Synthesis of Complex Organic Molecules in Soft X-Ray Irradiated Ices

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Abstract

We study the chemical evolution of H2O:CO:NH3 ice mixtures irradiated with soft X-rays, in the range of 250–1250 eV. We identify many nitrogen-bearing molecules such as, e.g., OCN−, NH3+, HNCO, CH3CN, HCONH2, and NH2COCONH2. Several infrared features are compatible with glycine or its isomers. During the irradiation, we detected through mass spectroscopy many species desorbing the ice. Such findings support the infrared identifications and reveal less abundant species without clear infrared features. Among them, m/z = 57 has been ascribed to methyl isocyanate (CH3NCO), a molecule of prebiotic relevance, recently detected in protostellar environments. During the warm-up after the irradiation, several infrared features including the 2168 cm−1 band of OCN−, the 1690 cm−1 band of formamide, and the 1590 cm−1 band associated with three different species, HCOO−, CH3NH2, and NH2CH2COO survive up to room temperature. Interestingly, many high masses have also been detected. Possible candidates are methylformate, (m/z = 60, HCOOCH3), ethanediamide (m/z = 88, NH2COCONH2), and N-acetyl-L-aspartic acid (m/z = 175). The latter species is compatible with the presence of the m/z = 43, 70, and 80 fragments. Photodesorption of organics is relevant for the detection of such species in the gas phase of cold environments, where organic synthesis in ice mantles should dominate. We estimate the gas-phase enrichment of some selected species in the light of a protoplanetary disk model around young solar-type stars.

Key words: ISM: molecules – methods: laboratory: solid state – X-rays: ISM

1. Introduction

Ice mantles covering cold dust particles in dense clouds and circumstellar regions are laboratories for chemistry giving rise to a plethora of chemical species (Herbst & van Dishoeck 2009). Processing of space ice analogs with ultraviolet photons (Bernstein et al. 1995, 2002; Muñoz Caro et al. 2002; Muñoz Caro & Schutte 2003; Meierhenrich et al. 2004; Nuevo et al. 2006; Chen et al. 2007; de Marcellus et al. 2011; Muñoz Caro & Dartois 2013; Vinogradoff et al. 2013; Meinert et al. 2016; Oba et al. 2016), and energetic particles (Palumbo et al. 1998; Loefller et al. 2005; Sicilia et al. 2012; Islam et al. 2014; Jones et al. 2014; Muñoz Caro et al. 2014; Förstel et al. 2016) have widely explored the cold solid state synthesis of complex organic molecules. Formation routes, mechanisms responsible for the production of new species, and efficiency of the different energetic processing have contributed to the interpretation of the observed interstellar ice features (Boogert et al. 2015). More recently X-ray processing of ice analogs has been studied given its relevance in circumstellar disks around young stars (Andrade et al. 2010; Ciaravella et al. 2010, 2010; Jiménez-Escobar et al. 2012, 2016, 2018; Chen et al. 2013; Pilling & Bergantini 2015; Ciaravella et al. 2016). In solar-type stars X-ray emission dominates over far extreme ultraviolet emissions for almost one billion years (Ribas et al. 2005) penetrating through the disk and reaching inner regions otherwise forbidden to less energetic photons (e.g., Walsh et al. 2012).

In this paper we present evidence for the synthesis of N-bearing organic molecules induced by soft X-rays in an H2O:CO:NH3 (1:0.9:0.7) ice mixture. The photodesorption of a similar mixture is discussed in Jiménez-Escobar et al. (2018).

The photochemistry of ices containing ammonia was first studied in atmospherically relevant ice mixtures by Hagen et al. (1979), who irradiated a CO ice containing traces of water, ammonia, and carbon dioxide. This early investigation and others that followed—changing the initial composition, the abundance ratios, and the energy source—had as major outcomes the formations of XCN compounds (in particular OCN−), and moderately complex amino containing molecules, which may be precursors for amino acids. The largest infrared detected molecule was C6H3N4 (Muñoz Caro & Schutte 2003). Subsequently, two independent studies formed amino acids by zapping dirty water ices with ultraviolet radiation (Bernstein et al. 2002; Muñoz Caro et al. 2002). The ices contained a fairly high amount of ammonia, methanol and hydrogen cyanide. In addition, the processing of nitrogen-bearing mixtures produced species with the peptide moiety, such as, e.g., isocyanic acid, HNCO, the smallest stable nitrogen-bearing mixture produced species with the peptide moiety, such as, e.g., isocyanic acid, HNCO, the smallest stable nitrogen-bearing mixture produced species with the peptide moiety, such as, e.g., isocyanic acid, HNCO, the smallest stable nitrogen-bearing mixture produced species with the peptide moiety, such as, e.g., isocyanic acid, HNCO, the smallest stable nitrogen-bearing mixture produced species with the peptide moiety, such as, e.g., isocyanic acid, HNCO, the smallest stable nitrogen-bearing mixture produced species with the peptide moiety, such as, e.g., isocyanic acid, HNCO.
During the photoexcitation of a core level, the electron is first promoted to an unoccupied orbital, with a resulting core-hole filled by an electron as in the normal Auger case. Then, an Auger electron is released with an energy corresponding to the excess energy of the transition.

