Electronic Sputtering Produced by Fission Fragments on Condensed CO and CO₂

C. R. Ponciano, R. Martinez, L. S. Farenzena, P. Iza, E. F. da Silveira

Department of Physics, Pontifícia Universidade Católica, Rio de Janeiro, Brazil

M. G. P. Homem and A. Naves de Brito

Laboratório Nacional de Luz Sincrotron, Campinas, Brazil

K. Wien

Institute of Nuclear Physics, Technical University, Darmstadt, Germany (Retired)

Condensed CO and CO₂ are bombarded by ~ 65 MeV ²⁵²Cf fission fragments and the desorbed ions are analyzed by time-of-flight mass spectrometry as a function of target temperature, in the ranges 25–33 K and 75–91 K, respectively. Absolute desorption yields are measured up to complete ice sublimation. The mass spectra of both ice targets reveal the emission of: (1) low mass ions, produced by direct Coulomb interaction of the highly charged projectiles and δ -electrons with CO and CO₂, and (2) pronounced series of cluster ions. The basic ice cluster structures (CO)_n and (CO₂)_n are present in the emitted cluster series such as (CO)_nCO⁺, (CO₂)_nCO₂⁺, or (CO₂)_nCO₃⁺. In the case of CO ice, however, the intense production of the series C_n⁺, C_n⁻, and (CO)_mC_n⁺ shows that C_n is the main cluster structure, consequence of a higher concentration of free carbon atoms in the nuclear track plasma of CO ice than in that of CO₂ ice. Ion cluster abundance is observed to decrease exponentially with cluster mass. The decay constant is $k_n \cong 0.13$, about the same for series based on (CO)_n and (CO₂)_n, but a factor 3.3 higher for the C_n series. The C_n clusters are formed by gas-phase condensation, but the (CO)_n and (CO₂)_n clusters are produced by fracturing of the highly excited solid around the nuclear track. A dramatic reduction of the ion desorption yield is observed near $T = 29$ K for CO and near $T = 85$ K for CO₂, when fast sublimation occurs and ice thickness vanishes. Close to sublimation temperature, the decay constant of the (CO)₂C_n⁺ series increases due to a decreasing formation probability of large C_n clusters. (J Am Soc Mass Spectrom 2006, 17, 1120–1128) © 2006 American Society for Mass Spectrometry

Small molecules constituted by the abundant elements H, C, N, and O have a large occurrence as ices in comets and in the outer solar system. For instance, H₂O, CO, and CO₂ are the three most abundant molecules in the comet Hale-Bopp [1]. These spatial ices are constantly bombarded by energetic photons and cosmic rays, which induce chemical reactions and sputtering on their surfaces. Early in 1978, Brown and coworkers reported the sputtering produced by MeV protons on ice [2]. Since this work, the study of sputtering of water ice has been pursued by many other groups (e.g., Baragiola et al. [3] and references therein). An overview of the radiation effects on ice chemistry has been published by Hudson and Moore [4] and the chemistry in CO₂-H₂O ice induced by magnetospheric plasma ion bombardment has been discussed by Delitsky and Lane [5]. Less attention has

been given to CO ice electronic sputtering, one of the reasons for which its secondary ion mass spectrometry (SIMS) analysis employing MeV heavy ion bombardment was revised recently by the authors [6].

The atmosphere composition above such frozen surfaces depends obviously on thermal desorption, but also on desorption induced by various types of radiation including heavy ions in the electronic sputtering regime. Understanding of the electronic sputtering process on ice mixtures, particularly knowing of the corresponding desorption yields, is required for studying such desorption phenomena. The aim of the present work is to contribute to such effort by studying and comparing ion emission from two ice films: frozen CO and frozen CO₂. Our experimental investigations started on pure frozen H₂O [7] and then on frozen gas mixtures of H₂O and CO₂ [8, 9] using targets at liquid nitrogen temperature, which is close to the sublimation temperature of solid CO₂. Very recently, a He cryostat became available, providing target temperatures down to ~ 25 K. Initially, the new instrumentation was used to investigate pure frozen CO targets at 25 K [6]. Then, the

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Address reprint requests to Dr. E. F. da Silveira, Department of Physics, Pontifícia Universidade Católica, 22543-970 Rio de Janeiro, Brazil. E-mail: enio@vldg.fis.puc-rio.br

studies were extended to frozen CO_2 to allow a comparison of the two carbon oxide ices. These experiments include studies of the temperature dependence of desorbed ion yields for both targets up to complete ice film sublimation.

