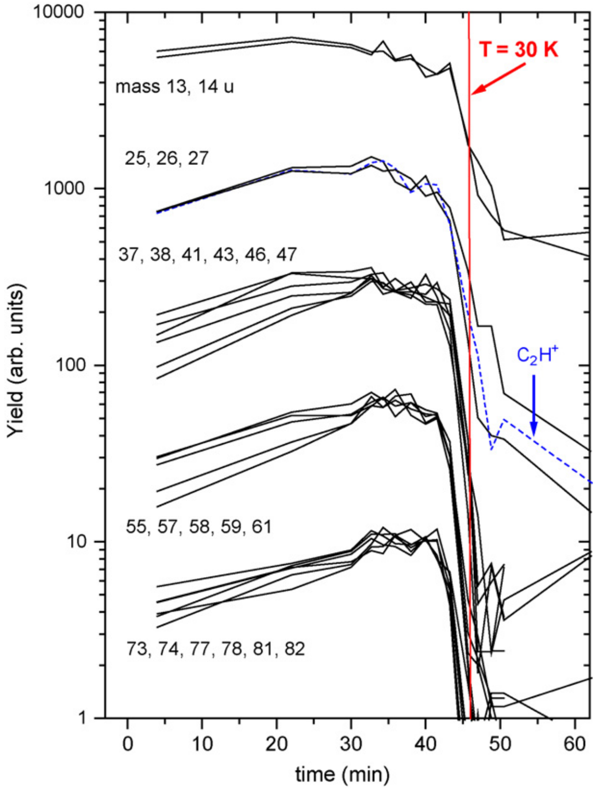

Fig. 9. TTY curves for 22 ions having supposedly the structure $C_nO_mH_l^+$. The curves are grouped with respect to five mass intervals. The TTY curves of each group are normalized to a mean curve of each group.

considered in Fig. 9, the pattern of $C_nO_nH_l^+$ mass lines (including lines of CO specific ions $\mathrm{C_nO_m}^+$) obviously continues until $m = 590$ u, as seen in Fig. 3. In the bar spectrum partially shown in Fig. 7, at higher masses the thin bars build a continuous pattern of lines, in which the lines of CO and NH_3 specific ions are embedded.

The $(NH)_nCO^+$ and $(NH)_nOH^+$ ions

By means of the underlying pure NH_3 spectrum and the normalized CO reference spectrum, the integral yields of CO specific-, NH_3 specific- and hybrid-molecular ions were estimated and are given in Table 1. The emission of NO^+ ions was already known from previous experiments on CO ice contaminated by N_2 [3,4]. Reaction products between the highly produced primarily ions, C^+, CO^+ and OH^+ with NH_3 are expected. Hybrid ions, such as NH_3C^+ or $(NH_3)_2C^+$, were not clearly observed, but NH_3OH^+ and $(NH_3)_2OH^+$ were indeed identified by means of the TTY curves. The series $(NH_3)_nCO^+$ members have a relatively small yield, as shown in Fig. 1, and their mass lines coincide with those of the very weak series $(NH_3)_nN_2^+$ present in the spectrum after the CO sublimation (see Fig. 6). As seen in Fig. 4, the TTY curve of the sum of the first five members of the $(NH_3)_nCO^+$ series has the expected shoulder at 29 K and above 30 K a shape similar to that of CO specific ions. Table 2 presents a rough estimate for the yield of the $(NH_3)_nCO^+$ series.

