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Photo-desorbed species produced by the UV/EUV irradiation of an H_2O:CO_2:NH_3 ice mixture

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Abstract

An H_2O:CO_2:NH_3 = 1:1:1 ice mixture, used as a model mixture for cometary and interstellar ices, was irradiated with ultraviolet (UV)/extreme ultraviolet (EUV) photons in the broad 4–20 eV (62–310 nm) energy range at 16 K. The desorbed species were detected in situ by mass spectrometry during photo-irradiation, and a quartz microbalance was used as a substrate to measure the mass of material remaining on the surface. The total mass desorption for this H_2O:CO_2:NH_3 = 1:1:1 ice mixture at 16 K was measured to be 1.8×10^{-18} μg photon^{-1}, which is comparable to the 1.5×10^{-18} μg photon^{-1} measured for pure H_2O ice irradiated under the same conditions. The main desorbed species produced during the photolysis of the ices were H_2, $NH_2^\bullet$, $OH^\bullet$, CO, and O_2, along with the starting components H_2O, NH_3, and CO_2. We also tentatively assigned minor mass peaks to larger species such as $OCN^\bullet/OCN^-$, HNCO, CH_4, H_2CO, CH_3OH, and HCOOH. This result supports the scenario in which complex organic molecules can be formed in cometary and/or astrophysical ices and desorbed to the gas phase, and helps to better understand the photochemical processes occurring at the surface of Solar System icy bodies such as comets, as well as in cold astrophysical environments such as star-forming regions and protostars.

Keywords: Ices; Photo-desorption; Comets; ISM; Prebiotic chemistry

1. Introduction

Our understanding of the evolution of organic molecules in the interstellar medium (ISM) (Ehrenfreund and Charnley, 2000; Snyder, 1997), in comets and meteorites (Cronin and Chang, 1993; Cronin and Pizzarello, 1999; Engel and Macko, 1997), and their voyage from interstellar molecular clouds to the early Solar System has changed dramatically within the last 15 years. Ground-based (Cernicharo et al., 2000; Turner, 1989, 1991) and space observations (Dartois et al., 2002; Gibb et al., 2000, 2004; Whittet et al., 1996), as well as laboratory simulation experiments (Gerakines et al., 1995; Hudson and Moore, 1993; Moore et al., 1983, 1991; Wu and Judge, 2002) and new methods for theoretical modeling (Gauss and Cremer, 1988; Woon, 1999, 2001) have provided information about the chemical processes and mechanisms for the formation of organic molecules in cold astrophysical environments including icy bodies in planetary systems.

Results obtained from space missions to Comet Halley during its last transit near the Sun in 1986 (Kissel et al., 1986; Knacke et al., 1986; Wickramasinghe and Allen, 1986), and more recent observations of the bright comets Hyakutake and Hale-Bopp (Brooke et al., 2003; Crovisier, 1998; Dello Russo et al., 1998, 2002; Mumma et al., 1996;

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Wouterloot et al., 1998) have allowed astronomers to reexamine the organic chemistry models of dust and volatile compounds in long-period comets. These objects are thought to be agglomerates of frozen gases, ices, and rocky debris, and are likely to be the most primitive bodies in the Solar System. It is now commonly accepted that comets were formed in outer regions of the Solar System, near giant planets and beyond, from remnants of dust and planetesimals that were not accreted into planets, although mixing of such interplanetary matter throughout the whole Solar System may have occurred as suggested by recent studies of grains of Comet Wild 2 returned by the NASA Stardust mission (McKeegan et al., 2006).

The knowledge of the chemical processes occurring in molecular clouds, comets, and meteorites provides constraints on the origin, the chemical composition, the evolution, and the distribution of organics in the Universe in general, and in our Solar System in particular. Laboratory simulations in which astrophysical ice analogs are irradiated with UV photons or energetic particles (protons, electrons, heavy ions) have strongly contributed to our current understanding of such processes connected with astrochemistry and astrobiology. In the last decade, these experiments have shown that organic molecules can be formed via UV photo-irradiation (Allamandola et al., 1999) and energetic proton bombardment (Hudson and Moore, 1999) of astrophysical ice analogs, including biological species such as amino acids (Bernstein et al., 2002; Muñoz Caro et al., 2002; Nuevo et al., 2008). However, such complex organic molecules are usually detected in the organic residues formed after warming up the irradiated ices to room temperature and a subsequent chemical protocol that may modify their original composition (Nuevo et al., 2008).

In this work, we present a laboratory study of the species desorbed during the irradiation of an H_2O:CO_2:NH_3 = 1:1:1 ice mixture with ultraviolet (UV)/extreme ultraviolet (EUV) photons in the 4–20 eV (62–310 nm) range at 16 K. Such a mixture was chosen because it contains three of the most abundant astrophysical solid species, H_2O being the most abundant ice component of cometary nuclei and interstellar grains (Allamandola et al., 1997; Crovisier, 1998; Dartois et al., 2002; Gibb et al., 2000, 2004). The mixing ratio between the ices was chosen as a model to demonstrate the feasibility of this type of experiment, and to evaluate the experimental constraints.

The masses of the species desorbed directly from the substrate were measured in situ during photo-irradiation at low temperature. The assignments of those detected masses to molecular species are discussed and compared with astronomical observations of the Solar System as well as other astrophysical environments such as star-forming regions and protostars. Finally, although the purpose of the present work is not to study the mechanisms of formation of the desorbed species, a few formation pathways reported in the literature are also suggested for some of the observed species.