Macfarlane and Torgerson [10] have shown that highly energetic heavy ions are capable of desorbing large molecules from an organic target as intact species or as their fragments. They developed a technique called ^{252}Cf -plasma desorption mass spectrometry (PDMS), which proved to be suitable for the analysis of ices, see for instance, [11–17]. In the presented work, the PDMS technique is applied to the study of the ion emission of CO and CO_2 ices under bombardment by fast projectiles. Both measurements were performed in the same analyzing chamber, using the same procedure and at the same UHV conditions, allowing a direct comparison of the results. The experimental methods are briefly described; then the experimental results obtained for pure CO and CO_2 targets are compared and discussed. Data correspond to mass spectra acquired at low—almost constant—temperature as well as yield measurements as a function of ice temperature. The temperature dependence of ion yields is used to complement the secondary ion species assignment by identifying their origin: e.g., are they only produced from the CO or CO_2 ice or are there also contributions from the rest gases? When sublimation/condensation is involved, temperature/time dependence measurements are often related to layer thickness dependence measurements.

Experimental

The experimental set-up used for these comparative measurements is presented in Figure 1 of reference [6]. It is a time-of-flight (TOF) spectrometer with a target connected to the cold finger of a He cryostat. ^{252}Cf fission fragments having energies of about 65 MeV (after passing the protection foil of the Cf source) were used for heavy ion bombardment of the ice target. They penetrated the ice layer at the target's front side, from where target ions were 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° was used to determine the thickness of the ice layer deposited on the target carrier. For further details see reference [6].

The Ice Targets

The substrate for the condensed gases was a thin Au foil (thickness $0.51\ \mu\text{m}$, diameter 8 mm) mounted onto a Cu frame, directly connected to the He-cryostat. To minimize IR radiation exchange with the chamber wall, the target was 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 range. A fresh layer of CO or CO_2 ice was condensed onto the target at a

Figure 1. TOF mass spectra of positive ions emitted from (a) CO ice at $T = 25\ \text{K}$ and (b) CO_2 ice at $T = 75\text{--}79\ \text{K}$. The arrows in (a) mark mass lines, which do not overlap mass lines of other ions. In (b) above, $m = 50\ \text{u}$ the ion yields have been multiplied by a factor of 6.

temperature of $T = 25\ \text{K}$ or $T = 75\ \text{K}$, respectively, until a thickness of about 200 nm was reached. The growth rate was about 20 nm/min. Then the CO or CO_2 gas dosing was stopped and the TOF measurements started.

Measuring the Temperature Dependence

For measuring the temperature dependence of positive desorbed ion yields, after dosing, the target temperature was slowly increased and acquisition of a series of 80–120 TOF spectra was started. During data acquisition, the temperature of the Cu frame was measured continuously by means of a Copper-Constantan thermocouple, which has a sensitivity of $\leq 0.008\ \text{mV}/1^\circ$ below 25 K. In case of CO ice, the periodical measurements were started at a target temperature of 25 K and stopped at 33 K, and in the case of CO_2 ice, at 75 K and at 91 K, respectively.

Ion Desorption from Frozen CO and CO_2

Positive ions. Figure 1a and b show mass spectra of positive ions emitted from CO ice and CO_2 ice, the first

Table 1. List of the primarily produced ions (PPI) and the observed cluster ion series (CIS). Absolute yields (ions/impact) of the PPI and of the CIS, the later summed over $n = 1$ –8, are given. The decay constant k_n is the exponential slope of the yields of cluster ions with $n > 1$

Ice	PPI	Y_{PPI} (ions/impact)	Cluster series	Y_{CIS} ($n = 1$ –8) (ions/impact)	k_n ($n > 1$)
CO	C ⁺	0.61	$C_n C^+$	0.46	0.58
	O ⁺	0.097	$C_n(\text{CO})^+$	0.37	0.48
	—	—	$C_n(\text{CO})_2^+$	0.46	0.21
	CO^+	0.21	$(\text{CO})_n \text{CO}^+$	0.24	0.17
	C [−]	0.0026	$C_n C^-$	0.011	—
	O [−]	0.0096			
CO ₂	C ⁺	0.37			
	O ⁺	0.23	$(\text{CO}_2)_n \text{O}^+$	0.074	0.11
	CO^+	0.51	$(\text{CO}_2)_n \text{CO}^+$	0.16	0.032
	O_2^+	0.72	$(\text{CO}_2)_n \text{O}_2^+$	0.23	0.23
	CO_2^+	0.58	$(\text{CO}_2)_n \text{CO}_2^+$	0.13	0.19
	C [−]	0.0066			
	O [−]	0.22			
	CO_3^-	0.31	$(\text{CO}_2)_n \text{CO}_3^-$	0.17	0.018