4. Discussion

In the preceding section, the flux of positive ions ejected from CO–NH_3 ice by fission fragment impact was sorted as CO specific ions, NH_3 specific ions and hybrid molecular ions. The spectral patterns of the first two components are observed to be quite similar to that observed with the pure ices. The dominant ion cluster series before and after the CO sublimation, $(NH_3)_nNH_4^+$, is created by attachment of H^+ in ammonia clusters, the protons being released by coulomb interaction of the impacting heavy ion with ammonia molecules. Since the source for both protons and $(NH_3)_n$ is the content of ammonia in the ice mixture, one should expect a much higher yield of $(NH_3)_nNH_4^+$ ions after the CO sublimation, once the molecular ratio of NH_3 and CO increases by two orders of magnitude after the CO sublimation (from 1:5, before, to 1:$\leq$0.05, after). However, data from Fig. 4 and Table 1 show that, instead, the $(NH_3)_nNH_4^+$ ion yield decreases slightly after CO sublimation. One possible explanation for this apparent contradiction is that the amorphous ice structure of the NH_3 component formed during condensation is preserved during the sublimation process of CO. It is very liked that the target porosity increases during the CO sublimation, changing the stopping power as well as formation and dynamics of secondary ions.

In the ice mixture, the CO molecules fill the relatively open NH_3 structure [6]; thus, two track-surrounding materials are subject to excitation (and ionization) by the passing projectile: one relative to the CO fraction and another one concerning the NH_3 fraction. This would explain why the yield of NH_3 specific ions remains nearly constant and why the total ion yield of positive ions is distinctly higher before CO sublimation than after (see Fig. 4). The total yield deceases by a factor of 3 and not 5, but one has to be aware that the capture probability for protons in $(NH_3)_n$ and the neutralization probability of primarily produced ions in mixed and pure ices can also play a role.

For fission fragments of 65 MeV energy penetrating the CO–NH_3 ice, δ-electrons carry electronic excitation about 45 nm deep into the material surrounding the nuclear track. In the track centre, the energy per molecule is about 60 eV and decreases in radial direction as $1/r^2$ (see, for instance, ref. [10]). At a radial distance of 2.5 nm, the energy density is still 11 eV/molecules, sufficient for dissociation of CO and NH_3 molecules. These estimated figures lead to some hundred dissociated molecules per nm track length, i.e., delivering a relatively high density of free carbon, oxygen and hydrogen, either atomic or molecular. In case of pure CO ice, the high carbon density generates a complex spectrum of $(CO)_mC_n^+$ ions up to masses of 450 u (see Fig. 5 of ref. [3]). A similar spectrum of CO specific ions is part of the mass spectrum shown in Figs. 2 and 7. Its integral yield is 1.5 ions per impact, 1.6 times lower than the yield obtained with the pure CO ice [3].

Dissociation of ammonia provides hydrogen atoms and molecules as well as N, NH and NH_2 in the track plasma. As mentioned in Section 3.2, in the case of NH_3 ice, reactions among the nitrogen containing species lead to the satellite ions contributing with only 3.4% to the total ion yield (see Table 1). The presence of unbound hydrogen in the track plasma is noticed

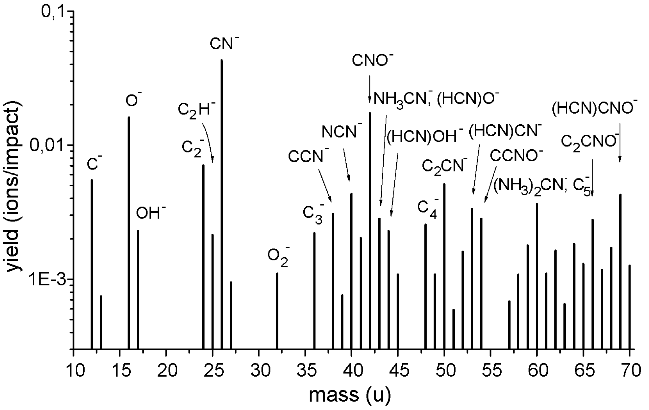

Fig. 10. Mass spectrum of negative ions ejected from CO–NH_3 ice before CO sublimation ($T = 25$ K). The chemical designation of mass lines $m > 36$ u is tentative.

by attachment of one H atom to the $(NH_3)_nNH_4^+$ clusters. Above $n = 8$, more than one attached H atom have been observed. Therefore, the cross section for H attachment seems to increase with the number of NH_3 molecules per cluster.