2. Experimental setup and protocol

2.1. Sample preparation and UV/EUV irradiation

The experiment was carried out in a ultrahigh-vacuum chamber evacuated by a turbo-molecular pump (Leybold TurboVac series, pumping speed: 600 L s^{-1}, background pressure $\sim 5 \times 10^{-9}$ torr), equipped with a gold-coated quartz crystal resonator microbalance (Leybold Inficon IPN750-171-P1) with a 0.1-ng sensitivity to measure the total mass of deposited ices, and mounted on a helium closed-cycle cryostat (CTI Model 22). The quartz crystal can be cooled down to a 16–170 K temperature range with an accuracy of ±0.5 K. A quadrupole mass spectrometer (QMS) (Pfeiffer Prisma QMS200), equipped with a secondary-electron multiplier (SEM), and controlled by the Balzers Quadstar 422™ software, is also connected to the vacuum chamber with an angle of 40° with respect to the surface of the substrate. This QMS is used to measure the mass of desorbed species in the 0–200 amu (atomic mass units) range, by recording mass spectra at a typical scan rate of 2 amu s^{-1}. A schematic diagram of the experimental setup is shown in Fig. 1.

The UV/EUV photons were provided by the high-flux beamline of the National Synchrotron Radiation Research Center (NSRRC) facility in Hsinchu, Taiwan, to which our vacuum system was directly connected. The incident zeroth order of the white light used in our experiment provides UV/EUV photons in the broad 4–20 eV (62–310 nm) energy range. The incident photon flux was constantly monitored using a ~90% optical-transmission in-line gold mesh, and measured to be 3×10^{16} photons s^{-1} cm^{-2} in average. The photon beam size at the ice sample was

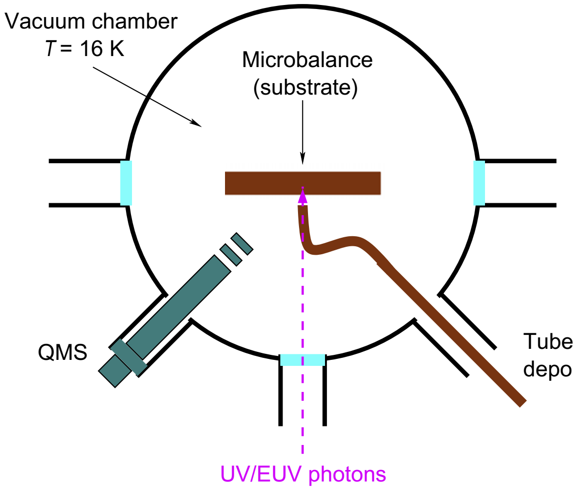

Fig. 1. Schematic diagram of the experimental setup seen from above. When an infrared-transparent substrate is used instead of the microbalance, this setup also allows us to monitor the evolution of the samples with infrared spectroscopy during photo-irradiation, using an FTIR spectrometer connected to the vacuum chamber. The gas tube handling system for gas deposition was mounted on a manipulator, that was retracted during photo-irradiation.

approximately $2 \times 4\ \mathrm{mm}^2$, and a typical experiment was run until a total integrated incident photon dose of about 3×10^{18} photons was reached. EUV photons are mainly emitted by stars, including the Sun, from atomic line transitions (Judge and Pietarila, 2004; Peter et al., 2006) such as He I and He II lines at 58.4 and 30.4 nm, respectively. Thus, circumstellar environments are affected by EUV radiation, although its intensity is expected to be 2–3 orders of magnitude lower than the hydrogen Lyman-α transition (vacuum UV range) (Meier, 1991; Rees, 1989).

Gas mixtures are prepared in a handling system equipped with a manifold connected to four stainless steel bottles, a vacuum pumping system, and a Baratron (MKS 122A) pressure gauge. For this study, the whole system was baked out under vacuum at 400 K for 12 h and cooled down to room temperature before use. Three stainless steel bottles were used to store each starting compound for our mixture, namely, water H_2O (liquid, triply distilled), carbon dioxide CO_2 (gas, Sigma–Aldrich, 99.999% purity), and ammonia NH_3 (gas, Sigma–Aldrich, 99.5% purity). Gases were admitted into their respective bottle by controlling their pre-determined partial pressures, and mixed together. Gas mixtures were then kept for typically 15 min before deposition. The mixture prepared for this study was $H_2O:CO_2:NH_3 = 1:1:1$ (same partial pressure for all three components). Although this mixture does not reflect the relative proportions between H_2O, CO_2, and NH_3 in interstellar or cometary environments (Crovisier, 1998; Gibb et al., 2000) (Table 1), it contains three of the most abundant ice species in astrophysical environments, and the four elements necessary to form organic molecules, namely, carbon, hydrogen, oxygen, and nitrogen. Such a mixture was also chosen because of experimental constraints, due to the vapor pressure of H_2O. Indeed, preparing a mixture with astrophysical relative abundances for CO_2 and NH_3 would imply smaller absolute quantities of the only carbon and nitrogen sources in the mixture, and thus smaller abundances for their photo-products, which would be significantly more difficult to detect with mass spectrometry.

In a parallel experiment, the quartz crystal microbalance was replaced by a KBr window so that infrared (IR) spectra of the ice samples could be recorded with a Fourier-transform infrared (FTIR) spectrometer (Perkin–Elmer FTIR-1600). From the FTIR absorbance spectrum we measured the column densities of the three starting components H_2O, CO, and NH_3, using their prominent absorbance bands at 3300, 2340, and $3375\ \mathrm{cm}^{-1}$, respectively, and determined a composition of $H_2O:CO:NH_3 = 1.00:0.99:1.02$ for the mixture. Therefore, the relative proportions between the starting components were found to be similar in the gas and solid mixtures within 2% under the present experimental conditions. This was expected because the gas mixture was directly deposited into the KBr substrate using a retractable manipulator, and because at 16 K the sticking coefficients for those three molecules are believed to be close to unity, so that every species hitting the cryosurface will stick on it.

A thin film of ice was prepared by depositing the $H_2O:CO_2:NH_3 = 1:1:1$ gas mixture onto the microbalance crystal at 16 K, the temperature kept constant during the whole experiment. The deposition rate was controlled to be about $0.1\ \mu\mathrm{g\ s}^{-1}$, and the pressure in the vacuum chamber was maintained at 1×10^{-8} torr. The total mass of the ice film was approximately 60 μg, which corresponds to about 4.6×10^{17} molecules, for a thickness of about 5 μm, i.e., thick enough for the incident photons not to reach and impinge on the surface of the microbalance crystal. After the gas deposition was completed, the vacuum chamber was left idling for a few hours to allow the residual gases to condense on the substrate or to be pumped out. The photolysis experiment was started only after the pressure inside the chamber reaches $\sim 1 \times 10^{-9}$ torr. During UV/EUV irradiation, we simultaneously monitored the frequency of the quartz microbalance to measure the total mass of the ice sample, the QMS scan speed of the ion signal for the desorbed species, and the incident photon flux.

