Exploring the Chemistry Induced by Energetic Processing of the H2-bearing, CO-rich Apolar Ice Layer

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Abstract

Interstellar ice mantles on the surfaces of dust grains are thought to have a bilayered structure, with a H2O-rich polar layer, covered by a CO-rich apolar layer that probably harbors H2 and other volatiles such as N2. In this work, we explore the chemistry induced by 2 keV electrons and Lyman photons in H2:CO:15N2 ice analogs of the CO-rich layer when exposed to similar fluences to those expected from the cosmic-ray-induced secondary electrons and UV photons during the typical lifetime of dense clouds. Six products were identified upon 2 keV electron irradiation: CO2, C2O (and other carbon chain oxides), CH4, H2CO, H2C5O, and H13NCO. The total product abundances corresponded to 5%–10% of the initial CO molecules exposed to electron irradiation. Lyα photon irradiation delivered one to two orders of magnitude lower yields with a similar product branching ratio, which may be due to the low UV-photon absorption cross section of the ice sample at this wavelength. Formation of additional N-bearing species, namely C215N2 and 15NH3, was only observed in the absence of H2 and CO molecules, respectively, suggesting that reactants derived from H2 and CO molecules preferentially react with each other instead of with 15N2 and its dissociation products. In summary, ice chemistry induced by energetic processing of the CO-rich apolar ice layer provides alternative formation pathways for several species detected in the interstellar medium, including some related to the complex organic molecule chemistry. Further quantification of these pathways will help astrochemical models constrain their relative contribution to the interstellar budget of, especially, the organic species H2CO and HNCO.

Unified Astronomy Thesaurus concepts: Interstellar molecules (849); Dense interstellar clouds (371); Cosmic rays (329); Laboratory astrophysics (2004); Experimental techniques (2078)

1. Introduction

In the interior of dense molecular clouds, interstellar ice mantles are formed on the surfaces of dust grains in two phases, leading to a bilayered structure. A H2O-rich polar layer that includes other molecules formed through grain surface chemistry such as CO2, CH4, or NH3, is covered by a CO-rich layer that probably contains other volatile species accreted from the gas phase such as N2 and O2 (Boogert et al. 2015). Molecular hydrogen (H2) is the most abundant molecule in the universe (Wooden et al. 2004). Even though it is a very volatile species, the presence of H2 in the interstellar ice mantles has been considered due to its large abundance in the interstellar medium (ISM; see, e.g., Sandford & Allamandola 1993; Kristensen et al. 2011). Chuang et al. (2018) recently suggested that under the conditions found in the innermost regions of the dense clouds (n > 10^4 cm^-3, T < 20 K), H2 could be co-deposited along with CO molecules during the CO accretion phase of ice mantle formation.

Interstellar ice mantles are characterized by a rich and diverse chemistry that can result in a wealth of complex organic molecules (COMs; see, e.g., Garrod 2013), the proposed organic precursors of more complex prebiotic species. These COMs are incorporated into protostellar and protoplanetary disks during star formation and detected in solar system comets (see, e.g., Altweig et al. 2015; Goessmann et al. 2015). Interstellar ice chemistry has been experimentally studied in the laboratory under astrophysically relevant conditions for a few decades (see, e.g., Gerakines et al. 1996). Most studies focus either on the H-atom addition reactions to molecules in the H2O-rich (Qasim et al. 2018, 2019b; Chuang et al. 2020; Qasim et al. 2020) or the CO-rich (Watanabe & Kouchi 2002, 2008; Fuchs et al. 2009; Hama & Watanabe 2013; Fedoseev et al. 2015a, 2017; Linnartz et al. 2015; Chuang et al. 2016, 2017; Qasim et al. 2019a, 2019c) ice layers, or on the chemistry induced by energetic processing of the H2O-rich layer (see the review in Öberg 2016). The energetic processing of ice mantles in the interior of dense clouds is driven by the secondary keV electrons and the secondary UV field produced by the interaction of the cosmic rays with the ice molecules (Bennett et al. 2005) and the gas-phase H2 molecules (Cecchi-Pestellini & Aiello 1992; Shen et al. 2004), respectively.

Only two works have recently addressed the photon-induced chemistry of binary ice mixtures, analogs to the CO-rich ice layer. Vacuum-ultraviolet (VUV) photon irradiation of 13CO:N2 ices only led to the formation of CO2 molecules (Carrascosa et al. 2019), while carbon chain oxides and nitrogen oxides were also formed when the CO:N2 ice was irradiated with protons (Sicilia et al. 2012). Photon irradiation of H2:CO ice samples led to the formation of CO2 and H2CO molecules (a COM precursor), along with unreacted HCO radicals (Chuang et al. 2018). This suggests that energetic processing of the CO-rich layer may contribute to the formation of COMs if H2 molecules are also present. In this work, we explore the chemistry induced by both 2 keV electron and Lyman photons irradiation of H2:CO:15N2 ice analogs of the CO-rich apolar ice layer in the cold, innermost regions of dense clouds. We use the experimental results to elucidate the contribution of this layer to the chemistry of the ISM and the interstellar budget of organic species in particular. The experimental setup is described in Section 2, and the resulting chemistry is presented in Section 3. The implications of the most important results are
Experiments 2
number of monolayers that absorb 95% of the incident energy

| Exp. | Ice Comp.            | Composition Ratio | Ice Thickness (ML) | Irradiation (×10^18 eV) | Irradiation Energy | Irrad. Energy |
|------|----------------------|-------------------|-------------------|-------------------------|--------------------|--------------|
| 1    | H₂:CO:¹⁵N₂           | 1.8:1:0.1:0.0     | 1500              | Processed: 380          | 2 keV e⁻           | 1.3          |
| 2    | H₂:CO:¹⁵N₂           | 1.6:1:0.1:0.0     | 1600              | Processed: 380          | 2 keV e⁻           | 1.3          |
| 3    | H₂:CO:¹⁵N₂           | 1.6:1:0.1:0.0     | 2400              | Processed: 380          | 2 keV e⁻           | 1.3          |
| 4    | H₂:CO:¹⁵N₂           | 1.5:1:1:1:1:0     | 1400              | Processed: 380          | 2 keV e⁻           | 1.5          |
| 5    | H₂:¹³CO:¹⁵N₂         | 1.1:1:0.1:0.1     | 2700              | Processed: 380          | 2 keV e⁻           | 1.5          |
| 6    | H₂:¹³CO:¹⁵N₂         | 1.4:1:0:1:0:1:2   | 2800              | Processed: 380          | 2 keV e⁻           | 1.3          |
| 7    | D₂:¹³CO:¹⁵N₂         | 1.1:1:1:1:0:1     | 2400              | Processed: 380          | 2 keV e⁻           | 1.3          |
| 8    | H₂:CO:¹⁵N₂           | 1.7:1:0:1:0:1:0   | 1900              | Processed: 1900         | Lyα                | 0.65         |
| 9    | H₂:CO                | 1.5:1:0:1:0:1:0   | 2100              | Processed: 420          | 2 keV e⁻           | 1.3          |
| 10   | H₂:CO                | 1.7:1:0:1:0:1:0   | 1700              | Processed: 1700         | Lyα                | 0.078        |
| 11   | CO:¹⁵N₂              | 1:0:1:0:1:0:1:0   | 2300              | Processed: 220          | 2 keV e⁻           | 1.3          |
| 12   | CO:¹⁵N₂              | 1:0:1:0:1:0:1:0   | 1400              | Processed: 1400         | Lyα                | 0.098        |
| 13   | H₂:¹⁵N₂              | 2:1:1:0:1:0:1:0   | 900               | Processed: 460          | 2 keV e⁻           | 1.3          |
| 14   | H₂:¹⁵N₂              | 2:3:1:0:1:0:1:0   | 1900              | Processed: 1900         | Lyα                | 5.2 × 10⁻⁵   |

Note. ¹ ML = 10¹⁵ molecules cm⁻². We assume a 20% error in the ice thickness (see Appendix A.2). ² In the 2 keV electron irradiation experiments, this is the number of monolayers that absorb 95% of the incident energy (Section 2.2). The electron penetration depth calculated for Experiment 1 was adopted throughout Experiments 2–7.

Table 1
Summary of the Experiments Simulating the Energetic Processing of the Apolar Ice Layer at 4 K

discussed in Section 4. Finally, the conclusions are summarized in Section 5.