The ejected electrons interact with the ice, producing a chain of (valence orbital) ionizations, freeing gradually other electrons of increasingly smaller energy, that, until they can, keep ionizing the ice material. This leads to the fragmentation of the ice molecules with a creation of a large number of ions and radicals, through a number of processes, such as, e.g., dissociative electron attachment, in which a molecule captures a low-energy electron in an excited resonant state, forming a transient molecular anion, that eventually dissociates (e.g., Munro et al. 2012).

We describe the experiment in Section 2. We present and discuss the results in Section 3: irradiation products, the warm-up phase followed through infrared and mass spectroscopy, and the refractory residue left on the window after the warm-up of the sample to room temperature. The conclusions and the astrophysical implications are in Section 4.

2. Experiment

The experiments were carried out in the Interstellar Photoprocess System (IPS), an ultrahigh vacuum (UHV) chamber of base pressure $1.3 \times 10^{-10}$ mbar. A mid-infrared Fourier Transform Infrared ABB FTLA-2000-104 spectrometer equipped with a mercury–cadmium–telluride infrared detector records infrared spectra in transmission of the ice sample. A Quadrupole Mass Spectrometer (QMS) in the 1–200 amu range (0.5 amu resolution) was used to monitor the ice and the composition of the gas in the chamber during the whole experiment. The gas line system baked out at 120 °C to eliminate organic and water contamination reaches a minimum pressure of $1.3 \times 10^{-7}$ mbar before preparing the gas mixture for the experiments. For a detailed description of the IPS facility, see Chen et al. (2014). As an X-ray source we used the Spherical Grating Monochromator beamline BL08B at National Synchrotron Radiation Research Center (NSRRC, Taiwan) covering photon energies from 250 to 1250 eV, whose spectrum is in Figure 1. During the experiments, X-ray photon flux is monitored by an in-line nickel mesh (about 90% optical transmission), calibrated by a traceable photodiode (International Radiation Detectors, Inc.).

![Figure 1. X-ray spectrum of the BL08B beamline at NSRRC used for the irradiation.](image1)

Figure 1. X-ray spectrum of the BL08B beamline at NSRRC used for the irradiation.

![Figure 2. Infrared spectra of the mixture in the range of 980–3800 cm$^{-1}$.](image2)

Figure 2. Infrared spectra of the mixture in the range of 980–3800 cm$^{-1}$. From the bottom the curves are the spectra of the ice before irradiation followed by those taken after 0.5, 1, 5, 10, 20, 40, 60, 80, 100, and 120 minute irradiation. The curves are shifted for clarity.

A KBr window cooled to 13 K was used as a substrate for a H$_2$O:CO:NH$_3$ (1:0.9:0.7) ice mixture. Such a mixture was irradiated with the soft X-ray spectrum of Figure 1 for a total of 120 minutes. In the mixture we used H$_2$O from Merck, GC-mass grade, freeze-pump-thaw degassing more than three times; CO and NH$_3$ from Matheson, 99.99% purity. The column densities of the ice components were $8.2 \times 10^{17}$ molecules cm$^{-2}$ for H$_2$O, derived using the 5018 cm$^{-1}$ band with a band strength $A$(H$_2$O) = $1.2 \times 10^{-18}$ cm molecule$^{-1}$ (Gerakines et al. 2005), $7.0 \times 10^{17}$ molecules cm$^{-2}$ for CO using the band at 2142 cm$^{-1}$ with $A$(CO) = $1.1 \times 10^{-17}$ cm molecule$^{-1}$ (Jiang et al. 1975), and $5.5 \times 10^{17}$ molecules cm$^{-2}$ for NH$_3$ using the band at 1112 cm$^{-1}$ with $A$(NH$_3$) = $1.7 \times 10^{-17}$ cm molecule$^{-1}$ (Sandford & Allamandola 1993). The total column density of the mixture is $N$(CO) + $N$(H$_2$O) + $N$(NH$_3$) = $2.1 \times 10^{18}$ molecules cm$^{-2}$.

Before and after irradiation, infrared spectra were collected with a resolution of 1, 2, and 4 cm$^{-1}$. The irradiation was stopped 10 times (0.5, 1, 5, 10, 20, 40, 60, 80, 100, 120 minutes) and infrared spectra were taken with a resolution of 2 cm$^{-1}$. At the end of the irradiation, the ice was heated up to room temperature at a rate of 2 K minute$^{-1}$. During the warm-up, infrared spectra were acquired every 10 K with a resolution of 4 cm$^{-1}$. The QMS was scanning masses from 1 to 200 amu during the whole experiment. We also ran a blank experiment using a similar ice mixture and no irradiation.