taken at $T = 25$ K and the second at $T = 75$ – 79 K, after gas condensation on target. All the mass lines of CO as well as of CO₂ specific ions should appear only at masses multiple of 4; thus, lines with intermediate values must be due to impurities in the ice, i.e., to contamination of the ice surface via condensation of the vacuum rest gases, mainly H₂O, N₂, and O₂. As shown in a later section on “Temperature Dependence of Ion Yields,” dedicated to ion yield dependence on ice temperature, the intensities of the rest gas ions H⁺, H₂O⁺, H₃O⁺, and NO⁺ increase with the warming-up time, whereas the intensity of CO and CO₂ specific ions decreases. Reaction products between contaminants and matrix constituents were found, such as the hybrid ions COH⁺ and COOH⁺, a result of CO₂ ice contamination by H₂O [8, 9]. Apart from background ions, mainly two types of ions contribute to the spectral pattern of Figure 1a and b: the primarily produced ions and the cluster ions. In the present context, primarily produced ions, PPI, are defined as the products of direct Coulomb interaction of the multiply charged projectiles as well as of δ -electrons with target atoms or molecules. For CO ice, the PPI are C⁺, O⁺, and CO⁺; for CO₂ ice, C⁺, O⁺, CO⁺, O₂⁺, and CO₂⁺. All these PPI can be explained by dissociation of the molecules CO and CO₂ or by the ionization of intact molecules themselves. Their ionization occurs mainly before or during dissociation. For further discussion of ion formation see the Discussion section.

In the range above the masses of the PPI, the spectra are dominated by series of cluster ions. For CO and CO₂ ices, the matrix molecules form neutral cluster series (CO)_n and (CO₂)_n, respectively. Both series become ionized by attachment of the PPI CO⁺ or O⁺, CO⁺, O₂⁺, and CO₂⁺, respectively. The corresponding series of cluster ions are (CO)_nCO⁺ in Figure 1a, and (CO₂)_nO⁺, (CO₂)_nCO⁺, (CO₂)_nO₂⁺, and (CO₂)_nCO₂⁺ in Figure 1b. This simple way of cluster ion formation is, however, not applicable to all PPI: O⁺ combines with (CO₂)_n, but

not with (CO)_n and, inversely, C⁺ combines with (CO)_n but not with (CO₂)_n. Furthermore, emitted carbon atoms exhibit in the case of CO ice desorption a strong tendency to form C_n clusters, whereas in the case of CO₂ ice hardly any C_{n > 1}⁺ or C_{n > 1}(CO)⁺ ion is observed. In Figure 1a, the pure carbon cluster series C_nC⁺ is well established; in Figure 1b, the C₃⁺ signal is already almost invisible. In the case of CO ice, C_n and (CO)_n combine and build the general series (CO)_mC_n⁺ with $m = 0, 1, 2, \dots$. Three of the cluster series marked in Figure 1a are attributed to $m = 0, 1$, and 2 : they are the series C_nC⁺, C_n(CO)⁺, and C_n(CO)₂⁺. Other series (CO)_mC_n⁺ with $m > 2$ were reported by recent experiments using pure CO ice [6]. The stability of the C_n⁺ cluster ion structures is discussed in reference [18].

The PPI with their respective ion cluster series are listed in Table 1 together with their absolute yields (emitted ions/impact). Table 2 presents the total ion yields and the ratio of total PPI yields to cluster ion yields summed over $n = 1$ –8.

Negative ions. The experiments were mainly addressed to desorbed positive ions, but a few mass spectra of negative ions have been acquired. The negative ion spectrum obtained with CO ice at $T = 25$ K has been published in a recent article on ion emission from condensed CO [6]. The total negative ion yield measured was 90 times smaller than that of the positive ions and the only negative cluster series observed is C_n[−]. Figure 2 presents a negative ion spectrum of CO₂ ice at $T = 25$ K. Note that above $m = 65$ u the yield scale has been multiplied by a factor of 10. For CO₂ ice, the total yield of negative ions (0.78 ions/impact) is 4.0 times smaller than the positive ion yield, and concentrated in two ions, O[−] and CO₃[−]. A pronounced background due to the so-called “hybrid molecular ions” appears above $m = 60$ u. These hybrid ions are attributed to reactions between CO₂ specific particles and H₂O specific particles [9], but as seen in the insert of Figure 2, nitrogen

Table 2. Total ion yields and relative total yields of the i) primarily produced ions PPI and ii) cluster ion series CIS ($n = 1-8$)

Ice target	Temperature (K)	Ion charge	Total yield (ions/impact)	Total PII yield (%)	Total CIS yield (%)
CO	25	positive	2,78	33	62
CO	25	negative	0,031	39	35
CO ₂	75–79	positive	3,15	77	19
CO ₂	25	positive	3,60 ^a		
CO ₂	25	negative	0,78	68	22

^aThe total yield of positive ions evaluated for a CO₂ target at T = 25 K was obtained by extrapolation from T = 77 K to 25 K (see Figure 7)

condensing at T = 25 K also leads to hybrid ions. All these hybrid ions form cluster series, for instance $(\text{CO}_2)_n(\text{CO}_4\text{H}_{0,1,2,3})^-$, with matrix molecules.

As shown in the next section, H₂O condenses steadily from rest gas onto the CO₂ ice surface. The formation of hybrid molecular ions in CO₂-H₂O ice has been recently studied as a function of H₂O concentration [9]. The results of these studies were used to estimate the H₂O content of the CO₂ ice target of the present work, yielding that the H₂O contamination of the ice surface is equivalent to a 2 to 4% H₂O concentration.