2. Methods

Table 1 summarizes the experimental simulations carried out for this paper. The irradiation of the H₂:CO:¹⁵N₂ ice analogs took place in Experiments 1−3 (2 keV electrons) and 8 (Lyα photons). Experiments 4−7 consisted in 2 keV electron irradiation of H₂:CO:N₂ ice mixtures using different combinations of molecular hydrogen (H₂ and D₂), carbon monoxide (CO, ¹³CO, and C¹⁸O), and molecular nitrogen (N₂ and ¹⁵N₂) isotopologs, and were used to confirm the ice chemistry product assignments in the previous experiments. In addition, we also performed 2 keV electron and Lyα photon irradiation of binary H₂:CO (Experiments 9 and 10, respectively), CO:¹⁵N₂ (Experiments 11 and 12), and H₂:¹⁵N₂ (Experiments 13 and 14) ice mixtures to understand how the presence of each component affects the chemistry of the apolar ice layer.

The experimental simulations were performed in the new SPACE TIGER¹ setup with a 500 mm diameter stainless steel, ultra-high-vacuum (UHV) chamber custom made by Pfeiffer Vacuum. The base pressure of ~2 × 10⁻¹⁰ Torr at room temperature is reached by a combination of magnetically levitated and scroll pumps. A detailed description of this setup can be found in P. Maksutienko (2020, in preparation), and the relevant features used for this work are described below.

2.1. Ice Sample Preparation

The ice samples were grown on a 12 mm diameter copper substrate (except for Experiments 1, 4, and 13, where a 10 mm diameter silver substrate was used) at a temperature of 4.3 K (achieved by means of a closed-cycle He cryostat, Model DE210b-g, Advance Research Systems, Inc.), by exposing the substrate to a gas mixture prepared in an independently pumped stainless steel mixing volume. The gas mixtures were introduced in the UHV chamber through a 10 mm diameter dosing pipe in close proximity (<2 mm) to the substrate. We thus assumed that the size of the deposited ice samples was 10 mm diameter. For a reproducible dosing rate, we employed a laser drilled 7 × 7, 4 μm diameter pinhole array (Lenox Laser, custom made) placed between the mixing volume and the UHV chamber. The dosing rate was proportional to the number of holes in the array and the pressure in the mixing volume (up to 20 Torr), and inversely proportional to the square root of the species molar masses. The dosing process was terminated by shutting off the valve that allowed the gas mixtures to go through this pinhole array and evacuating the small remaining volume between the valve and the array. The ice composition was estimated to be the same as the composition of the gas mixture, assuming a sticking coefficient value of 1 for all the species onto the surface at ~4 K. The gas mixture composition was measured in the UHV chamber before the ice deposition using a quadrupole mass spectrometer (QMS; Section 2.6). The measured QMS signals were transformed into partial pressures with a conversion factor previously calculated for the pure gases (see Appendix A.1 for the H₂, CO, and ¹⁵N₂ examples). The ice analogs in Experiments 1–3, and 8–14 were deposited from gas mixtures composed of H₂ (gas, >99.99% purity, Aldrich), CO (gas, 99.95%, Aldrich), and ¹⁵N₂ (gas, 98%, Aldrich). For the isotopically labeled ices in Experiments 4–7, we also used D₂ (gas, 99.96%, Aldrich), ¹³CO (gas, 99% ¹³C, <5% ¹⁸O, Aldrich), C¹⁸O (gas, 99% ¹²C, 95% ¹⁸O, Aldrich), and N₂ (gas, 99.99%, Aldrich).

2.2. Electron Irradiation of the Ice Samples

The deposited ice samples were electron-irradiated in Experiments 1–7, 9, 11, and 13 using an ELG-2/EPGS-1022 low-energy electron source system (Kimball Physics) with an average electron beam current of ~54 nA (relative uncertainty of 10%). The electron beam had an incidence angle of 56°, resulting in an elliptical spot at the sample position, with a minor axis the same size as the ice sample and

¹ Surface Photoprocessing Apparatus Creating Experiments To Investigate Grain Energetic Reactions.
a major axis \(\sim 35\%\) larger.\(^5\) The sample irradiation time was 45 minutes, so the ice samples were processed with \(\sim 6.5 \times 10^{14}\) electrons with a fixed energy of 2 keV, leading to a total incident energy of \(\sim 1.3 \times 10^{18}\) eV.

The length of the electron irradiation experiment was meant to match the energy fluence directly deposited by the cosmic rays into the interstellar ice mantles during the typical lifetime of a dense cloud (\(\sim 10^6\) yr). The total irradiated energy fluence of \(\sim 1.7 \times 10^{18}\) eV cm\(^{-2}\) is similar to the estimated energy fluence deposited by the cosmic rays into the interstellar ice mantles during \(\sim 1.3 \times 10^6\) yr (see Jones et al. 2011 and references therein).

The 2 keV electron penetration depth in the ice samples was lower than the total ice thickness and was calculated with the CASINO v2.42 code (Drouin et al. 2007) in terms of the number of monolayers \((1 \text{ ML} = 10^{15}\) molecules cm\(^{-2}\)). For example, in a H\(_2\):CO:15N\(_2\) ice analog with a 1.8:1.0:1.0 composition (Exp. 1, Table 1), 95\% of the irradiated energy is absorbed in the first 380 ML of the ice. This means that only a fraction of the ice should be considered chemically active, since the bottom monolayers are barely processed by the 2 keV electrons. The number of monolayers of the ice sample effectively processed by the 2 keV electrons is higher in ices with a lower density, such as the H\(_2\):CO ice of Exp. 9 (420 ML), while 95\% of the incident energy is absorbed in the first 220 ML of the CO:15N\(_2\) ice in Experiment 11, with a higher ice density. The electron penetration depth is indicated in the fifth column of Table 1. The number of monolayers that were chemically active was taken into account when estimating conversion yields (Section 2.5).

2.3. VUV Photoprocessing of the Ice Samples

The ice analogs were VUV photon-irradiated in Experiments 8, 10, 12, and 14. Tunable VUV photons are generated in SPACE TIGER with a laser-based system\(^8\) and 10, 12, and 14. Tunable VUV photons are generated in SPACE TIGER with a laser-based system (P. Maksisutenko 2020, in preparation). In particular, Ly\(\alpha\) photons were produced via two-photon resonance enhanced difference frequency mixing in krypton (Marangos et al. 1990). The number of irradiated Ly\(\alpha\) photons per second was measured with a Hamamatsu S10043 photodiode and varied between 1.8 and \(2.4 \times 10^{13}\) photons s\(^{-1}\) across the different experiments. The sample irradiation time in those experiments was set to 90 – 110 minutes. The ice samples were thus processed with \(\sim 1.4 \times 10^{17}\) photons of \(\sim 10.2\) eV energy, leading to a total incident energy of \(\sim 1.4 \times 10^{18}\) eV.

As in the electron irradiation experiments, the length of the photon irradiation was set to match the energy fluence irradiated into the ice mantles by the secondary UV field in dense cloud interiors. The laser beam had a normal incidence angle and was \(\sim 50\%\) the size of the ice sample surface, approximately. This resulted in a total incident energy fluence of \(\sim 3.5 \times 10^{18}\) eV cm\(^{-2}\) over the processed ice. For comparison, interstellar ices would be exposed to an energy fluence of \(\sim 3.2 \times 10^{18}\) eV cm\(^{-2}\) during a cloud lifetime of \(10^6\) yr, considering a secondary UV flux in the interior of dense clouds of \(\sim 10^4\) photons cm\(^{-2}\) s\(^{-1}\) (Shen et al. 2004), and a photon energy of 10.2 eV.

The ice sample Ly\(\alpha\) photon absorbances in Experiments 8, 10, 12, and 14 were calculated according to the Beer–Lambert law:

\[
1 - \frac{I(\text{Ly}\alpha)}{I_0(\text{Ly}\alpha)} = 1 - e^{-\sigma_{\text{abs}(\text{Ly}\alpha)}N},
\]

where \(I(\text{Ly}\alpha)\) and \(I_0(\text{Ly}\alpha)\) are the transmitted and incident Ly\(\alpha\) intensities, respectively; \(\sigma_{\text{abs}(\text{Ly}\alpha)}\) is the photon absorption cross section at the Ly\(\alpha\) wavelength in cm\(^2\); and \(N\) is the ice thickness in terms of molecules cm\(^{-2}\) (see Table 1). \(\sigma_{\text{abs}(\text{Ly}\alpha)}\) is expected to be negligible for solid H\(_2\) (Chuang et al. 2018) and for 15N\(_2\) ices (\(\leq 1.5 \times 10^{-21}\) cm\(^2\); Cruz-Díaz et al. 2014), while the value for CO ices is \(1.0 \times 10^{-19}\) cm\(^2\) (Cruz-Díaz et al. 2014b). The calculated Ly\(\alpha\) photon absorbances in Experiments 8, 10, and 12 was, approximately, 5\%, 6\%, and 7\%, respectively, while the absorbance in Exp. 14 was negligible. The absorbed energy in the Ly\(\alpha\) photon irradiation experiments is indicated in the last column of Table 1.