Table 1
Abundances of icy species in Comet Hale-Bopp, and the protostellar objects NGC 7538 IRS 9 and W33A. Sulfur-bearing species such as OCS and SO_2 were not studied in this work.

Species	Comet Hale-Bopp[a]	NGC 7538 IRS 9[b]	W33A[b]
H_2O	100	100	100
CO	20	16	9
CO_2	6	22	14
CH_3OH	2	5	22
H_2CO	1	4	1.7–7
CH_4	1	2	2
OCS/XCS	0.7	–	0.3
NH_3	0.6	13	15
C_2H_2	0.5	–	–
C_2H_6	0.5	–	–
OCN^-	0.37	1	3
SO_2	0.15	–	–
HCOOH	0.05	3	0.4–2

[a] Crovisier (1998).
[b] Gibb et al. (2000).

2.2. Estimate of the level of contamination

Under our experimental conditions, contamination during deposition is expected to be negligible, since ices were deposited by using a retractable manipulator (see Section 2.1), so that contamination probably mainly occurs during irradiation. According to Fig. 2 (see Section 3.2), the total irradiation time was approximately 6600 s (110 min). Using the Langmuir equation for the deposition of one monolayer (ML) of gas in our chamber at 1×10^{-9} torr and 16 K, we estimated that a maximum of 11 ML of residual gases could be deposited on the substrate during irradiation. However, mass spectra of desorbed species were recorded during the first ~1250 s (corresponding to the time for the total integrated photon

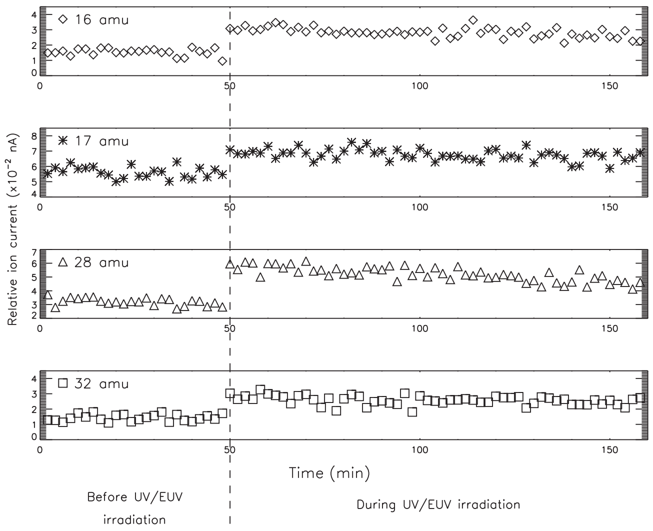

Fig. 2. QMS ion currents for several mass numbers recorded in a typical experimental run for our H_2O:CO_2:NH_3 = 1:1:1 ice mixture at 16 K. The vertical dashed line indicates the beginning of the UV/EUV photo-irradiation.

dose to reach 3×10^{18} photons, see Section 2.1), so that during QMS measurements only 2.1 ML of contaminants were deposited on the substrate.

In our system, 1 ML of deposited gas was estimated to be equivalent to a column density of $\sim 1 \times 10^{15}$ molecules cm^{-2} via FTIR measurements at 15 K, which corresponds to $\sim 5 \times 10^{14}$ molecules on the microbalance which has an area of about 0.5 cm^2. This means that the maximum amount of residual gases that can be deposited on the substrate during irradiation is approximately 1.1×10^{15} molecules. Compared with the 4.6×10^{17} molecules of ices deposited (see Section 2.1), this corresponds to a level of contamination smaller than 0.25%. Therefore, even if UV/EUV photons can penetrate layers of contaminants and photolyze them, the quantity of photo-products formed from their photolysis is small enough so that they would probably not be detectable with our QMS device.

2.3. Control and blank experiments

In desorption experiments induced by UV/EUV photons, it is important to verify that the desorbed species are only stemming from the photo-processes occurring in the ice matrix. For instance, NH_3 and CO_2 can in some cases react in the gas phase to form $NH_4NH_2CO_2$ (Khanna and Moore, 1999). A mass spectrum of the starting mixture H_2O:CO_2:NH_3 = 1:1:1 recorded with the QMS after deposition of the gases on the substrate showed only peaks corresponding to the individual ice components, indicating that $NH_4NH_2CO_2$ (78 amu) was not formed in our case. We also carried out a blank experiment where no ice was deposited on the substrate, which showed no difference between the mass spectra recorded before and after irradiation.

In the experiment where the quartz crystal microbalance was replaced by a KBr window in order to monitor the evolution of the ices with IR spectroscopy (see Section 2.1), the IR spectra recorded at 16 K did not show any other absorption feature besides those of H_2O, CO_2, and NH_3, confirming that no reaction is taking place in the handling system during the gas mixture preparation, nor in the vacuum chamber, after deposition of the ices and before photo-irradiation. Therefore, the desorbed photo-products observed in the present work result only from the UV/EUV photolysis of the starting ice mixture.

3. Results and discussion

3.1. Mass spectrometry analysis of desorbed species

The mass spectrum of the irradiated mixture indicates that the signal for molecular masses higher than 44 amu (corresponding to CO_2, i.e., the heaviest starting ice component) is weak. This means that under our experimental conditions, the detection of complex (heavier) molecules is more difficult via mass spectrometry because of their small abundances.