3. Results and Discussion

3.1. Irradiation and Products

During the radiation, infrared spectra and mass spectra of the photodesorbing species were recorded. It is worth mentioning that both techniques have a degree of degeneracy. Blending of the infrared features of different species prevent in many cases a unique identification. Mass spectra of less abundant and/or heavier species are more difficult to detect. We used infrared and mass spectra to identify the products and whenever necessary we based our identification on the most probable formation routes during the irradiation and the warm-up.
The primary effect of the X-rays is the core ionization of the atoms in the molecule as

\[ \text{H}_2\text{O} \xrightarrow{\nu} \text{H}_2\text{O}^{++} + e_\text{ph}^- \rightarrow \text{OH}^+ + \text{H}^+ + e_\text{ph}^- + e_{\text{A}}^- \]  

(Mase et al. 1998), and

\[ \text{CO} \xrightarrow{\nu} \text{CO}^{++} + e_\text{ph}^- \rightarrow \begin{cases} \text{CO}^2+ + e_\text{ph}^- + e_{\text{A}}^- \\ \text{C}^+ + \text{O}^+ + e_\text{ph}^- + e_{\text{A}}^- \end{cases} \]  

(Benndor et al. 1999). The star symbol (*) indicates an excited state. In a liquid solution of ammonia and water a nitrogen 1s core-level ionization results in

\[ \text{NH}_3 \xrightarrow{\nu} \text{NH}_3^+ + \text{H}^+ + e_\text{ph}^- \]  

(Unger et al. 2015). In the case of N 1s excitation to the 4\alpha 1 molecular orbital, the core-excited molecule de-excites primarily via resonant Auger decay into

\[ \text{NH}_3 \xrightarrow{\nu} \text{NH}_3^+ \rightarrow \begin{cases} \text{NH}_2^+ + \text{H}^+ + 2e_{\text{A}}^- \\ \text{NH}_3^+ + \text{H}^+ + \text{H} + 2e_{\text{A}}^- \end{cases} \]  

The ejected primary photoelectrons, \( e_\text{ph}^- \), and Auger electrons, \( e_{\text{A}}^- \), will further interact with the ice, giving rise to a cascade of secondary electrons that will drive the chemistry.

In Figure 2 the infrared spectra of the mixture sample and those taken at different steps during the irradiation are shown. From Figure 2, the range between 2400 and 1000 cm\(^{-1}\) is the richest in new features. A close-up view of this portion along with the region between 2750 and 3550 cm\(^{-1}\) is reported in Figure 3, in which we marked the most abundant species (see Table 1). The spectral region from 1800 to 1000 cm\(^{-1}\) is dominated by \( \text{NH}_3^+ \), -\( \text{NH}_2^+ \), and -\( \text{COO}^- \) stretches and C-H bending, found in a large variety of organic molecules, from simplest compounds to more complex molecules such as amino acids. In Figure 4 are shown the mass spectra of the main fragments desorbing during the irradiation. Along with the masses of the parent molecules (\( \text{CO} m/z = 28, \text{H}_2\text{O} m/z = 18 \) and \( \text{NH}_3 m/z = 17 \)) and their main fragments (having 10 desorption peaks as many as the number of the irradiation steps), we also detected many other molecules showing the same pattern. Although more noisy, less abundant species/fragments show similar patterns.

The majority of the infrared features appear after the first 30 s irradiation. \( \text{CO}_2 (2342 \text{ cm}^{-1}, m/z = 44) \) is the most abundant product. \( \text{HNCO} (2168 \text{ cm}^{-1}) \) is a second generation product formed by direct reaction of \( \text{CO} \) with \( \text{NH}_2 \) produced after the direct interaction of \( \text{NH}_3 \) with X-ray (reaction 3, see also Hudson & Moore 2000)

\[ \text{NH}_2 + \text{CO} \rightarrow \text{HNCO} + \text{H.} \]  

(5)

\( \text{OCN}^- (2168 \text{ cm}^{-1}) \) arises from the reaction between \( \text{NH}_3 \) and \( \text{HCO} \)

\[ \text{NH}_3 + \text{HNC} \rightarrow \text{OCN}^- + \text{NH}_4^+. \]  

(6)

The cyanate ion has been detected in many experiments of ice irradiation and radiolysis (Gerakines et al. 2004; van Broekhuizen et al. 2005; Chen et al. 2007; Pilling et al. 2010), and also observed in many astrophysical sources (Öberg & Boogert et al. 2011; Aikawa et al. 2012). The features at 2261 and 2242 cm\(^{-1}\) are associated with \( \text{HNCO} \) (Raunier et al. 2004). The detection of mass \( m/z = 43 \) during the irradiation and the warm-up support the presence of this species. In this region of the spectrum only a band at 2233 cm\(^{-1}\) has been detected in 46 MeV Ni ions irradiation of a similar mixture by Pilling et al. (2010), and has been assigned to \( \text{N}_2\text{O} \).

At 2260 cm\(^{-1}\) there is the \( \nu_2 \) CN-stretch feature of acetonitrile (\( \text{CH}_2\text{CN} \); Mencos & Krim 2016). Mass spectra of \( m/z = 41 \) have been detected during irradiation and warm up. Such mass is also associated with an isomer of acetonitrile \( \text{CH}_2\text{CNH} \) compatible with the infrared feature at 2038 cm\(^{-1}\) as listed in Table 1. Both species have been detected in space (McGuire 2018).
Another possible proton donor could be the hydronium ion H3O⁺, as it occurs in liquid solutions.