Discussion of the general pattern of the mass spectra. A general picture of ion formation and ion emission from CO ice by MeV ion impact has been developed in a recent article [6]. The basic emission process is the electronic sputtering, which is the same for the CO₂ ice; therefore, the pattern differences observed in the mass spectra of these two ices should depend on both the characteristics of the CO and CO₂ molecules (dipole moment, ionization potential, etc.) and the solid properties (density, stopping power, intermolecular binding energy, etc.) of the two ices.

Some relevant physical constants of CO and CO₂ compounds are presented in Table 3 (most extracted from [19]). These data lead to the following comments:

1. Bond length, energy loss, ionization potential and specific heat are about the same for CO and CO₂;

2. The dipolar moment of CO₂ is precisely zero (since it is a linear molecule with specular symmetry with respect to the carbon atom), while the dipolar moment of CO is relatively small (6% of the water one);
3. The sublimation temperature (see Figure 3) and the intermolecular binding energy are lower for CO ice than for CO₂ ice;
4. The critical temperature is a good indicator of the attraction force intensity in a gas: T_{cr} (CO) is 2.23 times lower than T_{cr} (CO₂);
5. CO is formed by a triple bond, much harder to break than one of the CO₂ double bonds.

The desorption of neutrals cannot be observed by the current technique but the very low value of the CO intermolecular binding energy supports the prediction that the desorption yield of CO neutral molecules (or clusters) should be higher than that of the CO₂ one. Using the formalism for electronic sputter yields developed by Johnson [20], it turns out that the desorption yield of CO neutral molecules should be 4.8 times higher than that of CO₂ neutral molecules. Since the number density n_B (molecules/volume) and also the specific energy loss are similar for both ices, the number of positive ions produced per track length unit should also be similar. The larger volume of CO ice ejected should therefore contain an equivalently higher number of positive ions than the ejected CO₂ volume. Actually, the opposite happens: the total yield of positive ions obtained with CO ice is slightly lower than that

Figure 2. TOF mass spectra of negative ions emitted from CO₂ ice at T = 25 K.

Table 3. Comparison between physical properties of CO and CO₂ molecules and ices

ICE	CO	CO ₂
Number density (10^{22} mol/cm ³)	2.2	2.3
Bond length (nm)	0,118	0,116
Sublimation temperature ^b (K)	~ 30	~ 85
at 10^{-8} torr		
Critical temperature T_{cr} (K)	132.9	304.1
Dissociation energy ^c (eV)	11.2 C≡O	7.20 C=O
(bond strength)		
Specific heat C_p (meV/molec)	0.301	0.384
Dipole moment (Debye)	0.110	0
Ionization potential (eV)	14.01	13.77
Energy loss (keV/nm) ^a	5.4	8.6

^afission fragment (65 MeV Ba) on ice;

^btemperature estimated from reference [19] and Figure 3;

^c1 eV/ molec = 96.5 kJ/mol.

Figure 3. Vapor pressure of CO and CO₂ as a function of temperature. The points represent data from reference [19]. Solid lines are fits from these data that allow, by extrapolation, to estimate the vapor pressure at high vacuum conditions.

obtained with CO₂ ice (see Table 2). It is generally assumed that the actual number of observed ions depends on their probability to desorb without being neutralized, which occurs mainly before expansion of the highly excited material into gas phase. The observed PPI that escape into gas phase are probably those which have been produced in the front part of the ejected volume.

In Figure 4, the ion yields of four cluster series versus the number n of cluster constituents are plotted, i.e., the number of C atoms, CO molecules, or CO₂ molecules. Similar to other cluster series distributions [7, 15, 17, 18], these yield curves are well described by single or double exponential decay curves, at least for $n > 1$. Considering that the desorption yield of each series varies as $Y = Y_0 \exp(-k_n n)$, both the yield of the corresponding series-head (i.e., the fitted Y value for $n = 0$), Y_0 , and the series exponential decay constant, k_n , are determined by fitting the experimental cluster distributions. The obtained slope values k_n are listed in Table 1. As seen, two groups of k_n values can be distinguished, having the mean values 0.41 and 0.13, respectively. Yield curves with k_n close to 0.41 are based on carbon clusters C_n , while those with k_n close to 0.13 are based on both clusters of matrix molecules, (CO) _{n} and (CO₂) _{n} . Figure 4 shows as an example for the first group the series $C_n(\text{CO})^+$, and as examples for the second group the series (CO) _{n} CO⁺, (CO₂) _{n} CO₂⁺ and (CO₂) _{n} CO₃⁻. In reference [6], we suggested that the C_n clusters are formed by condensation of free carbon atoms in gas-phase, whereas the clusters (CO) _{n} are emitted fragments of the solid CO ice. Figure 4 also illustrates that the exponential distributions of the (CO₂) _{n} CO₂⁺ and (CO₂) _{n} CO₃⁻ series have the same slope as that of the (CO) _{n} CO⁺ one, a strong argument supporting that the (CO₂) _{n} are formed and emitted simi-

larly to (CO) _{n} clusters, i.e., by fragmentation of the solid.

