13CO and 13CO2 ice mixtures with N2 in photon energy transfer studies

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ABSTRACT
In dense clouds of the interstellar medium, dust grains are covered by ice mantles, dominated by H2O. CO and CO2 are common ice components observed in infrared spectra, while infrared inactive N2 is expected to be present in the ice. Molecules in the ice can be dissociated, react or desorb by exposure to secondary ultraviolet photons. Thus, different physical scenarios lead to different ice mantle compositions. This work aims to understand the behaviour of 13CO : N2 and 13CO2 : N2 ice mixtures submitted to ultraviolet radiation in the laboratory. Photochemical processes and photodesorption were studied for various ratios of the ice components. Experiments were carried out under ultra-high vacuum conditions at 12K. Ices were irradiated with a continuous emission ultraviolet lamp simulating the secondary ultraviolet in dense interstellar clouds. During the irradiation periods, Fourier-transform infrared spectroscopy was used for monitoring changes in the ice, and quadrupole mass spectrometry for gas-phase molecules. In irradiated 13CO2 : N2 ice mixtures, 13CO, 13CO2, 13CO3, O2, and O3 photoproducts were detected in the infrared spectra. N2 molecules also take part in the photochemistry, and N-bearing molecules were also detected: NO, NO2, N2O, and N2O4. Photodesorption rates and their dependence on the presence of N2 were also studied. As it was previously reported, 13CO and 13CO2 molecules can transfer photon energy to N2 molecules. As a result, 13CO and 13CO2 photodesorption rates decrease as the fraction of N2 increases, while N2 photodesorption is enhanced with respect to the low UV-absorbing pure N2 ice.

Key words: Astrochemistry – ISM: molecules – Ultraviolet: ISM – Methods: laboratory: molecular

1 INTRODUCTION
In the Interstellar Medium (ISM), dense clouds are made of H2 and other gases, while sub-micron dust grains contribute about 1% of the cloud mass. As a consequence of the low temperatures, near 10 K in the cloud core, dust grains are covered by small molecules, leading to the formation of ice mantles. H2O is the main constituent of the ice and smaller amounts of CO, CO2, CH3OH, CH4, NH3, etc, are commonly observed (Mumma & Charnley 2011; Boogert et al. 2011). Molecules with weaker intermolecular forces such as CO, and presumably N2, are found in a larger extent on the surface of ice mantles, as they need lower temperatures to freeze out (T < 20 K) (Pontoppidan et al. 2008). In the cold astrophysical environments with temperatures below 20 K, non-thermal desorption processes induced by cosmic rays and secondary UV photons are the main processes contributing to the abundance of CO and N2 gases.

Secondary UV radiation is generated by the interaction of cosmic rays with hydrogen molecules present in dense clouds (Prasad & Tara 1983; Cecchi-Pestellini & Aiello 1992; Shen et al. 2004). As a consequence, mainly ion and photon induced desorption are the processes expected to contribute to the observed gas phase abundances below 20 K. Ice molecules can desorb by two different processes induced by UV photons. Desorption Induced by Electronic Transition (DIET) occurs when a molecule absorbs a photon, and it experiments an electronic transition to the excited state. Then, it can follow two different routes. If the molecule is located on the surface of the ice, it can use...
this energy to desorb, what is known as direct DIET. If the molecule is in the subsurface monolayers (MLs), the electronic energy is distributed to the surrounding species. Molecules in the surface can receive this energy, which is used to break the intermolecular bonds and photodesorb (Bertin et al. 2012; Martín-Doménech et al. 2015). This process is known as indirect DIET. Direct DIET is negligible in comparison with indirect DIET, as most photons are absorbed in the subsurface MLs compared to the absorption in the first ML of the ice. Photochemical desorption or photolysis is a different process. Some molecules do not desorb efficiently upon irradiation of the pure ice, but they photolysis as photoproducts of ices with a different composition (Martín-Doménech et al. (2015) and references therein).