The absorption at 1590 cm⁻¹ is widely contributed by the vibrational modes of the asymmetric stretching of HCOO⁻ and the -NH₂ scissor of species such as CH₃NH₂ (m/z = 31) (Holtom et al. 2005), an intermediate in the amino acids formation (Woon 2002) or even an amino acid such as glycine (Mate et al. 2018). The features at 1495 and 1590 together with the feature at 2900 cm⁻¹ are also associated with the zwitterionic, NH₃CH₂COO⁻ (Hudson & Moore 2000), or the neutral form of glycine, NH₂CH₂COOH (Gómez-Zavaglia & Fausto 2003; Mate et al. 2011). Formation of glycine is also supported by QMS detection of m/z = 75 desorbing in the range of 200–240 K (see Figure 9) during the warm-up. Glycine formation in ice mixtures have been inferred in ion irradiation (Pilling et al. 2010). However, as remarked by Oba et al. (2016) in ultraviolet-irradiated ice analogs, glycine is not a major component of m/z = 75, with many other isomers such as methylcarboxylic acid, CH₃NHCOOH, and glycamide, NH₂COCH₂OH, that dominate.

Table 1 summarizes all the infrared features identified in the spectra, their assignments, and for some species the band strengths. In Figure 5 we report the column densities of H₂O, CO, and NH₃ and four products CO₂ 2342 cm⁻¹, OCN⁻ 2168 cm⁻¹, HCO 1848 cm⁻¹, and HNCO 2242, 2261 cm⁻¹. Two Gaussian fitting is used to compute the integrated absorbances of CO and OCN⁻. HNCO is the sum of the 2241 and 2261 cm⁻¹ bands (Raunier et al. 2004). Three Gaussian fitting needs to separate the bands of HNCO from 13CO₂ at 2277 cm⁻¹. At the end of the irradiation ~73% of the H₂O, ~75% of the CO and ~85% of NH₃ have been destroyed. CO₂, OCN⁻, and HNCO increase for the first 60 minute irradiation. OCN⁻ species is always less abundant than CO₂. HCO increases during the first 5 minutes and then decreases. This species was not detected in heavy ion irradiation (Pilling et al. 2010).

During the irradiation, thanks to its high sensitivity, the QMS detected masses of low abundant species that have no clear infrared features. As an example, m/z = 55, 56, and 57 cannot be related to species listed in Table 1. A promising candidate for m/z = 57 is methane isocyanate (CH₃NCO). The most intense feature of this species at 2278 cm⁻¹ (Mate et al. 2017) overlaps with the 13CO₂. However, the detections of m/z = 57 along with the two fragments CH₃NCO (m/z = 56) and CHNCO (m/z = 55) support the presence of such species. This molecule has been recently detected in a low-mass solar-type protostellar binary (Ligerink et al. 2017; Martín-Doménech et al. 2017).

Following the analysis by Jiménez-Escobar et al. (2018) we identified the species associated with the masses detected during the irradiation, see Table 2. In the same table we also list the masses detected during the subsequent warm-up phase along with their possible candidate species.

3.2. Warm Up: Infrared and Mass Spectra

At the end of the irradiation the ice has been warmed up at a rate of 2 K minutes⁻¹. In Figure 6 the infrared spectra of the ice at different temperatures during this phase are reported. As a comparison we report similar spectra for the blank experiment in Figure 7.
The desorption temperatures of species in the mixture are generally higher than those in single component ices (Martín-Doménech et al. 2014). The CO band at 2145 cm$^{-1}$ disappears completely between 170 and 190 K in the irradiated sample, and between 130 and 150 K in the blank. In a thick ($\approx 10^{18}$ cm$^{-2}$) pure CO ice such infrared feature disappears between 40 and 50 K. As listed in Table 2 many masses were detected by the QMS during this phase.

OCN$^-$ at 2168 cm$^{-1}$ is still present at 300 K, its column density as a function of the ice temperature is shown in Figure 8. The column density of the HNCO in the same figure is, as in Figure 5, the sum of the 2241 and 2261 cm$^{-1}$ bands. Although band strengths may change with temperature (e.g., Luna et al. 2018), no measurements on either OCN$^-$ or HNCO are available. Data reported in Figure 8 are thus obtained taking the band strengths as constant. The band strengths at 15 K of $1.3 \times 10^{-16}$ cm molecule$^{-1}$ for OCN$^-$ (van Broekhuizen et al. 2004), and $7.8 \times 10^{-17}$ cm molecule$^{-1}$ for HNCO (van Broekhuizen et al. 2004) have been used. During the warm-up OCN$^-$ increases from 50 up to 170 K, then starts decreasing. Such an increase could be justified by further production of OCN$^-$ through the reaction HNCO + NH$_3$ $\rightarrow$ OCN$^-$ + NH$_3$. In agreement with the infrared spectra, starting from 170 K the ion current of mass $m/z = 42$ increases reaching a broad peak between 240 and 270 K, with a tail extending up to 300 K (see Figure 9).