The inset of Figure 4 shows the dependence of k_n on the CO ice temperature, for the $C_n(\text{CO})_2^+$ cluster series: it increases strongly near the point of sublimation, which means that the probability of producing larger clusters decreases. The relative smoothness of k_n on T is interpreted as the absence of bulk phase changes in the analyzed temperature range or, at least, that they are not affecting the cluster emission.

The fact that the mass spectra obtained with CO ice are dominated by C_n clusters led to the conclusion [6] that the highly excited material around the track must contain, during its expansion, a relatively high number of unbound carbon atoms.

In CO ice, one source of free carbon atoms is dissociation of excited CO molecules: $\text{CO}^* \rightarrow \text{C} + \text{O}$.

Another source is $\text{CO} + \text{CO} \rightarrow \text{C} + \text{CO}_2$, a reaction occurring between the most abundant matrix molecules CO. On the other hand, for CO₂ ice the dissociation of the linear molecule CO₂ leads preferentially to the formation of CO and O: $\text{CO}_2^* \rightarrow \text{CO} + \text{O}$.

The reaction between the matrix molecules, $\text{CO}_2 + \text{CO}_2 \rightarrow 2(\text{CO}) + 2\text{O}$, leads again to carbon monoxide, but not to carbon atoms.

The kinetic energy of the released CO molecule is probably too low to allow further dissociation by collisions. Kinetic energies of sputtered molecular ions were found to be in the order of 1 eV [21]. Both dissociation processes require a strong vibrational excitation (indicated by the asterisk *) of the matrix molecules. From the relatively low density of carbon atoms inside the volume of sputtered CO₂ molecules follows that the process $\text{CO}_2^* \rightarrow \text{C} + 2\text{O}$ or $\text{C} + \text{O}_2$ is of minor importance.

Because of both, the specific energy loss of the projectiles in CO₂ ice being 1.6 higher than in CO ice

Figure 4. Yields of cluster ions plotted versus n for two cluster series relative to CO ice and two cluster series relative to CO₂ ice. The curve of $C_n(\text{CO})^+$ was extrapolated from $n = 8$ to $n = 15$ because the corresponding yields were superposed with yields of other ions. In the insert, the dependence on temperature of the exponential slope constant, k_n , of the $C_n(\text{CO})_2^+$ series ejected from CO ice is shown.

Figure 5. Temperature dependence of positive desorbed ion yields of CO ice. The temperature is gradually increasing from 25 to 33 K; the sublimation temperature $T \approx 30$ K is reached after 12 min.

and the dissociation energy of C—O bond being (coincidentally) also 1.6 times smaller than that of C=O, one expects for the track plasma in CO₂ ice a density of CO molecules even higher than the free carbon density. Corresponding cluster series (CO)_n are, however, not observed in the mass spectra obtained with CO₂ ice: as seen in Figure 1b, the signal of the particularly stable (CO)₂⁺ ion [22] is already weak and the mass line of (CO)₃⁺ is missing. On the contrary, the very pronounced C_n cluster pattern in Figure 1a proves the strong tendency of free carbon atoms to cluster. The analysis of the total yields of ion emission, presented in Table 2, shows that for CO ice, the carbon clusters very likely attract the PPI C⁺, CO⁺, and (CO)₂⁺, so that most of the positive ionization ends up in cluster ions. For CO₂ ice, the opposite occurs: only 19% of the total positive ion yield accounts for cluster ions, 77% remaining as PPI. Similar results were obtained for negative ions. Regarding clustering of carbon atoms in the nuclear track plasma, a particular phenomenon is the synthesis of the fullerene C₆₀ in PVDF after heavy ion impact [23], but it was not observed for the current projectile-target systems.

The two dissociation processes mentioned above should lead to an oxygen concentration inside the track plasma comparable with the carbon concentration in the case of CO ice. O_n⁺ and O_n⁻ cluster series emission has been observed for irradiated O₂ ice [15], but regarding the mass spectra shown in Figures 1 and 2, there is no indication of clustering of oxygen. The production of O₂⁺ will be discussed in the next section 5. So far, the discussion of the mass spectra has been focused on dissociation and clustering of neutral molecules and atoms, the overwhelming fraction of the sputtered material.

Temperature Dependence of Ion Yields

The analysis of the desorption yield dependence on ice temperature is a convenient method to identify the

target *specific ions* (their yields tend to vanish at the CO or CO₂ sublimation temperatures), the *rest gas/substrate ions* (their yields increase or do not vanish at these temperatures) and the *hybrid ions* formed by chemical reactions between the other two species (their yields may show a maximum at the CO or CO₂ sublimation temperatures). Furthermore, the analysis of the yield dependence on ice temperature helps the understanding of the sputtering process(es).