Desorption induced by secondary UV radiation is a complex process, it varies depending on the molecules present in the ice, the interactions between them and the ice temperature, among others. A few works were dedicated to study the photon-induced desorption in multicomponent ices (Bertin et al. 2013; Fillion et al. 2014; Martín-Doménech et al. 2015, 2016; Cruz-Díaz et al. 2016, 2018). This work reports UV radiation of binary ices formed by $^{13}$CO and $^{13}$CO$_2$ mixed with N$_2$ were studied to explore the formation, photon-induced and thermal desorption of photoproducts. Irradiation experiments of ice mixtures with similar compositions were reported by Sandford & Allamandola (1990); Elsila et al. (1997) in high vacuum experiments, but, unfortunately, ultra-high vacuum (UHV) is required to study photon-induced desorption processes. N$_2$ has a very low vacuum ultraviolet (VUV) absorption cross section below 12 eV. Thus, photodesorption of pure N$_2$ ice is negligible in our experiments (see Sect. 2). Keeping the same $^{13}$CO or $^{13}$CO$_2$ ice thickness, different deposition ratios with N$_2$ were used, to investigate the photodesorption yield of the molecules.

Apart from photodesorption, secondary UV radiation within interstellar dense clouds and cold circumstellar regions can induce destruction and formation of covalent bonds in the ice. Consequently, new compounds appear in the ice mantles. Different species have been detected in the ISM and protoplanetary disks, but their formation pathway is still unknown. The processes of formation of photoproducts can be elucidated by experimental simulations. In this study, photoproducts obtained from the different mixtures are also discussed.

2 EXPERIMENTAL SETUP

The experiments were carried out using the UltraHigh Vacuum Interstellar Photoprocess System (UHV-IPS) at National Central University in Taiwan. The experimental protocol was described in Chen et al. (2014). During the experiments, the system was cooled down to 12 K, and the base pressure was around 3·10$^{-10}$ torr at room temperature. Fourier-Transform Infrared spectroscopy (FTIR) and Quadrupole Mass spectrometry (QMS) data were taken before and after cooling down to cryogenic temperatures to check the presence of any potential contaminants. A T-type microwave discharge hydrogen flow lamp (MDHL) was used to simulate the background UV radiation in dense clouds. Light source stability of MDHL was also checked before starting the experiments. The deposition substrate was irradiated to quantify the blank signal in the QMS, to substract it from the ice signal desorption afterwards. Using a gas line system, the ice mixtures for each experiment were prepared. High purity gases were used: $^{13}$CO$_2$ (99%), $^{13}$CO (99%), N$_2$ (99.999%). The gas flow was directed through stainless steel bellows, using a 1 mm diameter capillary to inject it into the chamber. The capillary was placed 20 mm away, aligned at normal angle of the CaF$_2$ substrate. Additionally, another MgF$_2$ window acted as interface between the MDHL and the chamber, leading to a cut-off at 114 nm (10.8 eV). The composition of the growing ice was monitored by a QMS, and the ice thickness with FTIR.

The ratio of the gas mixture components was measured before introducing them in the chamber. First, one of the components is introduced in a gas line system which has four bottles with the same volume, until it reached the desired pressure, and stored at the same pressure in an independent bottle. The gas line system is then evacuated. The same procedure is applied to the second gas component. Both gases are finally mixed in the gas line. However, the proportions obtained in the deposited ices were slightly different. The amount of each component was recalculated during deposition using the integrated area for the molecular $^2$P$_{1/2}$ fragments, giving the final composition (see Table 1) assuming that all molecular components share a similar sticky coefficient. This allowed to estimate the column density of IR-inactive N$_2$. All the experiments were repeated twice to ensure the results were reliable. During deposition of the ices, the column density of the components was controlled using FTIR, to obtain a value of 200 ML (1 ML is $10^{15}$ molecules cm$^{-2}$) of $^{13}$CO or $^{13}$CO$_2$.