A pertinent question is whether the hydrogen content in the track plasma is sufficient for the formation of the observed $C_nO_mH_l^+$ ions. It is already established that the projectile considered induces the production of carbon cluster ions, C_n^+ and C_n^-, as well as the hydrocarbon ions $C_nH_{m>0}^+$, $C_nH_{m=1-3}^-$, the latter being identified in the low mass regime with yields of $\cong$0.7 and 0.005 ions/impact, respectively. In a hot, high density gas consisting of carbon and hydrogen atoms, reactions between carbon species would lead to C_n and reactions between C_n and hydrogen to hydrocarbons C_nH_m. This has been studied by hydrodynamical calculations of a C-H-plasma relaxing into vacuum by adiabatic expansion [11,12]. In principle, the production of saturated hydrocarbons is favored. Regarding ionized species, this leads to a preferential production of $C(CH_2)_n^+$ and C_nH^- for even n, both being observed with ices of alkanes and other pure hydrocarbon compounds [11]. In the present spectra, the $C_n^{\pm}$ peaks are usually the highest of the $C_nH_m^{\pm}$ groups; the subsequent peaks ($m = 1$–3) decrease with m (see Figs. 6 and 9). It is concluded that in the track plasma the consumption of hydrogen by collisions with the C_nCO_m is too high to allow the production of species with a higher number of hydrogen adducts. At a CO/NH_3 ratio of 5:1, the relative density of unbound hydrogen in the track plasma should be distinctly lower than the density of CO specific species. After CO sublimation, the CO content of the ice decreases by more than two orders of magnitude, the very rare C_2^- ions collide with a relatively high density hydrogen gas and a pronounced C_2H^- signal appears in the negative ion mass spectrum, eight times higher than the C_2^- signal.

The negative ion spectrum obtained before CO sublimation (see Appendix A and Fig. 10) is governed by hybrid molecular ions, particularly the most intensive, very stable cyanide ion CN^- (0.05 ions/impact) and the weaker cyanate ion CNO^- (0.02 ions/impact), both of which seem to react with various species of the track plasma (see Fig. 10) including hydrogen cyanide HCN. Because the first three members of a cluster series $(HCN)_nCNO^-$ were identified, the production of relatively large amounts of hydrogen cyanide is required. Based on this, the reaction $CO + NH_3 \rightarrow HCN + H_2O$ is expected to occur between the matrix constituents.

The C^+ and CO^+ ions, the two main cations produced primarily by heavy ion impact in CO ice [2,3], do not react preferentially with NH_3 molecules. Such reaction would produce the NH_3C^+ species (mass 29 u), but the TTY curve corresponding to this mass and presented in Fig. 8 does not show a substantial contribution of NH_3 containing molecular ions; we suggest formation of the COH^+ ion. The $(NH_3)_nCO^+$ series is relatively weak (~0.15 ions/impact). This means that the high total ion yield, when the CO:NH_3 ice composition is 5:1, is due to the CO specific ions, particularly the three C_n cluster series and the hybrid ions having the $C_nO_mH_l^+$ structure; the contribution of the latter species is 35% of the total ion yield.

5. Conclusions

The essential results of the present experimental research concern the production of organic hybrid molecular ions in the nuclear track plasma. The results were mainly deduced from mass spectra of positive secondary ions ejected from a CO–NH_3 ice mixture bombarded by ^{252}Cf fission fragments. The spectra were measured as a function of temperature between $T = 25$ and 70 K, a range, which includes the CO ice sublimation around 30 K.