Figures 5 and 6 show ion yields as a function of the warming-up time, during which the ice layer temperature increased steadily. As seen in these figures, the ion yields drop suddenly at $T \approx 29$ K for CO ice and at $T \approx 85$ K for CO₂ ice. Beyond these temperatures, water vapor is still condensing but the ice layers have disappeared: the Na⁺ signal (see Figure 6) rises quickly, reaching its final level. Sodium is a common contaminant of bare target foils. The thickness of the ice layers starts to decrease when the rate of sublimation becomes higher than the rate of condensation. At a vapor pressure between 10⁻⁸ and 10⁻⁷ mbar—this was the pressure measured in the vacuum chamber—the so-called sublimation temperatures should have values of about 30 K for CO ice and 80 K for CO₂ ice as indicated in Figure 3, where the vapor pressure curves of both ices are extrapolated down to the measured vacuum pressures.

CO ice. After dosing CO gas, the target temperature was slowly increased and acquisition of 80 TOF spectra was started, each for 30 s. As seen in Figure 5, the measured yield (counts/30 s) of CO specific ions remains almost constant up to $T = 29$ K and drops then suddenly at 30 K. In this figure, two groups of positive

Figure 6. Temperature dependence of some positive desorbed ion yields of CO₂ ice. The temperature is gradually increasing from 75 to 91 K. The sublimation temperature $T \approx 85$ K is reached after 37 min. Three groups of ions are identified. The desorption yields of O₂⁺ and (CO₂)O₂⁺, (which are CO₂ specific ions), decrease to background level as temperature increases. The NO⁺, CO⁺, and N₂⁺ ion yields decrease but do not vanish. Yield of the condensed residual gas H₂O⁺ and that of the Na⁺ target contamination increase.

ions are recognized: (1) ions with relatively high yield, which decreases above 30 K by typically one order of magnitude and (2) molecular ions with lower yields, which decrease above 30 K down to the background level. All ions in the second group are members of $C_n(\text{CO})_m^+$ cluster series. Their disappearance above 30 K indicates that they are formed inside the nuclear track plasma of pure CO ice. This is particularly true for C_n clusters. An exception is recognized in the first group: the ion with mass $m = 36$ u, assigned as C_3^+ , remains on a level one order of magnitude above background. C_3^+ has an exceptional high yield in accordance with the odd-even periodicity of the C_n^+ cluster series [6, 18]. Also C^+ , the first member of this series, has above $T = 30$ K a yield clearly above the background and stems partially from organic impurities. Its yield is lower than that of the $m = 36$ u ion. Therefore, it is concluded that the $(\text{H}_2\text{O})_2^+$ mass peak is superimposed on the C_3^+ one. The yield curve of H_2O^+ , not shown in Figure 5, reaches a count rate of 320 ions/30 s for T above 30 K. Another mass line, which shows probably a foreign contribution, is the line at $m = 28$ u: the CO^+ signal coincides with that of N_2^+ , the ion of nitrogen, which condenses from rest gas.

The yield of the $(\text{CO})_2^+$ ions is relatively high and exhibits a peculiar behavior. Around 30 K the yield of $(\text{CO})_2^+$ decreases, but not as fast as that of CO^+ , and then reaches a level slightly above the count rate of CO^+ . Eventually, a monolayer of adsorbed CO molecules is left after sublimation of CO ice and is sufficient for the production of the unusually stable $(\text{CO})_2^+$ [6, 22]. Anyhow, the occurrence of an unidentified background ion is not excluded.

The intensity of the cluster series $C_n(\text{CO})_2^+$ was high enough for the study of the temperature dependence of the slope of the yield curves, i.e., of the decay constant k_n . The inset of Figure 4 illustrates that between $T = 25$ K and 28 K, k_n stays constant at 0.091, rises slowly above 28 K, and then, when the yields have dropped by more than a factor of 10, jumps up to values around 0.27. This means that the dependence of the cluster ion yield on n increases when the ice temperature approaches the sublimation temperature of about 29 K, probably because the number of carbon atoms available for (a nonplanar) clustering decreases with the decreasing thickness of the ice layer.

CO₂ ice. The procedure to produce a 200 nm thick CO₂ ice layer was similar to that of the CO ice layer. To avoid contamination with CO used for the former gas inlet, condensation was started above 40 K, then stopped at 75 K, and the measurement of a series of 120 spectra started, each for 30 s. As seen in Figure 6, again the yield curves measured with CO₂ ice can be divided into two groups: (1) curves which decline to background level, and (2) curves that decline to a counting rate distinctly higher than background. The ions of the first group, composed of CO₂ and O₂ structures, are attributed to reactions in the track plasma of pure CO₂ bulk which

generate TOF mass lines that disappear beyond the sublimation temperature (~ 85 K). These pure CO₂ specific ions have the typical behavior that their yields decrease with time even before rapid sublimation, which is caused by rest gas condensation resulting in a contamination layer steadily growing on top of the CO₂ ice layer. A similar decrease has been reported also for CO specific ions ejected from CO ice [6], but not observed in Figure 5, probably due to a lower rest gas pressure during the experiments with CO ice. The yield decrease is not the same for the various CO₂ specific ions: it is more relevant for the ions, which tend to react with rest gas molecules or for atoms diffused into the track plasma. Again, the typical behavior for the ions of the second group is that they can also stem from the rest gas condensate.