Thus, although the formation and desorption of heavy compounds cannot be ruled out, mass peaks assigned to the starting ice components, their photo-fragments, and photo-products with smaller molecular masses are expected to dominate the mass spectra during the photolysis. The contribution of the photo-fragments of the starting ices to the intensities of all mass peaks must therefore be subtracted to accurately measure the signal due to photo-products only. The procedure adopted to identify the photo-product candidates is as follows:

1. *Background subtraction:* The mass spectrum recorded before irradiation, characteristic of the starting ice mixture, was used as background spectrum. The absolute intensities in this spectrum were found to slowly decrease with time, and the decay rates for the peaks of each molecular mass of interest were measured. Working mass spectra were obtained after subtraction of the background spectrum.
2. *Choice of possible candidates:* The identification of the desorbed species was based on the most probable chemical processes during the photolysis of the ices (see Section 3.3). Table 2 lists the possible candidates assigned to the peaks observed in the mass spectrum of the UV/EUV-irradiated H_2O:CO_2:NH_3 = 1:1:1 ice mixture.
3. *Fragmentation spectra of pure ice samples:* Mass spectra from pure ices were recorded independently. The fragmentation mass spectrum of a given molecule was measured for a given condition of ionization of the QMS. Starting from the peak of highest mass for each starting compound, the fragmentation spectrum of a given compound was subtracted from the

Table 2
List of the most probable candidates for the desorbed photo-products observed in the mass spectra during the UV/EUV irradiation. Starting ice components are given in boldface.

Mass (amu)	Candidates	Mass (amu)	Candidates
1	$H^{\bullet}$	28	CO, N_2, C_2H_4[a]
2	H_2	29	$HCO^{\bullet}$[a], ^{13}CO
3	H_3^+	30	H_2CO[a]
12	$C^{\bullet}$	32	O_2, CH_3OH[a]
14	$N^{\bullet}$, $CH_2^{\bullet}$	42	$OCN^{\bullet}(OCN^-)$[a]
15	$NH^{\bullet}$, $CH_3^{\bullet}$	43	HNCO[a]
16	$O^{\bullet}$, $NH_2^{\bullet}$, CH_4[a]	44	$\mathbf{CO_2}$
17	$\mathbf{NH_3}$, $OH^{\bullet}$	45	$^{13}CO_2$, $HCONH_2$, $^{\bullet}COOH$
18	$\mathbf{H_2O}$, NH_4^+	46	HCOOH[a], C_2H_5OH[a]
27	HCN[a], HNC[a]		

[a] These species were tentatively identified.

working spectrum, in order to obtain a new working spectrum with peaks of smaller molecular masses.

(4) *After repeating Step 3 for each starting ice component*, we finally obtained a remaining mass spectrum, attributed to the desorbed products.

The candidates identified via this method are listed in Table 2. As expected, a significant number of the observed peaks are due to fragments produced by the photo-decomposition of the starting components. Other peaks can be assigned to products resulting from the recombination of photo-fragments and/or multi-photon processes. A more detailed analysis of the identified desorbed species is given in Sections 3.3 and 3.4.

3.2. Total mass desorption yields

The total mass of the ices was monitored by the quartz crystal resonator microbalance during the whole duration of the experiments. Before UV/EUV irradiation, ices remain in a stationary state between sublimation and condensation, defined by the given conditions of ultra-high vacuum in the chamber and the temperature of the cold finger, and no desorption is observed. Desorption process starts as soon as ices are subjected to photo-irradiation (Fig. 2). During desorption, the mass loss measured by the microbalance corresponds to the total mass of the species desorbed for a given photon dose. This measurement allows us to determine the photo-desorption yield, defined by the ratio between the mass loss per unit area and the increasing incident photon dose.

In order to verify that the observed desorption was not due to thermal effects transferred from the photons to the quartz crystal, we plotted the mass desorption rate as a function of the photon flux for our $H_2O:CO_2:NH_3 = 1:1:1$ mixture and for a pure H_2O ice (Fig. 3). The linear relationships obtained for both ices clearly indicate that the mass desorption yield is proportional to the photon dose. This behavior confirms previous results obtained for the photo-desorption of pure H_2O ice (Westley et al., 1995).

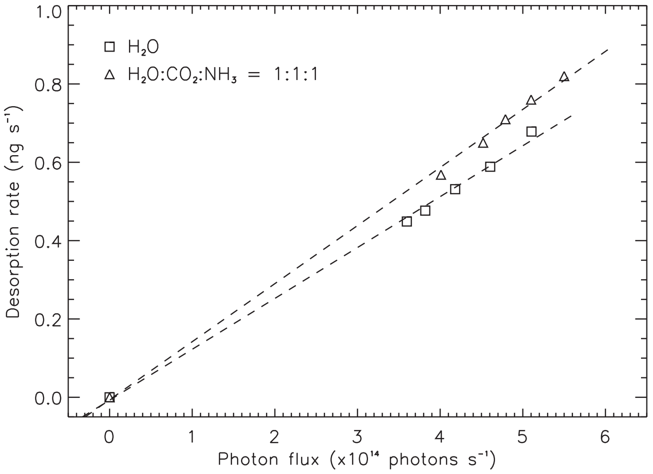

Fig. 3. Plot of the mass desorption flux as a function of the incident photon flux for pure H_2O ice (squares) and the $H_2O:CO_2:NH_3 = 1:1:1$ ice mixture (triangles) at 16 K, as well as their linear fits (dashed lines).

Figure 4 gives the mass desorption yields calculated for the $H_2O:CO_2:NH_3 = 1:1:1$ ice mixture and for pure H_2O ice as a function of the increasing photon dose. These data clearly show that desorption yields increase with the photon dose under our experimental conditions. The large error bars obtained at the beginning of the irradiation are due to the sudden response of the quartz crystal detector to the incident photons. The transient spikes gradually decrease in magnitude and become negligible after a few minutes. The typical uncertainties reach up to 40% at the beginning, and become smaller than 20% at photon doses higher than 1×10^{17} photons. The measured mass desorption yield for the $H_2O:CO_2:NH_3$ mixture was found to be $1.8\ (\pm 0.4) \times 10^{-18}$ µg photon^{-1}. Under the same experimental conditions, the mass desorption yield for pure H_2O ice was measured to be $1.5\ (\pm 0.3) \times 10^{-18}$ µg photon^{-1}, which corresponds to 5.0×10^{-2} molecules photon^{-1}. This