As mentioned in the previous section the infrared feature at 2260 cm$^{-1}$ is compatible with acetonitrile CH$_3$CN. During the warm-up $m/z = 41$ associated to such species or its isomer CH$_2$CNH is detected along with $m/z = 40$, see the second panel from the top in Figure 9. $m/z = 40$ is the largest fragment after $m/z = 41$ for both CH$_3$CN and CH$_2$CNH. Above $\sim 200$ K the profiles of such masses are very similar supporting the identification of the species.

The column density of CO$_2$ (2342 cm$^{-1}$) shown in Figure 10 as a function of the temperature during the warm-up phase indicates that about 90% of CO$_2$ desorbs between 150 and 190 K (see also Figure 6). Although the desorption peak of a pure CO$_2$ is around 85 K, a fraction of this molecule may be

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**Figure 4.** Ion current vs. cycle as detected by the QMS during the irradiation. The curves are all shifted for clarity. Left panel: $m/z = 12, 14, 15, 16, 17, 18, 26, 27, 28, 29,$ and 44. Right panel: $m/z = 30, 31, 39, 41, 42, 43, 45, 46, 55, 56,$ and 57. The ion current for $m/z = 30$ has been divided by 4.

**Figure 5.** Column density as a function of the irradiation time for the parent species H$_2$O (yellow dots), CO (green squares), and NH$_3$ (red asterisks), and the products CO$_2$ (blue diamonds), OCN$^-$ (orange triangles), HCO (light green crosses), and HNCO (light brown pluses).

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Table 2
QMS Detected Fragments

| m/z | Irrad. | Warm Up | Fragments |
|-----|--------|---------|-----------|
| 12  | y      | y       | C         |
| 13  | y      | y       | CH₃C      |
| 14  | y      | y       | N, CH₃    |
| 15  | y      | y       | HN, CH₃   |
| 16  | y      | y       | O, NH₃, CH₄|
| 17  | y      | y       | HO, NH₃   |
| 18  | y      | y       | H₂O       |
| 25  | ...    | ...     | CH₂C      |
| 26  | y      | y       | CO        |
| 27  | y      | y       | HCN       |
| 28  | y      | y       | CO, N₂    |
| 29  | y      | y       | HCO, ¹³CO, CH₃N |
| 30  | y      | y       | H₂CO, CH₃NH, NO |
| 31  | y      | y       | CH₂O,CH₃NH₂ |
| 32  | y      | y       | CH₂OH, O₂ |
| 33  | y      | y       | NH₂OH     |
| 34  | ...    | ...     | H₂O₂      |
| 36  | ...    | ...     | ?          |
| 38  | ...    | ...     | ?          |
| 39  | y      | y       | CHCN      |
| 40  | ...    | ...     | CH₃CN     |
| 41  | y      | y       | CH₂CN, CH₂CNH, CHCO |
| 42  | y      | y       | NCO, CH₂OC |
| 43  | y      | y       | HNCO, CH₂O |
| 44  | y      | y       | CO₂, N₂O, CONH₂, CH₃CHO |
| 45  | y      | y       | ¹³CO₂, CONH₂, HCOO |
| 46  | y      | y       | HCOOH     |
| 47  | ...    | ...     | HNO₂?     |
| 48  | ...    | ...     | ?          |
| 49  | y      | y       | CHNCO     |
| 50  | y      | y       | CH₃NCO    |
| 51  | y      | y       | CH₂NCO    |
| 52  | y      | y       | HCOHCO    |
| 53  | y      | y       | CH₄NO     |
| 54  | y      | y       | HCOOCH₃, NH₂CONH₂ |
| 55  | y      | y       | CH₃NO₂    |
| 56  | ...    | ...     | ?          |
| 57  | ...    | ...     | CH₂CH₂NCO |
| 58  | ...    | ...     | HCONHHCNO, HCOCONH₂ |
| 59  | ...    | ...     | NH₂CH₂COOH |
| 60  | ...    | ...     | NH₂COCONH₂, NH₂CONHCHO |
| 61  | ...    | ...     | CH₄NO₂   |

The mass spectrum of m/z = 44 shows a series of desorption peaks between 80 and 300 K. While the peaks between 80 and 200 K are in agreement with desorption of CO₂, as shown by the infrared spectra in Figure 6 and the column density in Figure 10, the broad and intense peak between 220 and 300 K suggests a contribution to m/z = 44 in fragmentation of larger compounds in the ice.

An upper limit to the contribution of N₂O to m/z = 44 can be estimated using m/z = 14 a fragment of either NH₃ and N₂. Assuming that m/z = 14 is only associated to the fragmentation of N₂O, we obtain a negligible contribution of N₂O to m/z = 44 (see red curve in the third panel from the top of Figure 9).

One of the carriers of the band at 1352 cm⁻¹ is CH₃CHO (m/z = 44). m/z = 44 of this species is ~83% of its main mass m/z = 29. Even assuming that m/z = 29 at high temperature is only related to CH₃CHO, an upper limit to its contribution is given by the green curve shown in panel (c) of Figure 9.