2.4. IR Ice Spectroscopy

The ice samples were monitored during the experimental simulations through reflection-absorption infrared spectroscopy (RAIRS) using a Bruker 70v Fourier transform infrared (FTIR) spectrometer and a liquid-nitrogen-cooled MCT detector. The spectra were averaged over 128 interferograms and collected with a resolution of 1 cm\(^{-1}\) in the 5000–800 cm\(^{-1}\) range after deposition of the ice samples, every 5 minutes during electron processing, every 10–20 minutes during VUV photon processing, and every 5 minutes during warm-up of the processed ices (Section 2.6).

The IR beam had an incidence angle of \(20^{\circ}\) with respect to the substrate surface, resulting in an elliptical beam at the sample position, with a 14.6 mm major axis and a 5 mm minor axis. This means that the IR beam was smaller than the size of the ice sample surface and the 2 keV electron beam, but larger than the Ly\(\alpha\) photon beam. The IR beam dilution of the ice chemistry products formed upon UV photon irradiation was taken into account for the quantification of the product conversion yields in Ly\(\alpha\) irradiated ices (Section 2.5).

2.5. Conversion Yields

To quantify the conversion of CO molecules into C-bearing products upon energetic processing of the H\(_2\):CO:15N\(_2\), H\(_2\):CO, and CO:15N\(_2\) ice samples, we calculated the ratio between the final product column density and the initial (active) CO column density \((N(X)/N(\text{CO}))\). The column densities of the species with detected IR bands are proportional to the integrated IR absorbances:

\[
N(X) = \frac{1}{A_X} \int_{\text{band}} \tau_\nu \, d\nu,
\]

where \(N(X)\) is the column density of the species X in molecules cm\(^{-2}\), \(\tau_\nu\) is the optical depth of the absorption band (2.3 times the absorbance), and \(A_X\) is the band strength of the IR feature in cm molecule\(^{-1}\).

The band strengths \(A_X\) of the IR features detected through RAIRS are different from those reported for the IR spectra collected in transmission mode but, similar to previous studies (e.g., Öberg et al. 2009), we assumed that the relative band strengths were the same in the IR spectra collected in
transmission and reflection-absorption mode:

$$
\frac{N_f(X)}{N_f(CO)} = \frac{\int \tau_v d\nu \cdot A_{CO}}{\int \tau_v d\nu \cdot A_X}. \quad (3)
$$

Table 2 presents the band strengths of selected IR features, with an assumed uncertainty of 20% (Bouilloud et al. 2015).

The IR absorbance in reflection mode shows a nonlinear behavior with the species column densities above a certain threshold (Öberg et al. 2009). When this happens, the integrated absorbance is not proportional to the species column density, and Equation (2) is not valid. In our experimental simulations, this nonlinear behavior prevented us from using the integrated absorbance of the CO IR feature ($\int \tau_v d\nu \cdot A_{CO}$) in Equation (3) to determine the product conversion yields for Experiments 1–12. Instead, we used the small fraction of $^{13}$CO molecules deposited along with the high purity CO in every experiment to calculate $N_f(X)/N_f(^{13}CO)$, using the integrated absorbance of the $^{13}$CO IR feature at $\sim$2092 cm$^{-1}$ in Equation (3). We subsequently multiplied this ratio by the $^{13}$CO/CO fraction of $1.4 \times 10^{-3}$, empirically determined using separate pure CO ice experiments where the IR spectra were collected in transmission mode. We assumed a 30% uncertainty in the calculated $^{13}$CO/CO fraction, due to the 20% uncertainty in the CO and $^{13}$CO IR band strengths (Bouilloud et al. 2015).

In addition to the systematic 20% uncertainty in the band strength of the product IR features and 30% uncertainty in the calculated $^{13}$CO/CO fraction, we also considered a 25% experimental uncertainty that accounted for the differences found in the conversion yields of experiments that should present the same results (Experiments 1–3, Appendix B.1). Several sources of errors contributed to this experimental uncertainty, such as the uncertainty in the integrated $^{13}$CO IR absorbances (due to the low signal-to-noise ratio of the feature), as well as day-to-day changes in the precise experimental conditions. Altogether, we estimated a total uncertainty of 45% in the reported product conversion yield values.

In addition, we also calculated the product ratios with respect to CO$_2$($N_f(X)/N_f(CO_2)$) and compared the product branching ratios in different experiments.

As for the product conversion yields, we considered the 20% systematic uncertainty in the band strengths of the product IR features and the additional 25% experimental uncertainty, leading to a total uncertainty of 35% in the reported product branching ratios. Only the additional experimental uncertainty needed to be taken into account when comparing conversion yields and product branching ratios of the same species across different experiments.

### 2.6. Temperature Programmed Desorption of the Processed Ice Samples

After the energetic processing of the ice analogs, the samples were warmed from 4 K up to 200 K using a 50 W silicon nitride cartridge heater rod (Bach Resistor Ceramics). A 2 K minute$^{-1}$ heating rate was applied until the complete sublimation of the ice samples was achieved. The temperature of the ice samples was monitored by a LakeShore 336 temperature controller using a calibrated Si diode sensor with a 2 K estimated accuracy and a 0.1 K relative uncertainty. The desorbing molecules were detected with a QMG 220M1 QMS (Pfeiffer, mass range 1100 amu, resolution of 0.5 amu, located at $\sim$13 cm from the substrate), leading to a temperature programmed desorption (TPD) curve for each species. This allowed us to detect additional chemical product features whose IR features could not be unambiguously detected. The initial ice components were monitored through their main mass fragments (m/z = 2, H$_2$; m/z = 4, D$_2$; m/z = 28, CO and N$_2$; m/z = 29, $^{13}$CO; and m/z = 30, $^{12}$C$_2$O and $^{15}$N$_2$). The chemical product features were also monitored through their main mass fragment, but we note that in the case of H$_2$CO and H$_2$C$_2$O, the main mass fragment was not the molecular ion (Section 3.1).

In addition, we used the area under the collected CO TPD curve ($A_{TPD}(m/z = 28)$) to estimate the initial amount of CO molecules in Experiments 1–12, measured as the CO ice column density ($N_f$(CO)) in molecules cm$^{-2}$. The correspondence between $A_{TPD}(m/z = 28)$ and $N_f$(CO) was previously calibrated (Appendix A.2). The initial H$_2$ and $^{12}$N$_2$ ice column densities were estimated from $N_f$(CO) assuming that the initial composition was the same as the composition of the gas mixture used for ice deposition. In Experiments 13 and 14, the $^{15}$N$_2$ column density was calculated from the area $A_{TPD}(m/z = 30)$ under the corresponding TPD curve (Appendix A.2).

### 3. Results

#### 3.1. Ice Chemistry Product Identification in Analogs of the Apolar Ice Layer

The black curve in the top panel of Figure 1 shows the IR difference spectrum in the 2500–950 cm$^{-1}$ range upon $\sim$1.3 $\times$ 10$^{18}$ eV irradiation with 2 keV electrons of the H$_2$:CO:$^{15}$N$_2$ ice analog in Experiment 3 (the results were similar in Experiments 1–3, Appendix B.1). The IR spectra in the 4000–950 cm$^{-1}$ range collected before and after irradiation are shown in Appendix B.2. The formation of CO$_2$, CH$_4$, and H$_2$CO at 4.3 K is evidenced by the growth of IR features at 2345 cm$^{-1}$, 1305 cm$^{-1}$, and 1725 cm$^{-1}$, respectively. Two features due to the presence of unreacted HCO radicals are also observed at 1855 cm$^{-1}$ and 1094 cm$^{-1}$. Additional IR features are detected in the 2310–1995 cm$^{-1}$ region of the spectrum, corresponding to carbon chain oxides. The formation of these species upon energetic processing of CO-bearing ice samples (including pure CO ices as shown in Appendix B.3) has been studied in Sicilia et al. (2012). Hereafter, we only discuss the formation of C$_2$O (see below) as a representative of the carbon chain oxide chemistry.
An inset of the CO₂, CH₄, and H₂CO IR bands is shown in black in the left panels of Figure 2. A local baseline around each IR feature was subtracted using a spline function with the IDL software. We note that a small amount of CO₂ contamination was present in the ice sample before irradiation, representing ~0.01% of the initial CO (see Appendix B.3). The double-peak structure of the H₂CO C=O stretching IR band at 1725 cm⁻¹ could be due to the apolar ice matrix in which the produced H₂CO was embedded as it was not observed for H₂CO molecules embedded in a H₂O polar ice matrix (Noble et al. 2012). In our experiments, the double-peak structure was not observed at high temperatures, after desorption of the majority of the H₂, CO, and ¹⁵N₂ molecules (see Figure B4 in Appendix B.4).