The ices were processed by UV-radiation with the MDHL. A hydrogen flux of 0.4 mbar was fixed in the MDHL circuit. MDHL photon flux is determined in situ by a nickel mesh (Chen et al. 2014). After each irradiation period, the photon dose was calculated, and an IR spectrum of the deposited ice was taken with a minimum resolution of 4 cm$^{-1}$. As the QMS spectrum was recorded during the whole irradiation sequence, both the solid and the gas phase were monitored.

The ices were irradiated leading to total irradiation times of 5, 10, 15, 20, 25, 35, 45, 55, 70, and 90 min. From these data, ice column densities of $^{13}$CO$_2$ and $^{13}$CO were calculated from their infrared absorption band, using equation 1 and integrating from 2320 cm$^{-1}$ to 2220 cm$^{-1}$ and from 2120 cm$^{-1}$ to 2075 cm$^{-1}$, respectively. In this formula, $N$ is the column density in molecules · cm$^{-2}$, $A$ is the band strength in cm · molecule$^{-1}$ (listed in Table 3), $\tau_\text{b}$ the optical depth of the band, and $d\nu$ the wavenumber differential in cm$^{-1}$.

\[
N = \frac{1}{A} \int_{\text{band}} \tau_\text{b} \, d\nu
\]
Table 1. \(^{13}\)CO: \(N_2\) and \(^{13}\)CO\(_2\): \(N_2\) ice mixture experiments performed for this study.

| Experiment | Ratio \(^{13}\)CO: \(N_2\)* | \(N\) \(^{13}\)CO (ML)** | Experiment | Ratio \(^{13}\)CO\(_2\): \(N_2\)* | \(N\) \(^{13}\)CO\(_2\) (ML)** |
|------------|-----------------|-----------------|------------|-----------------|-----------------|
| 1          | 1:0             | 200             | 7          | 1:0             | 196             |
| 2          | 2:1             | 201             | 8          | 2:1             | 201             |
| 3          | 1:1             | 201             | 9          | 1:1             | 201             |
| 4          | 1:2             | 198             | 10         | 1:2             | 199             |
| 5          | 1:4             | 199             | 11         | 1:4             | 199             |
| 6          | 0:1             | 0               |            |                 |                 |

* Rounded values are given to facilitate the discussion. Error was below 5% in all cases and the exact values were used for the graphs (e.g. the 1:1 ice mixture was 49% of \(^{13}\)CO and 51% of \(N_2\)).

** Average value between the two experiments was taken, the difference was below 6 ML in all cases.

3 RESULTS AND DISCUSSION

This section is divided into three different subsections. Sect. 3.1 introduces \(^{13}\)CO: \(N_2\) mixtures, as a prerequisite to interpret \(^{13}\)CO\(_2\): \(N_2\) mixtures. The experiments are presented in Sect. 3.2. A comparison of the results using both ice mixtures is provided in Sect. 3.3.

### 3.1 \(^{13}\)CO: \(N_2\) results

Figure 1 shows the spectra before irradiation for the different ice mixtures. Two peaks appear in the pure \(^{13}\)CO ice spectrum measured at 45° incidence angle, which converge as more \(N_2\) is added to the mixture. Thus, \(^{13}\)C=O stretching is split into two bands: one band belongs to the transverse optical (TO) mode and another one to the longitudinal optical (LO) mode, centered at 2091.2 cm\(^{-1}\) and 2095.5 cm\(^{-1}\), respectively (Palumbo et al. 2006). As the amount of \(N_2\) is increased, the shape of the bands changes. TO mode is redshifted while LO is blueshifted. When the fraction of \(N_2\) exceeds 0.66, both bands overlap and become indistinguishable. In other words, the LO and TO modes characteristic of cubic \(^{13}\)CO ice vanish when there is enough \(N_2\) in the ice mixture, as it might be expected. Additionally, the IR band of \(^{13}\)CO becomes narrower as the proportion of \(N_2\) is increased. \(N_2\) acts similar to noble gases used for dilution of ice molecules, therefore reducing intermolecular van der Waals forces between \(^{13}\)CO molecules.