Several bands in the range of 1000–1800 cm⁻¹ of the infrared spectra survive up to room temperature. In particular, the bands at 1690 cm⁻¹ of formamide is clearly present in the infrared spectra at 300 K. The associate mass m/z = 45 in panel (d) of Figure 9 shows a series of peaks within the temperature range. The red curve in the panel is the contribution of ¹³CO₂ to m/z = 45, computed as the 10% of m/z = 44. Assuming that CO₂ is the only carrier of m/z = 44, its isotopologue ¹³CO₂ can at most justify m/z = 45 only below 200 K. Pure formamide in thick ice has a desorption peak at 220 K that well fits with the broad feature between 200 and 300 K. In this range acetic acid (HCOOH—yellow curve) and acetaldehyde (CH₃CHO—green curve) may also contribute to this mass.

The band at 1590 cm⁻¹ is associated with three different species; HCOO⁻ that most probably desorbs after recombination with H as m/z = 46, see panel (e); CH₃NH₂ (m/z = 31), see panel (f); NH₂CH₂COO⁻ (m/z = 75). This band is still present in the infrared spectra at 300 K (Figure 7). These masses shown in Figure 9 and that of NH₃CH₃COO⁻ in Figure 11 have desorption peaks extending up to 300 K.

The QMS is much more sensitive than the infrared spectrometer and some of the detected masses during the warm-up have no clear features in the infrared spectra. Complex organic molecules produced in the experiment have generally low abundances and share similar fragments, and are therefore more challenging to identify. Masses such as m/z = 28, 29, 30, 31, 32, and 44 are common to many species and their intensities at high temperature require many contributors. For such species to be identified, we require the presence of the expected main mass fragments, and the existence of a consistent reaction channel in the ice.

Polymerization of two HCO radicals in the mixture will bring to glyoxal species (HCOHCO, m/z = 58)

$$2\text{HCO} \rightarrow \text{O} \sim \text{H}_2\text{O} \hspace{1cm} (9)$$

During warm-up, m/z = 58 show a desorption peak around 260 K (see Figure 11). Other fragments of such species, i.e., m/z = 29, 31, and 30, which are detected desorbing with m/z = 58, support the presence of glyoxal.

Vacuum ultraviolet irradiation experiments of CH₄:HNCO (Ligerink et al. 2018) produce the desorption of a fragment with m/z = 73 at ≈220 K, that have been assigned to several candidates, the most probable being propionamide, CH₃CH₂C(O)NH₃.

In our experiments m/z = 73 desorbs at higher temperatures, ≈270 K. Considering the different ice composition and thus the different first generation products, such as H₂CO and HCONH₂, m/z = 73 is readily explained by further energetic processing yielding a second generation of radicals

$$\text{HCO}^- + \text{HNCHO} \rightarrow \text{O} \sim \text{H}_2\text{O} \hspace{1cm} (10)$$

$$\text{HCO}^- + \text{NH}_2\text{CO} \rightarrow \text{O} \sim \text{H}_2\text{O} \hspace{1cm} (11)$$

Radical reactions of this species are among the most important routes in producing new molecules of astrobiological interest.
As mentioned in Section 3.1 and Table 1 several infrared features are compatible with glycine or other isomers. The thermal desorption of \( m/z = 75 \) further supports the infrared identification. As shown in Figure 11 this mass, although very weak, shows a desorption from 250 to 300 K. Its main fragment \( m/z = 30 \), presenting a desorption tail extending up to room temperature, supports this assignment.

As the chemical complexity induced by energetic processing increases, molecules with \( m/z = 88 \) can be produced by reactions involving second generation radicals. The reaction
between two formamide radicals bring to ethanediamide, NH₂CONH₂

\[
2\text{NH}_2\text{C}=\text{O} \rightarrow \begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array}
\]

Ethanediamide desorption is supported by detection of the fragment NH₂CONH₂ (\(m/z = 60\)). As Figure 11 shows, the two masses have similar profiles. Since the ratio (\(m/z = 60\))/(\(m/z = 88\)) is much larger than the value of 1.2 expected for ethanediamide, contributions from other species (e.g., urea) are required. The infrared bands of urea could be blended with the features around 1150 and 1500 cm\(^{-1}\). Reaction of urea radical with HCO produces formylurea (NH₂CONHCHO, \(m/z = 88\)),

\[
\begin{array}{c}
\text{NH}_2 \\
\text{C} = \text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array} + \begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{N} \\
\text{H}
\end{array}
\]

Methylformate, HCOOCH₃, is another candidate for \(m/z = 60\). This species could contribute to the 1717 cm\(^{-1}\) feature. Its main fragments \(m/z = 31, 32, 29\) are observed desorbing at the same temperature.

The largest mass detected during the warm-up is \(m/z = 175\). Such a large mass is difficult to identify. A possible candidate for \(m/z = 175\) could be N-acetyl-L-aspartic acid. Such species implies the presence of aspartic acid and other amino acids like alanine. Aspartic acid may in fact be present given the detection of the main fragments \(m/z = 88, 70, 43\). Alanine has the main fragment \(m/z = 44\), a mass common to many species. A more reliable identification of molecules having such large mass requires the use of other analytical techniques, and/or the characterization of the residue, which is beyond the scope of this work.