The TPD curves of CO₂, CH₄, and H₂CO are shown in Figure 3 and were also baseline-corrected using a spline function with the IDL software. H₂CO presented two desorption peaks: one at 105 K, slightly below the multilayer desorption peak temperature measured in Noble et al. (2012), and a second broad desorption peak above 130 K. We speculate that the second desorption peak could be due to the formation of H₂CO dimers at temperatures above 35 K (see also Appendix B.4), although contribution from the fragmentation of desorbing H¹⁵NCO molecules at ~150 K (see below) could not be ruled out.

Three additional products were detected using the QMS during the TPD of the processed ice analogs in Experiments 1–3: C₂O, H₂C₂O, and H¹⁵NCO. The TPD curves of these product main mass fragments (m/z = 40, C₂O; m/z = 14, H₂C₂O; and m/z = 44, H¹⁵NCO) in Experiment 3 are also shown in Figure 3. The C₂O IR feature at 1989 cm⁻¹ (Palumbo et al. 2008) was only tentatively detected at the edge of the hatched region in the top panel of Figure 1. The H₂C₂O and H¹⁵NCO IR features at 2129 cm⁻¹ and 2260 cm⁻¹, respectively (van Broekhuizen et al. 2004; Hudson & Ferrante 2020), overlapped with different CO and carbon chain oxide IR features in the hatched region and could not be unambiguously detected. In order to confirm the assignments of desorbing H¹⁵NCO molecules at ~150 K (see below) could not be ruled out.

Figure 1. IR difference spectra obtained upon irradiation of a similar incident energy with 2 keV electrons (black) and Lyα photons (purple) of H₂:CO:¹⁵N₂, H₂:CO, CO:¹⁵N₂, and H₂:¹⁵N₂ ice samples (from top to bottom). The IR spectra are offset for clarity. IR band assignments are indicated in the panels. The hatched region corresponds to the region of the spectrum dominated by CO and carbon chain oxide features (see Appendix B.3).

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An inset of the CO₂, CH₄, and H₂CO IR bands is shown in black in the left panels of Figure 2. A local baseline around each IR feature was subtracted using a spline function with the IDL software. We note that a small amount of CO₂ contamination was present in the ice sample before irradiation, representing ~0.01% of the initial CO (see Appendix B.3). The double-peak structure of the H₂CO C=O stretching IR band at 1725 cm⁻¹ could be due to the apolar ice matrix in which the produced H₂CO was embedded as it was not observed for H₂CO molecules embedded in a H₂O polar ice matrix (Noble et al. 2012). In our experiments, the double-peak structure was not observed at high temperatures, after desorption of the majority of the H₂, CO, and ¹⁵N₂ molecules (see Figure B4 in Appendix B.4).

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the $m/z = 40$, $m/z = 14$, and $m/z = 44$ desorptions in Figure 3, to C$_2$O, H$_2$C$_2$O, and H$^{15}$NCO (the thermal desorption detected at $T > 100$ K), respectively, we energetically processed four additional ice analogs composed of different combinations of isotopically labeled H$_2$, CO, and N$_2$ molecules with 2 keV electrons (Experiments 4–7; see Table 1), and checked that the same thermal desorption was observed for the expected mass fragments, considering the shift in the mass of the main fragments according to their isotopic composition in each experiment. The results are shown in Figure 4, confirming the formation of these species upon electron irradiation of H$_2$:CO:N$_2$ ice analogs.

After irradiation of similar incident energies with Ly$\alpha$ photons (Experiment 7), two of the six ice chemistry products formed upon electron irradiation were detected: CO$_2$ and H$_2$CO. The CO$_2$ IR feature, as well as the two features due to unreacted HCO. radicals, are observed in the corresponding IR difference spectrum in the top panel of Figure 1. The inset of the CO$_2$ IR band in the top-left panel of Figure 2 shows that the amount of CO$_2$ molecules formed upon Ly$\alpha$ photon irradiation is lower than in the 2 keV electron irradiation experiment. The formation of a small amount of H$_2$CO molecules is also observed in Figure 2. This suggests that the photon-induced chemistry took place to a lower extent, possibly due to the low photon absorption cross section of the ice sample at the Ly$\alpha$ wavelength (Section 2.3).

Figures 1, 2, and 3 also show the IR difference spectra, the inset of the detected IR features, and the TPD curves of the ice chemistry products formed upon energetic processing of the binary ice mixtures in Experiments 9–14. The energetic processing of H$_2$:CO ice samples led to the formation of the same species as in the H$_2$:CO:$^{15}$N$_2$ ice analogs, except for H$^{15}$NCO. We note that the C$_2$O IR feature at 1989 cm$^{-1}$ was observed in the corresponding IR difference spectrum (Figure 1), but it was blended with a CO IR band (Appendix B.3).

Due to the lack of H$_2$ in the CO:$^{15}$N$_2$ ice samples, the H-bearing species CH$_4$, H$_2$CO, H$_2$C$_2$O, and H$^{15}$NCO could not be formed in Experiments 11 and 12. The IR difference spectrum after $\sim 1.3 \times 10^{18}$ eV irradiation with 2 keV electrons shows the formation of CO$_2$ and C$_2$O, as well as the unreacted radicals OCN. and NCO. (Figure 1). In addition, thermal desorption of C$_2^{15}$N$_2$ was also detected (Figure 3, bottom panels), while only CO$_2$ formation was observed after irradiation with Ly$\alpha$ photons.

In H$_2$:^{15}$N$_2$ ices, $^{15}$NH$_3$ formation was observed after 2 keV electron irradiation in Experiment 13 by means of both IR spectroscopy (Figure 2, bottom-right panel) and mass...
Figure 3. TPD curves of the CO$_2$, C$_2$O, CH$_4$, NH$_3$, C$_2$N$_2$, H$_2$CO, H$_2$C$_2$O, and H$^{15}$NCO main mass fragments (from top to bottom, m/z = 44, m/z = 40, m/z = 16, m/z = 18, m/z=54, m/z = 29, m/z = 14, and m/z = 44, respectively) during the warm-up of H$_2$:CO:$^{15}$N$_2$ (Experiments 3 and 8), H$_2$:CO (Experiments 9 and 10), CO:$^{15}$N$_2$ (Experiments 11 and 12), and H$_2$:15N$_2$ (Experiments 13 and 14) ice samples (from left to right) after the irradiation of a similar incident energy with 2 keV electrons (black) and Ly$\alpha$ photons (purple).
spectrometry during the subsequent TPD (Figure 3). No other product was detected in this experiment (we note that the small amount of CO2 observed in the right panel of Figure 1 was due to contamination).

3.2. Conversion Yields and Product Branching Ratios in 2 keV Electron and Lyα Photon-irradiated Ices

As described in Section 2.5, we used the conversion yield \( (N_i(X)/N_i(CO)) \) to quantify the conversion of CO molecules into products. In order to get the conversion yields, the measured \( N_i(X)/N_i(\text{CO}) \) ratios were multiplied by the \(^{13}\text{CO}/\text{CO} \) fraction of \( \sim 1.4 \times 10^{-4} \). The CO, CH4, and H2CO IR bands in Figure 2, as well as the IR feature corresponding to the initial \(^{13}\text{CO} \) molecules, were numerically integrated using the composite Simpson’s rule (\texttt{integrate.simps} in Python). The resulting ratio of integrated absorbances \( \left( \int \tau_v \, dv/\int_{\text{CO}} \tau_v \, dv^2 \right) \) was used in Equation (3) along with the IR band strengths listed in Table 2. The integrated absorbances of the ice chemistry products formed upon Lyα photon irradiation were corrected for the IR beam dilution, as mentioned in Section 2.4. The \( N_i(X)/N_i(\text{CO}) \) percent yields at the end of Experiments 3 and 8−12 are presented in Figure 5 and Table 3. We note that the percent yields in Experiments 3, 9, and 11 are calculated with respect to the fraction of the ice that absorbs most (95%) of the incident energy from the 2 keV electrons. This fraction is \( \sim 15\% \) in Experiment 3, \( \sim 20\% \) in Experiment 9, and \( \sim 10\% \) in Experiment 11 (Section 2.2).

5 The contribution of the initial CO2 contamination to the final CO2 abundance was taken into account.
percent yields should be considered as average percent yields in the processed ice.