Fig. 2 and Table 4 show the IR features for the different \(^{13}\)CO: \(N_2\) ice mixtures. Direct \(^{13}\)CO dissociation requires an energy up to 11.1 eV (112 nm) that is not attained in our experiments using the MDHL with a MgF\(_2\) window interface. However, \(^{13}\)CO\(_2\) molecules can be produced triggered by an excited state of \(^{13}\)CO, as follows:
**Figure 1.** Comparison of IR spectra (resolution of 1 cm$^{-1}$) of the deposited ices, $^{13}$CO : N$_2$ ice mixtures on the right and $^{13}$CO$_2$ : N$_2$ ice mixtures on the left.

**Figure 2.** IR spectra before and after 90 min irradiation for the different $^{13}$CO : N$_2$ mixtures.
Table 3. Band strength values adopted for column density calculations.

| Species | Frequency (cm⁻¹) | Band strength (cm molecule⁻¹) |
|---------|-----------------|-----------------------------|
| ¹³CO    | 2093            | 1.3 · 10⁻¹⁷  
| ¹³CO₂   | 2280            | 7.8 · 10⁻¹⁷  
| ¹³CO₃   | 1989            | 1.5 · 10⁻¹⁷  
| O₃      | 1041            | 1.4 · 10⁻¹⁷  
| NO      | 1875            | 4.5 · 10⁻¹⁸  
| N₂O     | 2235            | 6.1 · 10⁻¹⁷  
| NO₂     | 1614            | 6.2 · 10⁻¹⁷  |

*a* From Gerasimenko et al. (1995)

*b* Value taken from ¹²CO₃ in Martín-Doménech et al. (2015)

*c* From Smith et al. (1985)

*d* From Sicilia et al. (2012)

*e* From Fulvio et al. (2009)

\[¹³CO + hν → ¹³CO^*\]
\[¹³CO^* + ¹³CO → ¹³CO₂ + ¹³C\] (3)

On the other hand, ¹³CO₂ dissociation energy is lower (5.44 eV, 228 nm) (Huebner et al., 1992), and becomes efficient in these experiments. As a consequence, the decrease of the pure ¹³CO ice band due to the formation of ¹³CO₂ is < 3%, and CO photodesorption consumes an important fraction of the absorbed photon energy during continued irradiation (Muñoz Caro et al., 2010).

\[¹³CO₂ + hν → ¹³CO + O^·\] (4)

From QMS measurements during ice deposition, it was possible to calculate the ¹³CO : N₂ ratio, obtaining the values shown in Table 1, which are slightly different from the ones measured in the gas line prior to deposition (see Sect. 2). QMS data (Fig. 3) allowed estimation of photodesorption ratios for each experiment. The results are shown in Figure 4. ¹³CO is not able to desorb directly from its own fragmentation in the excited state, as it is a non-dissociative state (Okabe 1978; Cottin et al. 2003). Thus, ¹³CO desorbs mainly through an indirect DIET mechanism.

As Chen et al. (2017) reported, N₂ and ¹³CO energy levels only overlap in the low wavelength emission range of the MDHL. N₂ ice VUV absorption ranges from 120 nm to 145 nm, and ¹³CO ice absorbs photons from 130 nm to 160 nm. From 120 nm to 130 nm, their absorption is relatively low. Bertin et al. (2013) studied this effect, concluding that direct energy transfer is barely possible between both molecules. Energy transfer follows an indirect DIET mechanism. Photoabsorption induces a transition from the electronic ground state to the first excited one. Energy from the relaxation of ¹³CO to the ground state can reach a N₂ molecule on the ice surface, where conversion to translational energy can lead to desorption.