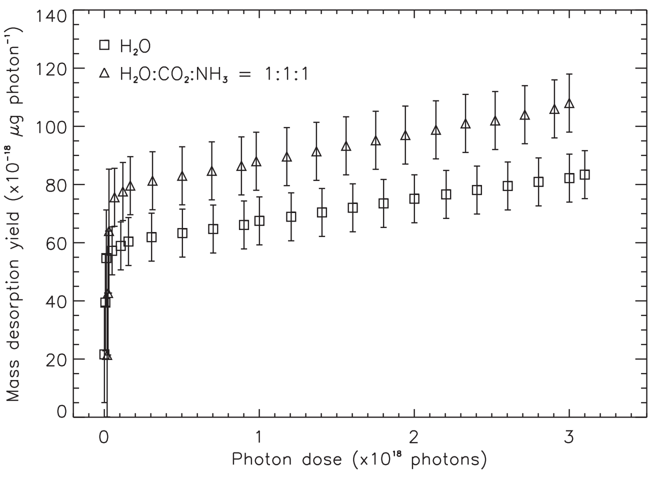

Fig. 4. Mass desorption yields as a function of the increasing photon dose for pure H_2O ice (squares) and the $H_2O:CO_2:NH_3 = 1:1:1$ ice mixture (triangles) at 16 K.

is about one order of magnitude higher than the value reported by Westley et al. (1995), and more recently by Öberg et al. (2009b), from which we can derive a value of 1.8×10^{-3} molecules photon^{-1} at 16 K (for a thick ice). This discrepancy could be due to the difference of incident photon energy. Indeed, a broad 4–20 eV photon energy range was chosen for our experiments, whereas Westley et al. (1995) and Öberg et al. (2009b) used a microwave-discharge H_2 lamp. Energetic EUV photons are expected to be more efficient than UV photons for desorption processes (Wu et al., 2002).

3.3. Photo-production of small molecules

The desorbed photo-products, formed from the photolysis of the H_2O:CO_2:NH_3 = 1:1:1 ice mixture, include: (1) the starting components H_2O, NH_3, and CO_2, (2) small closed-shell molecules such as H_2 (molecular hydrogen), CO (carbon monoxide), and O_2 (molecular oxygen), (3) radicals such as $OH^{\bullet}$, $NH^{\bullet}$, $NH_2^{\bullet}$, and $CH_3^{\bullet}$, which are photo-fragments of the starting ices, (4) $H^{\bullet}$, $C^{\bullet}$, $N^{\bullet}$, and $O^{\bullet}$ atoms, elementary constituents of the starting ices, and (5) photo-products of higher molecular masses, whose detection and identification will be discussed in Section 3.4. All those species are listed in Table 2 as a function of their increasing molecular mass.

Some of the proposed assignments are only tentative. For example, mass 16 amu can a priori be attributed to $O^{\bullet}$, $NH_2^{\bullet}$, or CH_4 (methane). However, the most abundant product among those three is expected to be the $NH_2^{\bullet}$ radical because it is a direct photo-fragment of NH_3. $O^{\bullet}$ atoms are also probably released from the full photo-dehydrogenation of H_2O and the photolysis of CO_2, but most probably with a lower abundance than $NH_2^{\bullet}$, because OC–O bonds are stronger than NH_2–H bonds, and because the full photo-dehydrogenation of H_2O is a 2-photon process. Consequently, the least abundant product with a mass of 16 amu is expected to be CH_4, since its formation from CO_2 (only source of carbon in the starting mixtures) requires a mechanism involving several photons and reactions (multiple photochemical processes) with other (hydrogenated) species. Similarly, mass 17 can be due to the desorption of either NH_3 (starting ice component) or the $OH^{\bullet}$ radical, readily formed from the photolysis of H_2O. However, it is difficult to estimate the relative proportions of the desorbed NH_3 and $OH^{\bullet}$, so we will assume that each species contributes to about half of the signal measured for mass 17.

Mass 28 can the same way be assigned to CO, molecular nitrogen N_2, or ethylene C_2H_4 (Table 2). In this case, CO appears to be the most probable candidate since it is a well-known direct photo-product of CO_2 (Okabe, 1978), including in ices (Gerakines et al., 1996; Wu et al., 2003). The presence of N_2 is less probable because its formation from NH_3, only source of nitrogen in the starting mixture involves a multi-photon mechanism. Similarly, the formation of C_2H_4 requires a multi-photon pathway from CO_2, only source of carbon in the starting mixture. In the following, we will thus assign this mass to CO only. Another interesting peak was observed for mass 32, which can be assigned to O_2 or CH_3OH (Table 2). Using similar arguments as mentioned above, O_2 is expected to be more abundant than CH_3OH, although the formation of both molecules requires several photochemical steps.

Figure 5 shows the ion currents for 6 selected mass peaks as a function of the photon dose for the H_2O:NH_3:CO_2 = 1:1:1 ice mixture. All curves quickly reach saturation for an integrated photon dose of about 1×10^{18} photons. The most abundant desorbed species is CO (28 amu), with an abundance ~1.4 times that of H_2 (2 amu). Figure 5 also indicates that the quantity of H_2 formed in this experiment is high, which is an information that cannot be obtained via other in situ techniques such as infrared spectroscopy, because H_2 desorbs quickly from the ice matrix and does not have any IR signature. This observation suggests that the formation of H_2 is favored over that of oxidized molecules because of the relatively high proportion of NH_3 in the starting ice mixture compared with cometary and interstellar abundances (Table 1). Indeed, previous theoretical calculations of chemical reactions occurring in icy mantles coating interstellar grains already suggested that H_2 is most likely produced from the photo-dehydrogenation of NH_3 and H_2O (d'Hendecourt et al., 1985; Tielens and Hagen, 1982), due to the low NH_2–H and HO–H dissociation energies of 4.60 (Mordaunt et al., 1996) and 5.10 eV (Woon, 2002), respectively.