After $\sim 1.3 \times 10^{18}$ eV irradiation with 2 keV electrons of the H$_2$:CO:15N$_2$ ices analog in Experiment 3, 3.0%, 0.7%, and 2.4% of the initial CO molecules were converted into CO$_2$, CH$_4$, and H$_2$CO, respectively. The total CO-to-product percent yield could be up to $\sim$10% in electron-irradiated ices, considering that the conversion yields of H$^2$NCO, H$_2$C$_2$O, C$_2$O, and the rest of carbon chain oxides were not calculated from the IR measurements. The CO$_2$ and H$_2$CO percent yields upon Ly$_\alpha$ photon irradiation of the same ice sample was 4.9%, 1.0% in the 2 keV electron- and Ly$_\alpha$ photon irradiation. The CO$_2$ percent yield was 4.3% in the 2 keV electron-irradiated CO:15N$_2$ ice sample.

The CO$_2$, CH$_4$, and H$_2$CO percent yields in the 2 keV electron-irradiated H$_2$:CO ice (Experiment 9) were 4.9%, 1.0%, and 2.0%, respectively. These percent yields were two orders of magnitude lower for CO$_2$ and H$_2$CO upon Ly$_\alpha$ photon irradiation of the same ice sample (Experiment 10). The relative formation of H$_2$CO with respect to CO$_2$ was similar in the 2 keV electron- and Ly$_\alpha$ photon-irradiated H$_2$:CO ices (Experiments 9 and 10). The CO$_2$ percent yield was 4.3% in the 2 keV electron-irradiated CO:15N$_2$ ice (Experiment 11), similar to the previous experiments, and two orders of magnitude lower (0.031%) upon Ly$_\alpha$ photon irradiation.

### 3.3. CO$_2$ Formation Kinetics

In the case of CO$_2$, we had sufficient signal-to-noise ratio from the beginning to the end of the experimental simulations to study the formation kinetics across the different experiments and use that to further explore the effects of the different energy sources and ice compositions. Figure 7 shows the CO$_2$ growth curves in terms of the conversion yield versus the incident energy fluence in the CO-bearing ice samples (Experiments 3 and 8–12), as well as in pure CO ices (Experiments A1 and A2, Appendix B.3). The CO$_2$ growth curves upon 2 keV electron irradiation of the studied ice samples (Figure 7, top panels) could be parameterized with a pseudo-first-order kinetic model (Ioppolo et al. 2009):

$$N(CO_2) - N_i(CO_2) = \frac{N_i(CO_2)}{N_i(CO)} \times (1 - e^{-\sigma_{form}E}),$$

where $E$ is the incident energy fluence in eV cm$^{-2}$, $N_i(CO_2)/N_i(CO)$ represents the CO$_2$ steady-state conversion yield, i.e., the highest conversion yield that could be reached in an environment where the ices were exposed to higher-energy fluences than the typical values expected in dense cloud interiors (Section 2.2). The parameter $\sigma_{form}$ is the apparent formation cross section in cm$^2$. In a pseudo-first-order kinetic model, this parameter indicates how fast the corresponding steady-state conversion yield is reached and cannot be used to determine the absolute formation rate. The best-fit steady-state conversion yields and apparent formation cross sections are presented in Table 4.

The formation of CO$_2$ molecules in the 2 keV electron-irradiated experiments seemed to be enhanced by the presence of H$_2$ molecules (Figure 7, top panels). The steady-state CO$_2$ percent yields in the H$_2$:CO:15N$_2$ ice sample (Experiment 3) and the H$_2$:CO binary mixture (Experiment 9) were more than a factor of 3 higher than the value in a pure CO ice (Experiment A1). The conversion from CO to CO$_2$ in the presence of H$_2$ molecules could proceed through the HO–CO intermediate, as it is the case in other proposed CO$_2$ ice formation scenarios (for example, the CO + OH reaction that is expected to take place in the H$_2$O-rich ice layer; Ioppolo et al. 2011). The formation of the HO–CO intermediate significantly decreases the CO$_2$ formation activation barrier compared to the CO + O reaction (Garrod & Pauly 2011) and could be the reason behind the observed enhancement in our experimental simulations.

Even though the presence of $^{15}$N$_2$ molecules in the ice samples seemed to increase the formation of CO$_2$ when...
Figure 7. CO₂ growth curves in terms of the conversion yield vs. the incident energy fluence upon electron (black, top panels) and VUV photon (purple, bottom panels) irradiation of H₂:CO:¹⁵N₂, H₂:CO, CO:¹⁵N₂, and pure CO ice samples (from left to right). The Lyα flux was not measured in Experiment A2, and we adopted the same value as in Experiment 7. The best-fit pseudo-first-order kinetic model is shown in the top panels (blue solid lines).

Table 4
Summary of the Best-fit CO₂ Formation Steady-state Percent Yields and Cross Sections upon Electron Irradiation of Different Ice Samples

| Exp. | Ice Comp.     | N₀(CO₂)/N₀(CO) (%) | σₓ₀ₓ (cm²) |
|------|---------------|--------------------|------------|
| 3    | H₂:CO:¹⁵N₂    | 15 ± 3             | [1.3 ± 0.3]×10⁻¹⁸ |
| 9    | H₂:CO        | 18 ± 3             | [2.0 ± 0.4]×10⁻¹⁹ |
| 11   | CO:¹⁵N₂      | 8.3 ± 0.2          | [4.3 ± 0.2]×10⁻¹⁹ |
| A1   | CO           | 4.1 ± 0.1          | [5.9 ± 0.2]×10⁻¹⁹ |

Note. Fit errors do not take into account the 45% total uncertainty in the conversion yield values.

Comparing the steady-state percent yield of the CO:¹⁵N₂ binary ice mixture (Experiment 11) with that of a pure CO ice (Experiment A1), the difference in the steady-state percent yields was not very significant considering the 25% uncertainty found between experiments (Appendix B.1). In addition, this effect was negligible in ice samples where H₂ molecules were also present (Experiments 3 and 9, Table 4). More experiments would be needed to constrain the effect of the ¹⁵N₂ molecules on the CO₂ formation.

The formation of CO₂ molecules upon Lyα photon irradiation also seemed to be enhanced in H₂-bearing ices when comparing the H₂:CO:¹⁵N₂ ice analog and the H₂:CO binary mixture with a pure CO ice and the CO:¹⁵N₂ binary mixture, while the presence of ¹⁵N₂ did not have any significant effect (Figure 7, bottom panels). However, the same kinetic model could not be used for the CO₂ growth curves in Lyα photon irradiation experiments.

4. Discussion

4.1. Electron and Photon Processing of the Apolar Ice Layer

Electrons and UV photon irradiation both resulted in chemical reactions in the apolar ice analogs. Based on the observed H₂CO product branching ratio with respect to CO₂, the induced chemistry was not significantly affected by the nature of the energetic processing (Section 3.2), even though, unlike the 2 keV electrons, the energy of the Lyα photons (∼10.2 eV) was not enough to directly dissociate the CO ice molecules (the CO dissociation energy is 11.09 eV; see Carrascosa et al. 2019 and references therein). Previous works comparing the energetic processing of H₂O-rich polar ices by cosmic-ray analogs and UV photons had found a general agreement in the induced ice chemistry (see, e.g., Gerakines et al. 2001). However, a significant decrease in the measured conversion yield is reported in the literature for selected products in UV-irradiated apolar ices after similar absorbed energies. For example, the formation of the carbon chain oxide C₃O₂ presented a 17 times lower yield upon UV photolysis of CO-bearing ices compared to proton irradiation of the same samples (Gerakines & Moore 2001), while the formation of N₂ radicals was not observed upon UV irradiation of N₂-rich ices, in contrast with radiolysis experiments of the same samples (Hudson & Moore 2002). The differences in the measured yields could indeed be linked to the inability of the UV photons to break the intramolecular bonds in CO and N₂ molecules. In our case, the ∼50–100 times lower conversion in Lyα photon-irradiated ices compared to the 2 keV electron irradiation experiments could to some extent be explained by the low photon absorption cross section of the ices at this particular wavelength, because only ∼5% (i.e., a 1/20 fraction) of the irradiated energy was absorbed by the CO molecules (Section 2.3). We speculate that broadband UV photon irradiation could lead to conversion yields within a factor of a few compared to the electron-irradiated ices, although this would need to be verified.

The CO₂ growth curves in 2 keV electron-irradiated ices could be parameterized with a pseudo-first-order kinetic model, but this model did not fit the growth curves in Lyα photon irradiation experiments (Section 3.3). However, these apparent differences in the formation kinetics could be misleading, as different parts of the CO₂ growth curves were probed in each case. If the CO₂ percent yields in Figure 7 were presented as a function of the absorbed energy fluence instead of the irradiated...
fluence, the complete growth curves of the Lyα photon irradiation experiments would roughly correspond to the first measured percent yield in the 2 keV electron-irradiated ices. We can thus speculate that the CO₂ formation in Lyα photon irradiation experiments could be in an earlier regime compared to the formation after similar irradiated energy fluences with 2 keV electrons, and it could eventually evolve to a pseudo-first-order kinetic curve at higher-energy fluences. Additional data using broadband UV irradiation and/or low-flux electron irradiation is needed to check whether there are any kinematic differences between the two types of energetic processing.