The search for hybrid molecular ions was very successful. About one third of the total ion yield (5.2 ions/impact) accounts for organic ions species having the $C_nO_mH_l^+$ structure. Positive hybrid molecular ions, which contain N or NH_3, are relatively rare: their yield is about 6% of the total positive ion yield. Only a few organic ions such as the hydrocarbons $C_{n\leq 3}H_{1,2,3}^+$ could be identified in the low mass region. However, the continuous spectral pattern of the hybrid molecular ions implies that with low yields other ions such as CH_4^+ (methane), COH_2^+ (formaldehyde) or CH_3OH^+ (methanol) are also generated and ejected. The basic reaction partners are CO, the dissociation product C of CO and the dissociation products H and H_2 of NH_3. The density of these atoms or molecules in the track plasma has to be high enough to allow, by fast gas phase reactions, the generation of $C_nO_mH_l^+$ ions with masses as high as 500 u. The relative hydrogen density in the track plasma is, however, not sufficiently high to allow the preferential production of saturated hydrocarbon species such as $(CH_2)_nC^+$ and C_nH^-. Up to 500 u, the spectrum of positive hybrid molecular ions seems to cover nearly the whole mass range.

The negative ion intensity is more than one order of magnitude lower than the intensity of positive ions. The very stable CN^- ion carries almost 20% of the negative ion yield; it is probably formed by dissociation of HCN into H^+ and CN^-. The presence of $(HCN)_n$ clusters indicates that a relatively high amount of HCN is formed in the track plasma and ejected. The total neutral molecule yield can be two to four orders of magnitude higher than the ion yield. A rough estimate leads then to 200–20000 hybrid molecular ions per impact in the flux of sputtered particles.

In contrast to the CO ice bombardment, for which case a high density of carbon atoms in the nuclear track has been reported recently, impacts on the CO_2 ice do not deliver free carbon [3,4]. It is therefore understandable that the mass spectrum obtained with CO_2–H_2O ice (ratio 1:1) exhibits a very low yield of C_n^+ clusters or of light hydrocarbons such as $C_2H_3^+$ ions (see Fig. 7 in ref. [2]). The main contribution-about 50%, to the yield of hybrid molecular ions stems from COH^+ and $COOH^+$, which require hydrogen in the track plasma, but not carbon.

From our findings it follows that CO in the icy state mixed with hydrogen compounds such as NH_3 and H_2O is much better suited for the production of organic material by MeV ion impact than CO_2. On the other hand, CO can be kept in the ice mixture only below an ice temperature of 30 K. Such temperatures are present on interstellar objects such as comets or grains, but not on planets or moons in the solar system.

Acknowledgements

The authors would like to acknowledge the Brazilian Agencies CNPq, FAPERJ and FAPESP for their support. P. Iza thanks CLAF for his scholarship. The LNLS staff is acknowledged for support during the experiments.

Appendix A

A.1. Negative ions

Within the sequence of positive ion spectra, some mass spectra of negative ions were measured by changing momentarily the polarity of the target voltage. In particular, a spectrum was taken before CO sublimation at $T = 25$ K and another shortly after CO sublimation at $T = 50$ K. It was observed that the relatively low total negative ion yield increased from ∼0.35 ions/impact to 0.6. Before CO sublimation, the mass spectrum, presented as a bar spectrum in Fig. 10, shows the CO specific ions $(C_{n=1\text{–}5})^-$ and $(O_{1,2})^-$ with an integral yield (0.040 ions/impact) two times higher than that obtained with pure CO ice [4]. With exception of the weak H^- signal (0.009 ions/impact), NH_3 specific negative ions were not observed. All other ions represented by mass lines in Fig. 10 seem to be hybrid molecular ions. Among the lightest ions, the (low intensity) hydrocarbon ions CH^-, $C_2H_{1\text{–}3}^-$ and, probably, $C_3H_{1\text{–}3}^-$ (whose integral yield is about 0.008 ions/impact) were identified. On the other hand, the CN^- and CNO^- ions were observed with relatively high yield: they probably also react with C, O, NH_3 and HCN, all of them being abundant species in the nuclear track plasma. The chemical designation of possible reaction products is tentatively assigned in Fig. 10. On account of the generally low yields of the negative ions, the cluster series based on $(NH_3)_n$, C_n and $(HCN)_n$ are difficult to identify. An exception is the series $(HCN)_nCNO^-$, for which the first three members of the series were clearly observable (the integral yield is 0.004 ions/impact).