The [CO]/[CO_2] ratio of the ion current between masses 28 (CO) and 44 amu (CO_2) was found to be ~11.2 for our H_2O:NH_3:CO_2 mixture after the saturation plateau was

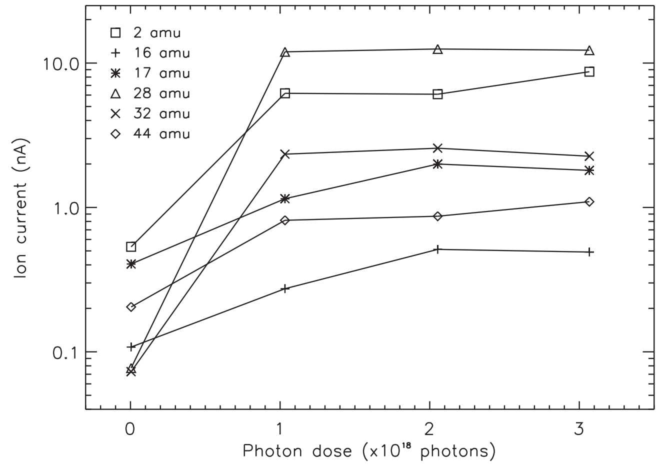

Fig. 5. QMS ion currents for 6 selected molecular masses of desorbed photo-products, namely, 2 amu (H_2), 16 amu ($NH_2^{\bullet}$ and/or $O^{\bullet}$), 17 amu (NH_3 and/or $OH^{\bullet}$), 28 amu (CO), 32 amu (O_2), and 44 amu (CO_2), as a function of the increasing photon dose after UV/EUV irradiation of the H_2O:CO_2:NH_3 = 1:1:1 ice mixture at 16 K. Except for NH_3 and CO_2, these compounds were formed from the photolysis of the starting ice mixture. A saturation plateau for the formation of those species appears when the integrated photon dose reaches about 1×10^{18} photons.

reached (Fig. 5). CO is a very volatile compound that can be easily desorbed from ices even at 16 K as recently confirmed by photo-desorption experiments of pure CO ices (Öberg et al., 2007). Moreover, CO can only be a product of photolysis of CO_2 in our experiment, since CO_2 is the only source of carbon in the starting mixture. Öberg et al. (2009a) also showed that pure CO ice and pure CO_2 ice have similar desorption yields, although in our case their absolute yields might differ because CO_2 is in excess compared with CO, since it is a photo-product of CO_2 that can be trapped in the ice matrix. The photolysis of CO_2 leads to the formation of CO and O_2, the latter being most probably produced via the recombination of two $O^\bullet$ atoms (Okabe, 1978; Smardzewski, 1978):

$$CO_2 + h\nu \rightarrow CO_2^* \rightarrow CO + O^\bullet, \tag{1}$$

$$2\ O^\bullet \rightarrow O_2, \tag{2}$$

where the asterisk indicates that CO is in an excited state after absorption of the photon $h\nu$. The global photochemical pathway for the formation of O_2 from the photolysis of CO_2 can thus be re-written as:

$$2\ CO_2 + 2\ h\nu \rightarrow 2\ CO + O_2. \tag{3}$$

Therefore, according to Eq. (3), a $[CO]/[O_2]$ ratio of 2 is expected at the saturation level if O_2 is only photo-produced via this pathway. However, the $[CO]/[O_2]$ ratio found in our experiment was ~5.4 (Fig. 5), indicating that the $O^\bullet$ atoms formed from the photolysis of CO_2 do not all recombine to form O_2, but rather recombine with CO to form CO_2 again, and/or are involved in the formation of other complex molecular species. It is to be noted that $O^\bullet$ atoms can also be produced from the full dehydrogenation of H_2O, although such $O^\bullet$ atoms may be most probably involved in the formation of complex molecules rather than O_2.

Assuming that half of the signal for mass 17 is due to the desorption of NH_3 as discussed earlier, the abundances of the photo-desorbed NH_3 and $NH_2^\bullet$ result in a $[NH_3]/[NH_2^\bullet]$ ratio of ~1.9 (Fig. 5), indicating that about one third of the ammonia is converted into $NH_2^\bullet$ radicals. This ratio may however vary since $O^\bullet$ atoms and/or CH_4 molecules may slightly contribute to the ion current for mass 16, although $NH_2^\bullet$ is expected to be the main contributor to this ion current. The photo-produced $NH_2^\bullet$ radical is a very reactive species, even at low temperature, that can either recombine with $H^\bullet$ atoms to form NH_3 again, or react with other species to form complex molecules. Therefore, only a small fraction of $NH_2^\bullet$ is expected to be desorbed. Understanding the formation pathways for $NH_2^\bullet$ is interesting because this radical is used for the classification of comets along with C_2 and $CN^\bullet$. $[NH_2^\bullet]/[H_2O]$ ratios have sometimes been used as a parameter to compare comets (Fink and Hicks, 1996).

The photolysis of NH_3 and H_2O produce $H^\bullet$ atoms that can subsequently lead to the formation of H_2 by radical–radical recombination. Such reaction processes have been previously reported and discussed (Hudson and Moore, 2000; Westley et al., 1995):

$$NH_3 + h\nu \rightarrow NH_3^* \rightarrow NH_2^\bullet + H^\bullet, \tag{4}$$

$$H_2O + h\nu \rightarrow H_2O^* \rightarrow OH^\bullet + H^\bullet, \tag{5}$$

$$2\ H^\bullet \rightarrow H_2. \tag{6}$$

The global equations for the formation of H_2 via the photolysis of NH_3 and H_2O can thus be re-written as:

$$2\ NH_3 + 2\ h\nu \rightarrow 2\ NH_2^\bullet + H_2, \tag{7}$$

$$2\ H_2O + 2\ h\nu \rightarrow 2\ OH^\bullet + H_2. \tag{8}$$

According to Eqs. (7) and (8), we expect $[H_2]/[NH_2^\bullet]$ and $[H_2]/[OH^\bullet]$ ratios to be 0.5 at the saturation level. This assumes that H_2 is equally formed from the photo-decompositions of NH_3 and H_2O, because NH_2–H and HO–H bonds have similar dissociation energies (Mordaunt et al., 1996; Woon, 2002).