On the other hand, an unexpected feature occurs for a CO₂ specific ion, concerning the mass line $m = 72$ u and assigned as $(\text{CO}_2)\text{CO}^+$: its yield (not shown) remains almost constant over the whole temperature range. A possible explanation is that the distinct peak at $m = 72$ u in the spectrum shown in Figure 2b contains to a large extent a contribution of $(\text{CO}_2)\text{N}_2^+$.

Ions originating from the rest gas condensate can be easily recognized by means of the temperature dependence of their yields. In Figure 6, the yield curves of various rest gas ions are compared with that of O_2^+ found to be a pure CO₂ specific ion. The rest gas ions H_2O^+ , as well as the H^+ and H_3O^+ ions (yield curves not shown), are known to originate from water condensate [7]. Their yields increase continuously and are not very sensitive to the sublimation point of CO₂. The yield of the mass line at $m = 28$ u decreases but not as strongly the O_2^+ ion, supporting the interpretation that it is formed by the rest gas N_2^+ (which decreases in time) and also by the CO^+ ions whose yield may increase due to the oxygen from water. The weak organic ion CH^+ is also a hybrid ion: the CO₂ contributes with the carbon atom and the H₂O with the hydrogen atom (see also reference [7]); this explains why its yield increases with time (H₂O increases) but decreases afterwards (CO₂ has sublimated). The ion of mass 30 u should be also a hybrid ion, but not the ion of formaldehyde (COH_2^+)—this can be excluded from recent investigations of CO₂-H₂O mixtures [9]; its designation is supposedly NO^+ : the oxygen atom comes (partially) from the CO₂ ice dissociation since its yield decreases beyond the sublimation point.

Discussion of Ion Formation

The main mechanism of positive ion formation has already been stated in a previous section. The positive primarily produced ions are produced by direct Coulomb interaction between the projectile and δ -electrons with target atoms or molecules. As shown in the following, some of these ions need further reactions to be produced with the observed intensity. The cluster ions

originate from reactions among these PPI and clusters or reactions between cluster ions and clusters.

It is useful to review the ion formation data obtained with CO and CO₂ in other conditions. Fragmentation of these molecules in gas phase has been extensively studied by electron-, photon-, and ion-impact. The electron impact mass spectrum of CO gas shows a dominant CO⁺ peak, followed by three peaks of about the same intensity: C⁺, O⁺, and CO₂⁺ [24]. The fragmentation of CO by 1 MeV/u F⁴⁺ ions has CO⁺ as the main final product, followed by the C⁺ + O⁰ and C⁰ + O⁺ by channels with cross sections 6 to 7 times of magnitude lower [25], whereas 2.4 MeV/u Ar¹⁴⁺ projectiles result in cross sections about 3 to 5 times lower [26]; C⁺ and C²⁺ ion production is enhanced with respect to O⁺ and O²⁺, respectively. For CO₂ dissociation after collision with 3.6 MeV/u Si⁸⁺ projectiles, it was reported that the peripheral O ions have larger kinetic energies than the central C ions [27].

In the present work, the C⁺ ion has by far the highest yield (see Figure 1a and Table 1). The Coulomb interaction of the multi-charged ~0.6 MeV/u fission fragment with CO molecules in the close vicinity of the track is a very energetic process ionizing and dissociating most of the molecules within a radius of 0.5 nm. Abundant (CO)_n⁺ production was also observed by 1.5 MeV/u Ar¹³⁺ projectiles impact [28]. In particular, the electronic stopping power process induces emission of multi-charged C and O ions, which are indeed observed [6]. Around the fission fragment track, the PPI C⁺, O⁺, and CO⁺ react with the abundant CO bulk molecules; occurrence of the reaction CO⁺ + CO → CO₂ + C⁺ will enhance C⁺ production. Dissociation of CO⁺ into C⁺ and O is less probable, because it requires a relatively high excitation energy (11.2 eV).

The CO₂⁺ ion found in the electron impact mass spectrum of CO gas [21] is also seen in Figure 1a. The reactions occurring promptly like in the described CO gas experiments and leading to CO₂⁺ ions are CO⁺ + CO → CO₂⁺ + C and/or O⁺ + CO → CO₂⁺.

Electron impact on CO₂ gas produces about the same spectrum as that of CO gas: a CO⁺ peak much higher than the three others. This pattern is a consequence of the fragility of the CO₂ molecule, compared to the CO one. Both CO₂⁺ and CO⁺ peaks are seen in the CO₂ ice mass spectra, since CO⁺ is a dissociation product of CO₂⁺. Note that the ionization of CO₂ can occur in the same Coulomb interaction process as its dissociation and that O₂⁺ PPI have the highest yield. Results shown in Figure 6 prove that O₂⁺ is a pure CO₂ derivate: reactions in which O or O⁺ are involved should not contribute to O₂⁺ production, because oxygen (either atoms or ions) can also be delivered from the contaminant H₂O. The exothermic reaction most likely to occur in this system is CO₂⁺ + CO₂ → O₂⁺ + 2CO.