After CO sublimation ($T = 50$ K), the yields of the CO specific ions C^- and C_2^- decrease by a factor of about 5, while those of the carbon containing hybrid ions CN^- and CNO^- decrease by only a factor of 2. The latter two ions react with the ammonia clusters, which are relatively more abundant after the CO sublimation, and generate two pronounced cluster series $(NH_3)_nCN^-$ and $(NH_3)_nCNO^-$. These two series have also been observed before CO sublimation but with much lower intensity. After CO sublimation, the series $(HCN)_nCNO^-$ vanishes.

Two other findings attract attention: (i) the series $(NH_3)_nNH_2^-$, well established from our previous studies of pure NH_3 ice [5], forms at $T = 50$ K (after the CO sublimation) again a relatively strong spectral structure, which is, however, not visible before the CO sublimation; (ii) the yield ratio of the $(C_{n=1\text{–}4})^-$ and $(C_{n=1\text{–}4}H)^-$ ions decreases by a factor 5 after the CO sublimation (from ∼4 to ∼0.8). This phenomenon is particularly expressed for C_2^- and C_2H^-, whose yield ratio decreases from 3.3 to 0.12. The C_2H^- signal becomes one of the strongest signals after CO sublimation.

References

[1] L.S. Farenzena, V.M. Collado, C.R. Ponciano, E.F. da Silveira, K. Wien, Int. J. Mass Spectrom. 243 (2005) 85.

[2] C.R. Ponciano, L.S. Farenzena, V.M. Collado, E.F. da Silveira, K. Wien, Int. J. Mass. Spectrom. 244 (2005) 41.

[3] L.S. Farenzena, R. Martinez, P. Iza, C.R. Ponciano, M.G.P. Homem, A. Naves de Brito, E.F. da Silveira, K. Wien, Int. J. Mass. Spectrom. 251 (2006) 1.

[4] C.R. Ponciano, R. Martinez, L.S. Farenzena, P. Iza, E.F. da Silveira, M.G.P. Homem, A. Naves de Brito, K. Wien, J. Am. Soc. Mass Spectrom. 17 (2006) 1120.

[5] R. Martinez, C.R. Ponciano, L.S. Farenzena, P. Iza, M.G.P. Homem, A. Naves de Brito, K. Wien, E.F. da Silveira, Int. J. Mass. Spectrom. 253 (2006) 112.

[6] R. Martinez, C.R. Ponciano, L.S. Farenzena, P. Iza, M.G.P. Homem, A. Naves de Brito, E. F. da Silveira, K. Wien, in preparation.

[7] K. Wien, Nucl. Instrum. Meth. B 131 (1997) 38.

[8] V.M. Collado, L.S. Farenzena, C.R. Ponciano, E.F. da Silveira, K. Wien, Surf. Sci. 569 (2004) 149.

[9] L.S. Farenzena, P. Iza, R. Martinez, F.A. Fernandez-Lima, E. Seperuelo Duarte, G.S. Faraudo, C.R. Ponciano, M.G.P. Homem, A. Naves de Brito, K. Wien, E.F. da Silveira, Earth, Moon, and Planets 97 (2005) 311–329.

[10] C.C. Watson, T.A. Tombrello, Rad. Eff. 89 (1985) 263.

[11] E.R. Hilf, W. Tuszynski, B. Curdes, J. Curdes, M. Wagner, K. Wien, Int. J. Mass Spectrom. Ion Proc. 125 (1993) 101.

[12] M. Wagner, K. Wien, B. Curdes, E.R. Hilf, Nucl. Inst. Meth. B82 (1993) 362.