The $[H_2]/([NH_2^\bullet] + [OH^\bullet])$ ratio is thus expected to be ~1, NH_3 and H_2O having the same abundances in the starting ice mixture and roughly the same probability to be photolyzed by an incoming photon. However, from Fig. 5, we could derive for our mixture lower limits of ~17.7, ~4.8, and ~3.8 for the $[H_2]/[NH_2^\bullet]$, $[H_2]/[OH^\bullet]$, and $[H_2]/([NH_2^\bullet] + [OH^\bullet])$ ratios, respectively. These values indicate that $NH_2^\bullet$ and $OH^\bullet$ radicals either are trapped in the ice matrix and not efficiently desorbed, or, most probably, react efficiently with other species, themselves, or each other. This result also suggests that H_2 is not formed only from the photolysis of NH_3 and H_2O, but also via other more complex and indirect pathways that still need to be identified. Once it is formed, H_2 will escape from the ice matrix, due to its low sublimation temperature (14 K), as well as its small size and molecular weight.

These results indicate that a large fraction of the UV/EUV photons absorbed by the $H_2O:CO_2:NH_3 = 1:1:1$ mixture is involved in the dissociation of hydrogenated compounds, which can be the starting ice components and/or some of their photo-products. Only the presence of CO_2 in the starting mixture seems to favor the formation of oxidized compounds such as CO and O_2 with high abundances (Fig. 5). This suggests that in astronomical objects where hydrogenated compounds such as NH_3 are less abundant, the production of oxidized molecules, including O_2 and organic molecules, may be favored. However, solid O_2 was so far only tentatively and indirectly detected in the ISM (Vandenbussche et al., 1999), due mainly to the fact that O_2 has no IR signature.

3.4. Photo-production of more complex molecules

More complex organic molecules are also expected to be produced, with however smaller abundances than the species mentioned in Section 3.3. As summarized in Table 2, we have tentatively assigned masses 27, 29, 30, 32, 42, 43, and 45 amu to hydrogen cyanide and/or isocyanide HCN/HNC, the formyl radical $HCO^\bullet$, formaldehyde

H_2CO, methanol CH_3OH, the cyanate radical $OCN^\bullet$ and/or its anion OCN^-, isocyanic acid HNCO, and formamide $HCONH_2$, respectively, and mass 46 amu to formic acid HCOOH and/or ethanol C_2H_5OH. Most of these species are stable, neutral, closed-shell organic molecules, and are known to be formed in ice mixtures subject to VUV (Gerakines et al., 2001; Hudson and Moore, 2000) and UV/EUV photo-irradiation (Wu et al., 2002, 2003, 2006). Note that the photo-desorbed $OCN^\bullet$ radical might actually stem from the OCN^- anion in the ice matrix. However, since our quadrupole mass spectrometer can only detect positive ions, either directly desorbed from the ice or produced by ionization of neutral species, OCN^- cannot be directly detected in our study. OCN (radical or anion) and $HCO^\bullet$ (radical) are very reactive species likely to recombine promptly with other compounds. Therefore, only small amounts of these molecules are expected to be detected among photo-desorbed species during UV/EUV irradiation.

Finally, assignments to larger organic molecules such as CH_3OH, $HCONH_2$, HCOOH, and C_2H_5OH in Table 2 are only tentative because of their very weak peak intensities. It is however to be mentioned that the presence of CH_3OH is likely, since it is one of the most abundant ice components in cometary and interstellar ices (Table 1) that can be formed via hydrogenation of CO_2 (starting ice component) and/or its photo-product CO (Fuchs et al., 2009; Watanabe et al., 2003) (see Section 3.5). Further studies, using complementary and independent experimental techniques, will be carried out in order to confirm the identification of such products in photo-desorption experiments under our experimental conditions.

3.5. Astrochemical considerations

Most of the organic molecules that have been observed or tentatively identified in our photo-desorption experiment have also been detected in space. Indeed, observations from the European Infrared Space Observatory (ISO) in the IR range showed that those species are present in Solar System icy bodies such as comets, and in interstellar environments where icy mantles are coating cold silicate or carbonaceous grains (Bernstein et al., 1999; Crovisier, 1998; Dartois et al., 2002; Gibb et al., 2000, 2004; Moore et al., 1996; and references therein).

Those species have also been shown to be present in samples formed in the laboratory from the UV irradiation of ices containing molecules known to be abundant in astrophysical environments, namely, H_2O, CO, CO_2, CH_3OH, NH_3, HCN, etc. (see Table 1) at low temperature. Such experimental simulations showed in particular that the UV irradiation of these ices always leads to the formation of organic residues consisting of complex organics (Bernstein et al., 1995, 1997; Muñoz Caro and Schutte, 2003). The composition of these residues seems to be mostly independent from the temperature at which the ices are irradiated in the ~10–80 K range, the substrate, and the composition of the starting ice mixture, as long as it contains the four elements required to form organic molecules, namely, carbon, hydrogen, oxygen, and nitrogen, as shown in the study of the formation of the amino acids present in organic residues (Nuevo et al., 2008).

HCN, its isomer HNC, as well as the $CN^\bullet$ radical and other CN-bearing molecules have been observed in comets (Crovisier, 1998; Mumma et al., 2001), interstellar clouds (gas phase) (Pirogov, 1999; Sohn, 2004; and references therein), and circumstellar environments (solid phase) (Aoki et al., 1999; Wiedemann et al., 1991). Nitrile-bearing compounds, including HCN and salts such as NH_4CN are believed to be the precursors of biological compounds including nucleobases, the informational subunits of DNA and RNA (Borquez et al., 2005; Minard et al., 1998), and proteins (Matthews, 1975). However, it has been shown that their formation may not be favored in the overly reducing atmosphere of the early Earth (Whittet et al., 2001a). Therefore, they are thought to be formed in astrophysical environments before being delivered to the Earth, and probably other planets, via comets and meteorites (Chyba and Sagan, 1992; Oró, 1961), where they may have played a significant role in the first prebiotic reactions that led to the emergence of life on our planet.