The N₂ photodesorption rate increases as a function of the fraction of N₂ up to a maximum, for a fraction of N₂ of 0.5 (red line in Fig. 4). Simultaneously, ¹³CO photodesorption rate decreases (blue line). Interestingly, the CO+N₂ photodesorption rate follows a linear trend; its slope is related to the number of photons absorbed by ¹³CO, since N₂ absorption is negligible. Additionally, Fig. 4 shows that both CO and N₂ have the same possibilities to desorb (e.g. a fraction of N₂ of 0.8 is traduced into a 81% of N₂ photodesorption and 19% of CO photodesorption, and so on for the other ratios). Knowing that, only, the top 5±1 MLs contribute to the photodesorption of pure CO ice (Muñoz Caro et al. 2010; Fayolle et al. 2011; Chen et al. 2014), two different effects lead to the observed values. First, as the proportion of N₂ is increased, there will be fewer ¹³CO molecules and more N₂ molecules on the ice surface ready to photodesorb. Second, the lower number of ¹³CO molecules on the top 5±1 MLs reduces the number of absorbed photons that contribute to photodesorption. Thus, the energy available for photodesorption decreases and the overall value of photodesorption is reduced (black line).

### 3.2 ¹³CO₂ : N₂ ice mixtures

In Figure 1 various ¹³CO₂ : N₂ ice spectra after deposition are shown. The profile of the ¹³C=O stretching band of ¹³CO₂ is altered by the presence of N₂. In a way analogous to ¹³CO : N₂ ice mixtures, two bands, belonging to the TO and LO modes at 2277 cm⁻¹ and 2314 cm⁻¹, respectively, are seen in the pure ¹³CO₂ ice, and they converge into one band for large N₂ ratios, although a shoulder in the band shows that it is not a single isolated peak.

Table 5 shows the different IR features after 90 min irradiation for different ¹³CO₂ : N₂ mixtures (see scheme 5 and Table 5). Howev-er, O₂ has no dipole moment, neither intrinsic or induced by IR photons. Thus, its presence was confirmed by QMS (θ = 32) during the irradiation of the ices and temperature programmed desorption (TPD) experiments, while O₃ was identified from IR spectra.

\[O^· + O^· → O₂\]
\[O₂ + hν → O^· + O^·\]
\[O₂ + O^· → O₃\]
\[O₃ + hν → O₂ + O^·\] (5)

¹³CO₂ is formed as shown in Scheme 6. ¹³CO₂ abun-
Figure 3. Ion current obtained for three different \( \text{m} \text{z} \) fragments during the irradiation of a \(^{13}\text{CO} : \text{N}_2 = 1:2\) mixture in Experiment 4 (left) and four fragments from a \(^{13}\text{CO}_2 : \text{N}_2 = 1:1\) mixture in Experiment 9 (right), see Table 1. A 5-point median smooth was applied to \( \text{m} \text{z} = 45 \) in both graphs for clarity.

Table 4. IR bands (cm\(^{-1}\)) detected after 90 min irradiation for different \(^{13}\text{CO} : \text{N}_2\) mixtures, experiments 1-5.

| Pure \(^{13}\text{CO}\) | \(^{13}\text{CO}:\text{N}_2\) (2:1) | \(^{13}\text{CO}:\text{N}_2\) (1:1) | \(^{13}\text{CO}:\text{N}_2\) (1:2) | \(^{13}\text{CO}:\text{N}_2\) (1:4) | Assignment | References |
|-----------------|----------------|----------------|----------------|----------------|-----------|-----------|
| 2345            | 2347           | 2347           | 2347           | 2348           | \(^{12}\text{CO}_2\) | Yamada & Person (1964) |
| 2281            | 2282           | 2282           | 2282           | 2282           | \(^{13}\text{CO}_2\) | Sandford & Allamandola (1990) |
| 2264            | 2264           | 2264           | 2265           | 2265           | \(^{13}\text{C}^{18}\text{O}^{16}\text{O}\) | This work |
| 2140            | 2140           | 2140           | 2140           | 2140           | \(^{12}\text{CO}\) | Jiang et al. (1975) |
| 2092            | 2092           | 2092           | 2093           | 2093           | \(^{13}\text{CO}\) | Gerakines et al. (1995) |
| 2065            | 2065           | 2065           | 2065           | 2065           | \(^{13}\text{C}^{17}\text{O}\) | Loeffler et al. (2005) |
| 2040            | 2040           | 2040           | 2040           | 2040           | \(^{13}\text{C}^{18}\text{O}\) | Öberg et al. (2009) |
| 1820            | 1820           | 1820           | 1820           | 1820           | 1821       | ?         |
|--              | --             | --             | --             | 1085           | ?         | ?         |