During the dense cloud lifetime, the energy directly transferred from the incoming cosmic rays into the electronic system of the ice molecules is thought to be similar to the incident energy experienced by the ice mantles from the cosmic-ray-induced secondary UV field (Moore et al. 2001). From the results presented in this paper, keV electrons produced by the interaction of cosmic rays with the ice molecules (Bennett et al. 2005) are probably more important for the apolar ice layer processing than the secondary UV field induced by the interaction of the cosmic rays with the gas-phase H₂ molecules (Cecchi-Pestellini & Aiello 1992; Shen et al. 2004).

4.2. Effect of the Different Components in the Ice Chemistry

Experiments with binary ice mixtures were performed to understand how the presence of the different components affects the chemistry. In the absence of H₂ molecules, C₁₂¹⁵N₂ was detected following electron irradiation of the CO:¹⁵N₂ ice sample (Figure 3). In addition, ¹⁵NH₃ molecules were only observed in the H₂:¹⁵N₂ processed ice, while neither was detected in the mixture with three components. This suggests that the products of CO and H₂ irradiation preferentially react with each other instead of with ¹⁵N₂ or its dissociation products, leading to a quenched formation of ¹⁵NH₃ and C₁₂¹⁵N₂ in H₂:CO:¹⁵N₂ ices. Formation of ¹⁵NH₃ in H₂:CO:¹⁵N₂ ice samples and subsequent reaction with H:¹⁵NCO leading to the formation of OCN⁻ and NH₄⁺ probably did not take place, because the NH₂⁺ IR feature at 1485 cm⁻¹ was not observed in Experiment 3 (Figure 1). The OCN⁻ IR feature at 2166 cm⁻¹ overlaps with different CO and carbon chain oxide IR bands, and it could not be unambiguously detected either.

The CH₄ and H₂CO product branching ratios with respect to CO₂ upon energetic processing of H₂:CO:¹⁵N₂ ice analogs and H₂:CO binary mixtures were used to explore the effect that the ¹⁵N₂ molecules had on the chemistry. The relative product formation of H₂CO with respect to CO₂ could be decreased in the absence of ¹⁵N₂ molecules (Figure 6, left panel). However, we note that the difference found in the product branching ratios was just above the 25% experimental uncertainty. The CH₄ product branching ratio was the same, within the experimental uncertainties, upon 2 keV electron irradiation of H₂-bearing CO ices with or without ¹⁵N₂. On the other hand, a higher carbon chain oxide production in the 2 keV electron-irradiated H₂:CO and CO:¹⁵N₂ binary ice mixtures compared to the H₂:CO:¹⁵N₂ ice analog was evidenced by the stronger C₂O IR feature observed in the corresponding IR difference spectra (at the edge of the hatched region in Figure 1). This was confirmed by the higher QMS signal detected during thermal desorption of this species in the corresponding experiments (Figure 3).

4.3. Alternative Pathways to H-atom Addition Reactions for the CH₄, NH₃, and H₂CO Ice Formation

CH₄ has been detected in interstellar ice mantles with abundances of ∼5% with respect to H₂O ice (Boogert et al. 2015 and references therein). The strong correlation between the observed CH₄ and H₂O ice column densities, along with the broad profile of the solid-phase CH₄ IR feature, suggests that this species is present in the H₂O-rich polar ice layer and supports a scenario where CH₄ molecules are formed on the surface of dust grains through successive H-atom additions to C atoms during the formation of the H₂O-rich ice layer (Öberg et al. 2008). This formation pathway has been recently probed through experimental simulations in Qasim et al. (2020). In this work, we show that CH₄ molecules are also formed upon energetic processing of H₂-bearing CO ices. The produced CH₄ molecules represented less than 1% of the initial CO molecules (Table 3). Therefore, we do not expect this formation pathway to significantly contribute to the total formation of CH₄ ice, in line with the weak correlation of the observed CH₄ and CO ice column densities (Öberg et al. 2008).

The observed NH₃ ice abundance with respect to H₂O ice molecules is ∼7%. NH₃ is also believed to be present in the H₂O-rich polar ice layer after formation through H-atom hydrogenation of N atoms during the accretion of the H₂O-rich ice layer (Boogert et al. 2015). As explained above, ¹⁵NH₃ molecules are not formed in the presence of CO molecules, and we thus do not expect the NH₃ molecules to be present in the CO-rich ice layer. The formation through apolar ice energetic processing would only be expected if CO and N₂ ices were partially segregated, which may occur due to the slightly lower binding energy of N₂ molecules compared to CO molecules in pure and mixed CO:N₂ ices (Bisschop et al. 2006).

H₂CO has been likely detected in interstellar ice mantles, with estimated abundances ranging from 2% to 7% with respect to H₂O ice in different environments (Boogert et al. 2015 and references therein). However, current observations are not of sufficient quality to determine if H₂CO would be present in the H₂O-rich or the CO-rich ice layers (Qasim et al. 2019c and references therein). The most accepted H₂CO ice formation pathway is the H-atom hydrogenation of CO molecules (see, e.g., Watanabe & Kouchi 2002; Fuchs et al. 2009). H₂CO is thus more likely to be found in the CO-rich apolar ice layer (Cuppen et al. 2009). More recently, Chuang et al. (2018) proposed the VUV photon processing of H₂CO ices as an additional H₂CO ice formation pathway. In this work, we show that H₂CO also forms upon electron irradiation of H₂-bearing CO ices. The conversion with respect to the initial CO molecules in a H₂:CO:¹⁵N₂ ice analog (∼25%, Table 3) and the product branching ratio with respect to CO₂ (Figure 6, left panel) are enhanced compared to H₂CO ices. More experimental simulations aiming to characterize this formation pathway are needed in order to properly address the relative contribution of the different H₂CO formation scenarios.

4.4. H₂C₂O and HNCO Formation in the Interstellar Medium

H₂C₂O is thought to be chemically related to other organics such as CH₃CHO and CH₃CHOH, which belong to the family

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6 We note that approximately one-third of the observed CO₂ ice in the interstellar medium is present in a CO environment (Pontoppidan et al. 2008) and could be formed upon cosmic-ray irradiation of CO ices (Jamieson et al. 2006).
The formation of HNCO in the ISM is of particular interest from a prebiotic chemistry perspective, as it contains the peptide bond (\(-\text{H}--\text{N}--\text{C}(=\text{O})--\)) that links amino acids into proteins. The observed HNCO (and two of its metastable isomers, HOCN and HCNO) gas-phase abundances across different astrophysical environments cannot be explained with current gas-phase astrochemical models, and contribution from solid-phase formation pathways is needed to some degree depending on the environment (Tideswell et al. 2010; Quan et al. 2010; Quénard et al. 2018). HNCO has been observed in comets (Mumma and Charnley 2011), but in interstellar ices, only the related species OCN\(^-\) has been detected (Pontoppidan et al. 2003; van Broekhuizen et al. 2005) with a typical abundance of \(~0.6\%\) with respect to H\(_2\)O (Boogert et al. 2015). van Broekhuizen et al. (2004) proposed that solid-phase OCN\(^-\) is formed from HNCO in the presence of NH\(_3\) molecules, through an acid-base-like reaction that would take place in the H\(_2\)O-rich polar ice layer. However, a possible correlation between CO and OCN\(^-\) is reported in Öberg et al. (2011), and strong enhancements of the OCN\(^-\) ice abundance are observed in cold regions after accretion of the CO-rich apolar layer (Boogert et al. 2015), which suggests that OCN\(^-\), and in extension HNCO formation, is occurring in the apolar ice layer. Based on laboratory experiments, the hydrogenation of N atoms and the simultaneous hydrogenation and UV irradiation of NO molecules in CO-rich ice analogs have been proposed as possible formation pathways for HNCO in the apolar ice layer (Fedoseev et al. 2015b, 2016). However, it is not obvious that these pathways can account for the observed abundance of HNCO in the ISM. In this work, we show that the electron irradiation of a H\(_2\)CO:15N\(_2\) ice analog also results in H\(^{15}\)NCO formation. Even though the formation of other \(^{15}\)N-bearing species was quenched upon energetic processing of a H\(_2\)CO:15N\(_2\) ice analog (Section 4.2), the formation of 15N=CO was confirmed during the TPD of the processed ice sample (Figure 4). However, the overlapping of the corresponding IR feature with different CO and and carbon chain oxide IR bands prevented us from calculating the conversion yield. A proper quantification of the HNCO conversion yield will help to properly estimate the contribution of this formation pathway to the budget of this species in the ISM.