Table 2 summarizes the species identified as carriers of the observed mass spectra.

### 3.3. The Refractory Residue

Infrared spectra of the residue are shown in Figure 12. The two spectra were obtained at 300 K, the first just after the warm-up and the second one day after keeping the window for 20 hr in the vacuum chamber. Although the spectrum after 20 hr is significantly reduced, in the range 1000–2400 cm\(^{-1}\) all the features are still present. The broadband around 3000 cm\(^{-1}\)
is shared by species containing the hydroxyl functional group, such as alcohols and carboxylic acids frequently present in processed ice residues. After 20 hr, this band displays a clear tail that extends beyond 2500 cm$^{-1}$, suggesting the presence of carboxylic acids. Indeed, alcohols are expected to desorb gradually at room temperature, which likely accounts for the decrease of the band around 3000 cm$^{-1}$ and the band peaking around 1100 cm$^{-1}$. The feature at 2165 cm$^{-1}$ typical of the C=N stretch in OCN$^-$ is still present after 20 hr. The COO$^-$ feature at 1588 cm$^{-1}$ typical of carboxylic acid salts is significantly reduced after 20 hr compared to the 1679 cm$^{-1}$. The C=O stretching at 1679 cm$^{-1}$ suggests the presence of amides. Hexamethylenetetramine (HMT) in the spectrum corresponds to the bands at 2897, 2832, and 1238 cm$^{-1}$. The main HMT band peaks around 1007 cm$^{-1}$, in this spectrum it would be a small narrow band superposed on the larger band that appears at this wavenumber. In ultraviolet experiments with ice of the present composition, HMT is a very minor species, which makes sense because HMT has six CH$_2$ groups, and CO is not a good precursor; the presence of methanol would be much more favorable for its formation. In addition, the formaldehyde precursor of HMT is more efficiently formed when methanol is included in the ice. Furthermore, HMT forms at room temperature, and it would not be expected in the fresh residue. The feature at $\sim$1105 cm$^{-1}$ that shifts at lower wavenumber in the spectrum after 20 hr is associated with HOCH$_2$COO$^-$ (Muñoz Caro & Schutte 2003). The bands identified in the infrared spectrum of the residue are in Table 3.

### Table 3

| Label | Band (cm$^{-1}$) | Assignment | Reference |
|-------|-----------------|------------|-----------|
| 1     | 3192            | NH$_4^+$   | 1         |
| 2     | 3063            | ?          | ?         |
| 3     | 2897            | HMT?       | 1         |
| 4     | 2832            | HMT, NH$_4^+$ | 1     |
| 5     | 2165            | OCN$^-$     | 2         |
| 6     | 1679            | Amides     | 1, 2      |
| 7     | 1588            | COO$^-$ str. in carboxylic acid salts | 1, 2 |
| 8     | 1447            | NH$_4^+$    | 1         |
| 9     | 1341            | COO$^-$ str. in carboxylic acid salts | 1, 2 |
| 10    | 1238            | HMT         | 1         |
| 11    | 1105            | HOCH$_2$COO$^-$ | 1     |

References. (1) Muñoz Caro & Schutte (2003); (2) Pilling et al. (2010).

### 4. Conclusions and Astrophysical Implications

We have studied the chemical evolution induced by soft X-rays in the range of 250–1250 eV in a mixture containing nitrogen, H$_2$O:CO:NH$_3$. Among the products of the irradiation there are many N-bearing molecules such as, e.g., OCN$^-$ (2168 cm$^{-1}$), HNCO and CH$_3$CN (2261 cm$^{-1}$), HCONH$_2$ (1690 cm$^{-1}$), and NH$_4^+$ (1478 cm$^{-1}$). Several features of the irradiated mixture are compatible with the presence of glycine or its isomers (see, e.g., Oba et al. 2016). The products detected in the infrared spectra are common to other irradiation experiments of similar mixtures with ultraviolet (Hudson & Moore 2000) and energetic particles (Hudson & Moore 2000; Pilling et al. 2010).

Detection of several masses in gas phase during the irradiation and the warm-up revealed a number of complex organics with no clear features in the infrared spectra of the irradiated ice. Photo- and thermal-desorptions are of great
interest as they offer the possibility that complex organics formed in the solid phase can enrich the gas-phase molecular distribution.

Acetonitrile CH$_3$CN detected through the 2260 cm$^{-1}$ infrared feature and $m/z = 41$ has been observed in Sgr B2 and Sgr A (Solomon et al. 1971) while its isomer CH$_3$CHN (compatible with 2038 cm$^{-1}$) in Sgr B2 (Lovas et al. 2006). More recently acetonitrile has been observed in a protoplanetary disk around MWC480 by Öberg et al. (2015).

Formamide HCONH$_2$ is also produced and its mass ($m/z = 45$) is among the most intense during thermal desorption. Formamide with its peptide moiety may be a building block for species of astrobiological interest such as sugars and amino acids. This species has been identified in hot cores, and external galaxies (see McGuire 2018), and also around the SVS13-A protostar by Bianchi et al. (2019). These authors also detected acetaldehyde (CH$_3$CHO), methanol (CH$_3$OH), and methylformate (HCOOCH$_3$), all of them produced in the present experiments, and revealed through QMS in the gas phase either during the irradiation or warm-up (see Table 2).