Figure 4. Photodesorption rate per incident photon for \( \text{CO}, \text{N}_2 \) and \( \text{CO}+\text{N}_2 \) in \(^{13}\text{CO} : \text{N}_2\) mixtures.

Photodissociation decreases as more \( \text{N}_2 \) is introduced in the ice mixture, as a consequence of the lower number of intermolecular \(^{13}\text{CO}_2 - ^{13}\text{CO}_2\) interactions. As QMS was recorded from \( \frac{\%}{5} = 1 \) to \( \frac{\%}{5} = 50 \), \(^{13}\text{CO}_3\) was only detected by an infrared absorption band at 1989 cm\(^{-1}\), and confirmed by the position and evolution of this band. The IR band position looks coherent with the bathochromic shift observed for \(^{13}\text{CO}_2\) and \(^{13}\text{CO}\) from the corresponding \(^{12}\text{CO}_2\) and \(^{12}\text{CO}\) molecules (see Table 4). Additionally, \(^{13}\text{CO}_3\) is formed at short irradiation times and its abundance decreases for longer irradiation periods (Martín-Doménech et al. 2015).

\[^{13}\text{CO}_2 + \text{O} \rightarrow ^{13}\text{CO}_3\]
\[^{13}\text{CO}_3 + h\nu \rightarrow ^{13}\text{CO}_2 + \text{O} \cdot\]

These photoproducts had also been detected in pure \( \text{CO}_2\) ices in previous works (Öberg et al. 2009; Bahr & Baragiola 2012; Martín-Doménech et al. 2015). Additionally, up to four different N-bearing molecules formed from \(^{13}\text{CO}_2 - \text{N}_2\) interactions, have been detected in this work: \( \text{NO}, \text{N}_2\text{O}, \text{NO}_2\) and \( \text{N}_2\text{O}_4\). Their abundances as a function of photon dose (molecules per induced photon) are represented in Fig. 4.
6. $N_2O$ is supposed to be formed easily, as its formation does not require $N_2$ dissociation (see Scheme 7). However, it is not the most abundant species found.

$$N_2 + O \rightarrow N_2O$$
$$N_2O + h\nu \rightarrow N_2 + O.$$  \hfill (7)

Other $N_2$ oxides can only be produced after dissociation of $N_2$ molecules, which implies a photon energy of 9.74 eV (127 nm), covered by the MDHL emission spectrum.

$$N_2 + h\nu \rightarrow N + N.$$ 
$$N + N \rightarrow N_2.$$  \hfill (8)

From $N$ radicals, other nitrogen oxides can be formed.

$$N + O \rightarrow NO$$
$$NO + h\nu \rightarrow N + O.$$ 
$$N + O_2 \rightarrow NO_2$$
$$NO_2 + h\nu \rightarrow N + O_2$$
$$NO_2 + NO_2 \rightarrow NO_4$$
$$N_2O_4 + h\nu \rightarrow NO_2 + NO_2.$$  \hfill (9)

During UV irradiation, nitrogen oxides can be dissociated. NO is the most stable one with a dissociation energy of 6.46 eV (191 nm), while NO$_2$ requires 3.11 eV (399 nm) and N$_2$O 3.63 eV (341 nm) (Huebner et al. 1992).

**Figure 5.** IR spectra before and after 90 min irradiation for $^{13}CO : N_2$ ice mixtures.

**Figure 6.** Evolution of the column densities of $^{13}CO_2$ and its photoproducts (Exp. 11) as a function of the photon dose using the band strength values shown in Table 3.