### 5. Conclusions

1. Interstellar ice mantles are characterized by H\(_2\)O-rich (polar) and CO-rich (apolar) layers. Energetic processing of polar ices have long been known to induce a complex organic chemistry. In this study, we show that a complex ice chemistry can also be induced by energetic processing of the CO-rich apolar layer if H\(_2\) molecules are present and can proceed in very cold environments (down to \(~4\ K\)).

2. Several products were identified in our experiments simulating the electron processing of a H\(_2\):CO:15N\(_2\) ice analog, including simple species such as CO\(_2\), C\(_2\)O (among other carbon chain oxides), and CH\(_4\), and the more complex organics H\(_2\)CO (a COM precursor), H\(_2\)C\(_2\)O, and H\(^{15}\)NCO. In particular, H\(^{15}\)NCO is an interesting molecule from a prebiotic chemistry perspective, as it contains the peptide bond (\(\sim\text{H}--\text{N}--\text{C}(=\text{O})--\)).

3. The CO conversion into these products in the 2 keV electron irradiation experiment accounts for \(~5\%--10\%\) of the initial CO exposed to the irradiation. More experimental simulations aiming to quantitatively characterize these formation pathways are needed in order to assess their relative contribution to the interstellar budget of, especially, the organics H\(_2\)CO, and H\(^{15}\)NCO.

4. The CO\(_2\) and H\(_2\)CO formation is one to two orders of magnitude lower in Ly\(_\alpha\) photon-irradiated ices compared to 2 keV electron-irradiated ices when the incident energy is similar, which may be due to the low UV-photon absorption cross section of the ice at this wavelength, while the relative branching ratio is similar in both cases. From the results presented in this paper, keV electrons produced by the interaction of cosmic rays with the ice molecules probably contribute to the apolar ice layer chemistry to a larger extent than the cosmic-ray-induced secondary UV field.

5. Formation of \(^{15}\)NH\(_3\) and C\(_2\)\(^{15}\)N\(_2\) is only observed in the absence of CO and H\(_2\) molecules, respectively. This suggests that chemical pathways involving both H\(_2\) and CO molecules are preferred over those involving only H\(_2\) and \(^{15}\)N\(_2\) or CO and \(^{15}\)N\(_2\) molecules.

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### Appendix A

#### Ice Sample Preparation

**A.1. Ice Composition**

In order to estimate the ice composition from the partial pressures of the different components in the gas mixtures, we derived a conversion factor for each species that transformed the QMS signal of the ice component main mass fragments into partial pressures. To that end, we previously introduced different pressures of the pure gases in the UHV chamber and measured the QMS signal of the species main mass fragment. We note that the pressure read by the baratron gauge was corrected by the relative probability of ionization with respect to N\(_2\), as indicated by the manufacturer. The 12CO relative probability of ionization was used for the 13CO and C\(_{18}\)O isotopologs as an approximation. Figure A1 shows the linear relation between the corrected gas pressure and the corresponding QMS signal of H\(_2\), CO, and \(^{15}\)N\(_2\) molecules. In Experiments 4 and 6, the carbon monoxide and molecular nitrogen molecules shared their main mass fragments (m/z = 28 and m/z = 30, respectively), and
alternative mass fragments were used \((m/z = 12\) for CO and \(^{13}\)C\(^{15}\)O, \(m/z = 14\) for \(^{15}\)N\(_2\), and \(m/z = 15\) for \(^{13}\)N\(_2\)).

### A.2. Ice Thickness

The total thicknesses of the ice samples in Experiments 1–14, A1, and A2 were calculated in terms of molecule column densities (molecules cm\(^{-2}\)). Due to the nonlinear behavior of the IR absorbance with the species column densities above a certain threshold in the IR spectra collected in reflection-absorption mode, the CO IR feature at \(\sim 2140\) cm\(^{-1}\) could not be used to determine the initial CO ice column density (see, e.g., Öberg et al. 2009). As mentioned in Section 2.6, the initial CO ice column density \((N(\text{CO}))\) was estimated instead from the area under the TPD curve measured with the QMS \((A_{\text{TPD}}(m/z = 28))\), while the initial H\(_2\) and \(^{15}\)N\(_2\) ice column densities were estimated from \(N(\text{CO})\) assuming that the initial ice composition was the same as the composition of the gas mixture used for ice deposition. We note that the error made in the approximation of the initial CO ice column density as the CO column density calculated with the TPD curve after processing of the ice samples (below 10\%) according to the CO conversion into products in the 2 keV electron irradiation experiments (Section 3.2) was lower than the uncertainty in the estimation of the CO column density (20\%; see below).

The area under the CO TPD curve \((A_{\text{TPD}}(m/z = 28))\) was proportional to the CO ice column density. We calibrated the QMS to extract the proportionality constant \(k_{\text{CO}}\):

\[
k_{\text{CO}} = \frac{A_{\text{TPD}}(m/z = 28)}{N(\text{CO})}. \tag{A1}
\]

The same proportionality constant was used for the \(^{13}\)CO isotopolog in Experiments 5 and 6, as a first approximation. The constant \(k_{\text{CO}}\) was calculated from a series of seven calibration experiments in which pure CO ice samples were deposited on top of a CsI IR transparent substrate that allowed the collection of the IR spectrum in transmission mode (Experiments C1–C7; Table 5). The CO ice column density \((N(\text{CO}))\) was subsequently estimated from the \(\sim 2140\) cm\(^{-1}\) IR feature using Equation (2). The \(\sim 2140\) cm\(^{-1}\) IR feature absorbance was numerically integrated using the composite Simpson’s rule (integrate.simps in Python). The band strength \(A\) of this feature is \(1.1 \times 10^{-17}\) cm molecule\(^{-1}\) (Table 2). After deposition, a heating rate of 2 K min\(^{-1}\) was applied to the pure CO ice until complete sublimation was achieved. The area under the CO TPD curve was also calculated with the integrate.simps function in Python. A linear fit was subsequently performed to the seven experimental data points in Figure A2, using the curvefit function in Python. The proportionality constant \(k_{\text{CO}}\) was found to be \([5.56 \pm 0.11]\) \(\times 10^{-11}\) A K ML\(^{-1}\). A 20\% uncertainty was assumed due to the 20\% uncertainty of the CO IR band strength (Bouiloud et al. 2015).

In Experiments 4 and 6 the carbon monoxide and molecular nitrogen molecules shared their main mass fragments \((m/z = 28\) and \(m/z = 30\)) at different pressures of the pure gases in SPACE TIGER (black dots). Similar fits were determined for the rest of the isotopologs used in this work.

**Figure A1.** Linear fit (solid blue line) to the measured QMS signal of the main mass fragments of H\(_2\) \((m/z = 2\) (left panel)), CO \((m/z = 28\) (middle panel), and \(^{15}\)N\(_2\) \((m/z = 30\) (right panel) at different pressures of the pure gases in SPACE TIGER (black dots). Similar fits were determined for the rest of the isotopologs used in this work.

**Figure A2.** Linear relation (solid blue line) between the area under the TPD curve of a pure CO ice in SPACE TIGER \((A(m/z = 28))\) and the CO ice column density \(N(\text{CO})\), extracted from a series of seven calibration experiments (black dots).

**Table 5**

| Exp. | Ice comp. | Thickness (ML) | Irradiation | Incident energy (\(\times 10^{15}\) eV) |
|------|-----------|---------------|-------------|------------------|
| A1   | CO        | 1000          | 2 keV e\(^{-}\) | 1.4               |
| A2   | CO        | 400           | Ly\(_{\alpha}\) | not measured      |
| C1−C7| CO        | 217−924\(^{a}\)| blank      |                   |

\(^{a}\) 1 ML = 10\(^{15}\) molecules cm\(^{-2}\). We assume a 20\% error in the ice thickness in Experiments A1−A2 (see Section A.2). The ice thickness was calculated using Equation (2) from the IR spectra collected in transmission mode.
and \( m/z = 30 \), respectively), and the ice thickness was determined from \( A(m/z = 12) \), for which a similar calibration was performed.

On the other hand, the total thickness of the ice samples in Experiments 13 and 14 was calculated from the \( ^{15}\text{N}_2 \) ice column density \( (N(^{15}\text{N}_2)) \). The \( ^{15}\text{N}_2 \) initial column density was calculated from the area \( A_{\text{TPD}}(m/z = 30) \) under the corresponding TPD curve. The proportionality constant \( k_{^1\text{N}_2} \) was averaged from the \( A_{\text{TPD}}(m/z = 30)/N(^{15}\text{N}_2) \) measured in Experiments 1–3, 5, 7, 8, 11, and 12 and had a value of \( 8.1 \times 10^{-11} \text{ A K ML}^{-1} \).