OCN^- (anion) was tentatively detected in the spectrum of the embedded protostar W33A (Gibb et al., 2000) as well as in Comet Hale-Bopp (Crovisier, 1998) with abundances of 3% and 0.37% relative to H_2O, respectively (Table 1). It was also probably detected together with its counter-cation NH_4^+ in the astronomical sources MonR2:IRS3 (Schutte and Khanna, 2003) and NGC 7538 IRS 9 (Gibb et al., 2000). OCN^- is believed to form only from the photolysis of astronomical ices, so that it is sometimes used as a tracer of the photochemical evolution of organics in the ISM (Pendleton et al., 1999; Whittet et al., 2001b). In addition, OCN^- was observed around low-mass stars in the IR range (van Broekhuizen et al., 2005), where it is usually thought to be in acid/base equilibrium with HNCO.

HNCO was observed in the gas phase of the ISM (Rubin et al., 1971; Turner, 1991; Zinchenko et al., 2000), and was shown to be easily formed from NH_3 and CO via the following photochemical process (Hudson et al., 2001):

$$NH_3 + h\nu \rightarrow NH_3^* \rightarrow NH_2^\bullet + H^\bullet, \tag{9}$$

$$NH_2^\bullet + CO \rightarrow HNCO + H^\bullet. \tag{10}$$

OCN^-/HNCO and NH_4^+ are potential candidates for the precursors of urea (NH_2CONH_2) (Wöhler, 1828), an organic molecule of prebiotic interest, that has been tentatively detected in the protostellar source NGC 7538 IRS 9 (Raunier et al., 2004), as well as in organic residues formed from the UV photo-irradiation of ice mixtures containing H_2O, CH_3OH, and NH_3 at low temperature (Nuevo et al., 2010).

Formaldehyde (H_2CO) is a relatively abundant component of interstellar and cometary ices with respect to H_2O. It is believed to condense onto cold interstellar grains before being incorporated into comets during the formation of stellar nebulae. H_2CO was first detected in Comet Halley with a production rate of a few percents with respect to H_2O in the IR (Combes et al., 1986; Knacke et al., 1986) and radio ranges (Snyder et al., 1989). Subsequently, H_2CO has also been observed in other comets (Bockelée-Morvan et al., 1994). In cometary and interstellar environments, formaldehyde may also be present in its polymeric form, namely, polyoxymethylene (POM), as suggested by recent studies by Cottin et al. (2001, 2004). H_2CO is generally expected to form via hydrogenation of CO ice at low temperature, as reported in recent laboratory and theoretical studies (Fuchs et al., 2009; Watanabe et al., 2003). This formation pathway is compatible with what is observed in our experiment, where CO is the main photo-product of CO_2, and where $H^\bullet$ atoms and H_2 molecules are produced from the photolysis of H_2O and NH_3.

Methanol (CH_3OH) is one of the most abundant components of interstellar and circumstellar ices after H_2O, CO, and CO_2 (Table 1). In some cases, CH_3OH can even be the second most abundant component after H_2O (Dartois et al., 1999; Gibb et al., 2000; d'Hendecourt et al., 1996; Pontoppidan et al., 2004; Skinner et al., 1992; Whittet et al., 1996). It has also been observed in the coma of comets (Bockelée-Morvan et al., 1994; Crovisier, 1998; Ikeda et al., 2002). Methanol is believed to be the hydrogenation product of H_2CO, formed via the same pathway from CO (Fuchs et al., 2009; Watanabe et al., 2003).

Formamide ($HCONH_2$; Rubin et al., 1971; Gottlieb et al., 1973), ethanol (C_2H_5OH; Millar et al., 1988, 1995), and formic acid (HCOOH; Liu et al., 2001, 2002) are among the largest organic molecules that have been observed in the ISM in the gas phase. Only formamide has tentatively been detected in the solid phase (ice) in the protostellar source NGC 7538 IRS 9 (Raunier et al., 2004). In the laboratory, formamide has been produced and detected in the solid phase after irradiation of interstellar ice analogs with UV photons and energetic protons (Chen et al., 2007; Gerakines et al., 2004), confirming that this compound can be formed via photochemical processes. The detection of larger molecules in astrophysical environments and in laboratory simulations is more challenging due to their high molecular weight and thus smaller abundances.

Finally, other complex organic molecules may have been formed in our experiments, but their detection via mass spectrometry is difficult because of their low volatility and/or small abundances. However, our study completes the database of organic species that might be detected by future radio-astronomical (gas phase) observations of interstellar environments where ice-coated cold grains are exposed to UV photon irradiation and desorbed from the grains. All species mentioned in the present study constitute interesting targets for the COSAC instrument onboard the lander Philae of the European mission ROSETTA, that will probe in situ the nucleus of Comet 67P/Churyumov–Gerasimenko in 2014 (Goesmann et al., 2005, 2007; Thiemann and Meierhenrich, 2001).

4. Conclusion

An $H_2O:CO_2:NH_3 = 1:1:1$ ice mixture was irradiated at 16 K with UV/EUV 4–20 eV photons provided by a synchrotron radiation source. Using a quartz crystal resonator microbalance, we measured the total mass photo-desorption rate of this ice mixture during irradiation. Mass spectrometry was employed to monitor the desorption of some photo-products including H_2, $OH^\bullet$, $NH_2^\bullet$, CO, and O_2, along with the starting ice components H_2O, NH_3, and CO_2. We also tentatively detected larger species with smaller abundances such as HCN, $HCO^\bullet$, H_2CO, CH_3OH, $OCN^\bullet/OCN^-$, HNCO, $HCONH_2$, HCOOH, and C_2H_5OH. Although their presence in our samples must be confirmed, the relevance of the identification of these species is strongly supported by their observation in the interstellar medium and in comets, indicating that the processes occurring in astrophysical media can be reproduced in the laboratory. Future work will include a more detailed study of the mechanisms of formation of such species, their production yields, their formation rates, as well as their desorption efficiencies in various astrophysical environments.

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