In the above analysis, only the most abundant matrix molecules are involved. The electron impact spectra show a very small O₂⁺ peak. This proves that the

fragmentation CO₂⁺ → O₂⁺ + C does not occur with comparative intensity.

The CO₂⁺ + CO₂ → O₂⁺ + (CO)₂⁺ reaction among matrix molecules can also lead to the strongly bound (CO)₂⁺ ion, whose mass peak is seen in Figure 1b.

Negative ions are not produced by direct Coulomb interaction with projectiles: they are the result of electron capture away from the central hot core of the nuclear track. The total yield of negative CO specific ions is about 35 times lower than that of negative CO₂ specific ions. The reason for this large difference in yields is probably the availability of O⁻, which is much lower in the track plasma of CO ice than in that of CO₂ ice where it is partially consumed for the reaction O⁻ + CO₂ → CO₃⁻ [8, 9]. It is assumed that, in the track plasma of CO ice, a certain fraction of the primarily produced δ-electrons is captured by carbon atoms and therefore lost for the production of O⁻. The series (CO₂)_nO⁻ and (CO₂)_nO₂⁻ produced by 1.5 MeV/u Ar¹³⁺ projectiles impact were reported by Tawara et al. [29].

Conclusions

Desorbed ion mass spectra of condensed CO and CO₂ are measured and compared. The ice samples were irradiated by ~65 MeV ²⁵²Cf fission fragments. Such heavy ion projectiles create nuclear track plasma along their trajectory inside the solid. Fast expansion of the CO ice target material at the surface ejects into vacuum an equivalent of about 2.4 × 10⁵ CO molecules/impact, five times more than for the CO₂ ice target. Only a very small fraction (0.001% for CO ice and 0.009% for CO₂ ice at T = 25 K) of these particles is charged [23].

Two types of ions can be recognized in these spectra: ions which are primarily produced along the nuclear track by direct Coulomb interaction with the passing projectile and those which originate from fast chemical reactions between these ions and the most abundant atoms or molecules in the nuclear track plasma. The CO-ice ion mass spectra show, apart from the primarily produced ions C⁺, O⁺, CO⁺, O⁻, and C⁻, a rich variety of cluster ions of type C_n⁺, C_n⁻, (CO)_nCO⁺, and C_n(CO)_m⁺. Similarly, the CO₂-ice ion mass spectra show the C⁺, O⁺, O⁻, CO⁺, O₂⁺, and CO₂⁺ ion peaks and cluster series (CO₂)_nCO₂⁺, (CO₂)_nO⁺, (CO₂)_nCO⁺, (CO₂)_nO₂⁺, and (CO₂)_nCO₃⁻.

The cluster series yields decrease with n, the number of cluster constituents, generally as an exponential decay. Two types of decay constants were observed: k_n ≅ 0.41 for fast-decay series based on carbon clusters C_n and k_n ≅ 0.13 for slow-decay series based on clusters of matrix molecules (CO)_n and (CO₂)_n. The fast-decay series are interpreted as cluster formation by gas-phase condensation of carbon atoms and the slow-decay series as cluster formation by fragmentation of the excited solid around the nuclear track into aggregates of matrix molecules. Further discussion is presented in reference [17].

The pronounced C_n cluster pattern obtained for CO ice is remarkable. It requires a high concentration of

unbound carbon in the nuclear track plasma. Free carbon is probably produced by dissociation of CO, but the reaction $\text{CO} + \text{CO} \rightarrow \text{CO}_2 + \text{C}$ might also lead to carbon atoms. For CO_2 ice, in which case equivalent reactions of matrix molecules do not lead to unbound carbon, strong C_n clustering was not observed. CO molecules or O atoms do not exhibit such a strong clustering tendency. Another pronounced difference between the carbon monoxide and dioxide sputtering is the ratio of the total positive ion yield to the total negative ion yield: it is about 90 for CO and ~ 4 for CO_2 .

In accordance with the measured residual gas pressure, CO ice is found to sublime at about 29 K and CO_2 ice at about 85 K. Ion yields measured during temperature increase show a corresponding sudden decrease for CO and CO_2 specific ions, whereas ions originating from a rest gas condensate showed increasing count rates, also when the CO or CO_2 ice layers had disappeared. This allowed identification of ice specific ions, rest gas ions, and hybrid ions. The decay constant k_n was measured as a function of temperature for the $\text{C}_n(\text{CO})_2^+$ cluster series: it increases strongly near the point of sublimation, when the ice layer vanishes; the conclusion is that k_n is inversely connected with the free carbon density in the ejecta.

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