Another species detected in the gas phase during the experiments is methyl isocyanate (CH$_3$NCO), $m/z = 57$, a molecule of prebiotic relevance. This species has been detected in protostellar environments (Ligerink et al. 2017; Martín-Doménech et al. 2017), the Orion cloud (Cernicharo et al. 2016), and comets (Goessmann et al. 2015). Ligerink et al. (2017) estimated the column density of CH$_3$NCO toward the binary low-mass protostar IRAS 16293−2422 to be ∼(3−4) × 10$^{15}$ and ∼(6−9) × 10$^{15}$ cm$^{-2}$ for sources B and A, respectively. A similar value, 4 × 10$^{15}$ cm$^{-2}$, has been derived toward IRAS 16293−2422 B by Martín-Doménech et al. (2017). The fractional abundance with respect to hydrogen nuclei results $\lesssim 1.4 \times 10^{-10}$ (Martín-Doménech et al. 2017).

Following the QMS quantification and calibration by Martín-Doménech et al. (2015), we estimated the photodesorption yields in molecules ph$^{-1}$ for the molecules listed in Table 4. The quantitative calibration of QMS for the present facility has been detailed in Sie et al. (2019). We then exploit the chemical model of protoplanetary disk around classical T Tauri stars put forward by Walsh et al. (2012). These authors investigated an axisymmetric region surrounding a star with half the mass and twice the radius of the Sun. The effective temperature is 4000 K, and the X-ray luminosity, $1 \times 10^{30}$ erg s$^{-1}$, is taken constant throughout the disk evolution. The stellar X-ray spectrum used in the disk modeling (Nomura et al. 2007) covers energies from 0.1 to 10 keV with a dominant broad and intense peak in the range between 200 and 900 eV, similar in shape to the spectrum used in our experiments (see Figure 1).

The gas-phase fractional density of a particular species $i$ produced by photodesorption is given by

$$f_i = Y_i \langle A_i \rangle F_X \tau_X,$$  \hspace{1cm} (14)

where $Y_i$ is the photodesorption yield reported in Table 4, $\langle A_i \rangle \sim 1 \times 10^{-22}$ cm$^2$ is the average dust geometrical cross-section per hydrogen nucleus, $F_X$ the local X-ray flux in photons cm$^{-2}$ s$^{-1}$, and $\tau_X$ the irradiation time.

Methyl isocyanate emission has been detected toward IRAS 16293−2422 on solar system scales, i.e., within ∼60 au from the protostar (Ligerink et al. 2017). At radial distances between 10 and 50 au, and within 50 au of altitude from the plane of the disk, dust temperatures are between 20 and 40 K, consistent with a long residence time of mixed water ices. The X-ray flux results $F_X \sim 10^{-4}−10^{-3}$ ergs cm$^{-2}$ s$^{-1}$ (Walsh et al. 2012). Assuming an average photon energy of 600 eV, we obtain $F_X = 10^{-2}−10^0$ photons cm$^{-2}$ s$^{-1}$. Using Equation (14), we derive an irradiation time $\tau_X \gtrsim 200$−20,000 yr. Such times are compatible with the disk dynamical age of 40,000 yr reported in Martín-Doménech et al. (2017), and with other estimates for this source (Bottinelli et al. 2014; Majumdar et al. 2016).

On the base of Table 4 we may estimate the CH$_3$NCO/HNCO ratio to be ∼0.6, about a factor of 3 bigger than the largest observational estimate 0.25 (Ligerink et al. 2017). However, we did not expect to find a close agreement with the observational data, as the two species, CH$_3$NCO and HNCO formed on the surface of dust grains, are photodesorbed and incorporated into the gas phase without any further interaction. Our results show that the photodesorption may be an efficient nonthermal source of such species, and other organic molecules. Thus, around young solar-type stars, known to emit many more X-rays than the present-day Sun, X-ray irradiation has a potential role in prebiotic chemistry.

In conclusion, the present results show that X-ray irradiation of a water mixed (H$_2$O:CO:NH$_3$) ice may originate a chemistry rich in organic compounds, most of them likely to be desorbed to the gas phase via photo and/or thermal desorption. Such species have been detected in many astrophysical environments and in particular in circumstellar regions. In this latter case, X-rays can permeate the disk and reach deeper regions, where less energetic radiation such as ultraviolet is inhibited, triggering a solid phase chemistry that through photodesorption can enrich dilute medium of complex organics. Future experiments will be aimed at a more detailed identification of the species including the solid and gas-phase production yields in order to provide a more accurate comparison with observations.

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### Table 4

| $m/z$ | Molecule       | Molecules/Photon |
|-------|----------------|-----------------|
| 31    | CH$_3$NH$_2$   | 1.94 × 10$^{-3}$ |
| 41    | CH$_3$CN       | 3.62 × 10$^{-3}$ |
| 43    | HNCO           | 3.17 × 10$^{-3}$ |
| 57    | CH$_3$NCO      | 2.03 × 10$^{-5}$ |

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