### Appendix B

#### Ice Chemistry in the Apolar Ice Layer

**B.1. Uncertainties in The Product Conversion Yields**

The 2 keV electron irradiation of \( \text{H}_2: \text{CO}:^{15}\text{N}_2 \) ice analogs in Experiments 1, 2, and 3 were performed under the same conditions, and the same results were thus expected. The left panel of Figure B1 shows the \( \text{CO}_2, \text{CH}_4, \) and \( \text{H}_2\text{CO} \) conversion yields \( (N(X)/N(\text{CO})) \) (Section 2.5). We found a 25% experimental uncertainty (indicated as red error bars) in the product conversion yields measured in Experiments 1–3, on top of the systematic uncertainties in the product IR band strengths and the calculated \( ^{13}\text{CO}/\text{CO} \) fraction, described in Section 2.5. The systematic uncertainties have the same effect in all experiments and should not be taken into account when comparing the conversion yields (or product branching ratios) of the same species in different experiments. Several sources of errors contributed to this experimental uncertainty, for example, the uncertainty in the integrated \( ^{13}\text{CO} \) IR absorbance (due to the low signal-to-noise ratio of this feature), or other day-to-day changes in the precise experimental conditions, such as the noise level in the collected IR spectra. The right panel of Figure B1 shows the \( \text{CH}_4 \) and \( \text{H}_2\text{CO} \) product branching ratios with respect to \( \text{CO}_2 \) in terms of conversion yield ratios. The additional \( \sim 25\% \) experimental uncertainty mentioned above was able to account for the differences found between Experiments 1–3.

**B.2. Ice Chemistry in Analogs of the Apolar Ice Layer**

Figure B2 shows the IR spectra collected before and after the energetic processing of the analogs of the apolar ice layer in Experiments 3 and 8–12 in the mid-IR range. The difference spectra, along with the identification of the more relevant features, are presented in Section 3.1. A broad feature above 3000 cm\(^{-1} \) was usually observed after irradiation of the different ice samples, regardless of their composition. This feature was probably due to the condensation of \( \text{H}_2\text{O} \) molecules on the walls of the IR detector during the experimental simulations. Contribution from background contamination inside the UHV chamber was not expected to be significant. Unfortunately, this prevented us from studying the potential formation of \( \text{H}_2\text{O} \) molecules in the processed ice samples.

**B.3. Ice Chemistry of a Pure CO Ice Sample**

The top panel of Figure B3 shows the IR spectrum of a 1000 ML pure CO ice (Experiment A1, Table 5) in the 2500–950 cm\(^{-1} \) region of the spectrum. The CO IR features were confined to the 2310–1995 cm\(^{-1} \) region, and only a small \( \text{CO}_2 \) feature due to contamination was observed outside that region. The \( \text{CO}_2 \) contamination represented \( \sim 0.01\% \) of the initial CO molecules, as measured from the IR spectra in transmission mode in Experiments C1–C7. After a total deposited energy of \( \sim 1.3 \times 10^{18} \) eV through 2 keV electron irradiation, the most abundant formed species was \( \text{CO}_2 \) (Ioppolo et al. 2009). A bunch of additional IR features were detected, most of them (but not all) in the 2310–1995 cm\(^{-1} \) region of the spectrum (middle panel of Figure B3), corresponding to carbon chain oxides including \( \text{C}_2\text{O}, \text{C}_2\text{O}_2, \text{C}_3\text{O}, \text{C}_3\text{O}_2, \text{C}_4\text{O}, \text{C}_4\text{O}_2, \text{C}_5, \text{C}_5\text{O}, \text{C}_5\text{O}_2, \text{C}_7\text{O}, \text{C}_7\text{O}_2 \). A \( \text{C}_2\text{O} \) IR feature was detected at the edge of this region (at 1989 cm\(^{-1} \), Palumbo et al. 2008), blended with a CO IR band. A complete analysis of the formation of carbon chain oxides upon energetic processing of CO-bearing ice samples is presented in Sicilìa et al. (2012), and it is beyond the scope of this paper.

In addition, the difference spectrum (bottom panel of Figure B3) shows that the 2140 cm\(^{-1} \) CO feature does not decrease, but increases its intensity upon energetic processing of the pure CO ice. A similar increase is observed after energetic processing of \( \text{H}_2: \text{CO}:^{15}\text{N}_2, \text{H}_2: \text{CO}, \) and \( \text{CO}:^{15}\text{N}_2 \) ice samples (Figure 2). This is probably due to a change in the \( \text{C}=\text{O} \) stretching IR band strength as a result of structural changes taking place in the ice sample, combined with the limited chemistry undergone by the CO molecules.

**B.4. Product Identification in Different Isotopically Labeled Ice Mixtures**

In order to confirm the assignments of the thermal desorption peaks observed in the left panels of Figure 3, we irradiated four additional ice analogs composed of different combinations of isotopically labeled \( \text{H}_2, \text{CO}, \) and \( \text{N}_2 \) molecules with 2 keV electrons (Experiments 4–7 in Table 1). The positions of the IR bands detected after irradiation of the ice samples, and the mass fragments showing thermal desorption during the TPD of the processed ices were shifted according to the particular isotopic composition of the products in the different ice samples. This is shown in Figure 4 for \( \text{H}_2\text{CN}, \text{H}_2\text{C}_2\text{O}, \) and \( \text{C}_3\text{O} \) (only TPD curves), and in Figure B4 for \( \text{CO}_2, \text{H}_2\text{CO}, \) and \( \text{CH}_4 \). For example, the \( \text{C}=\text{O} \) stretching IR band corresponding to \( \text{CO}_2 \) shifted from 2345 cm\(^{-1} \) to 2310 cm\(^{-1} \) for \( ^{13}\text{CO}_2 \), and 2280 cm\(^{-1} \) for \( ^{15}\text{CO}_2 \), while the thermal desorption was observed for the mass fragments \( m/z = 44, 48, \) and 45, respectively.
Figure B2. IR spectra obtained before (dashed lines) and after (solid lines) irradiation of a similar incident energy with 2 keV electrons (black) and Lyα photons (purple) of H₂:CO:¹⁵N₂, H₂:CO, CO:¹⁵N₂, and H₂:¹⁵N₂ ice samples (from top to bottom). The IR spectra are offset for clarity.

Figure B3. IR spectrum before (top panel) and after (middle panel) a total deposited energy of \( \sim 1.3 \times 10^{18} \) eV through 2 keV electron irradiation of a 1000 ML pure CO ice (Experiment A1; Table 5), along with the IR difference spectrum (bottom panel). The 2310–1995 cm\(^{-1}\) region, where the CO and most of the carbon chain oxides IR features are located, is highlighted in every panel.
Figure B4. TPD curves and IR features of the CO$_2$, CH$_4$, and H$_2$CO (from top to bottom) produced upon 2 keV electron irradiation of different isotopically labeled three-component ice samples, from left to right: H$_2$:CO:15N$_2$, H$_2$:CO:N$_2$, H$_2$:C$^{18}$O:15N$_2$, H$_2$:13CO:15N$_2$, and D$_2$:13CO:15N$_2$. The H$_2$CO TPD curves are shown for both the main mass fragment (black) and the molecular mass fragment (gray). The H$_2$CO IR feature observed at 4.3 K (black) is shown along with that detected at 120 K (red).
The double-peaked H$_2$CO C=O stretching IR band at 1725 cm$^{-1}$ was also redshifted for H$_2$C$^{18}$O, H$_2$D$^{18}$CO, and D$_2$C$^{18}$O. However, the double-peak structure was not observed at higher temperatures (only one peak was detected; see Figure B4). This double-peak structure could be thus due to the apolar ice matrix in which the produced H$_2$CO molecules were embedded, because the majority of the H$_2$, CO, and N$_2$ molecules conforming to this apolar ice matrix had already desorbed at higher temperatures. In addition, as mentioned in Section 3.1, the thermal desorption of H$_2$CO presented two desorption peaks. We speculate that the second desorption peak could be due to the formation of H$_2$CO dimers with a higher binding energy, as the H$_2$CO IR feature was detected at temperatures higher than the multilayer H$_2$CO thermal desorption peak temperature. However, the two desorption peaks were only observed for the mass fragments corresponding to HCO$^+$ and H$_2$CO$^+$ (and the corresponding isotopologs), but not to the (H$_2$CO)$_2$ dimers (not shown in Figure B4).

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