TPD data from QMS were used to confirm the presence of NO, $N_2O$ and NO$_2$. The thermal desorption temperature of these photoproducts found in our experiments is coherent with previous works where these species were warmed up from pure ices (Fulvio et al. 2009).

The QMS ion current measured during irradiation is related to the photodesorption rate, see Sect. 2. The highest amount of photodesorbing $N_2$ was reached at the end of the irradiation. QMS data shows a correlation between...
CO/ML

2

0.0

0.5

1.0

1.5

2.0

3.0

ion current of fragment NO\textsuperscript{+} molecule could not be confirmed in our experiments. The photon-induced desorption of a specific nitrogen oxide obtained from integration of the IR bands using Formula 1. Table 5. IR bands (cm\textsuperscript{-1}) detected after 90 min irradiations for different \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} mixtures, experiments 7-11.

| Pure \textsuperscript{13}CO\textsubscript{2} | \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} (2:1) | \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} (1:1) | \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} (1:2) | \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} (1:4) | Assignment | References |
|----------------------------------------|-----------------|-----------------|-----------------|-----------------|-------------|-----------|
| \textsuperscript{13}CO\textsubscript{2} | 3630            | 3629            | 3627            | 3629            | \textsuperscript{13}CO\textsubscript{2} | This work  |
| \textsuperscript{13}CO\textsubscript{2} | 3513            | 3514            | 3514            | 3516            | \textsuperscript{13}CO\textsubscript{2} | This work  |
| \textsuperscript{13}CO\textsubscript{2} | 2349            | 2347            | 2346            | 2347            | \textsuperscript{13}CO\textsubscript{2} | Yamada \& Penson (1964) |
| \textsuperscript{13}CO\textsubscript{2} | 2294            | 2287            | -               | -               | \textsuperscript{13}CO\textsubscript{2} | Gerakines et al. (1995) |
| \textsuperscript{13}CO\textsubscript{2} | 2276            | 2279            | 2280            | 2281            | \textsuperscript{13}CO\textsubscript{2} | Sandford \& Allamandola (1990) |
| \textsuperscript{13}CO\textsubscript{2} | 2264            | 2264            | 2263            | 2264            | \textsuperscript{13}CO\textsubscript{2} | Sandford \& Allamandola (1990); Fulvio et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | 2141            | 2141            | 2141            | 2140            | \textsuperscript{13}CO\textsubscript{2} | Jiang et al. (1975) |
| \textsuperscript{13}CO\textsubscript{2} | 2093            | 2093            | 2093            | 2093            | \textsuperscript{13}CO\textsubscript{2} | Hudgins et al. (1993); Gerakines et al. (1996) |
| \textsuperscript{13}CO\textsubscript{2} | 2042            | 2041            | 2041            | 2041            | \textsuperscript{13}CO\textsubscript{2} | \textsuperscript{13}CO\textsubscript{2} | Öberg et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | 1989            | 1989            | 1989            | 1989            | \textsuperscript{13}CO\textsubscript{2} | This work  |
| \textsuperscript{13}CO\textsubscript{2} | 1875            | 1873            | 1873            | 1873            | NO            | Pugh \& Narahari Rao (1976); Sicilia et al. (2012) |
| \textsuperscript{13}CO\textsubscript{2} | -               | -               | 1854            | 1850            | NO\textsubscript{2}O\textsubscript{4} | Fulvio et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | -               | -               | 1739            | 1740            | N\textsubscript{2}O\textsubscript{4} | Fulvio et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | -               | -               | 1614            | 1614            | NO\textsubscript{2}O\textsubscript{4} | Fulvio et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | -               | -               | 1302            | 1303            | NO\textsubscript{2}O\textsubscript{4} | Fulvio et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | -               | -               | 1262            | 1262            | N\textsubscript{2}O\textsubscript{4} | Fulvio et al. (2009) |
| \textsuperscript{13}CO\textsubscript{2} | -               | -               | 1041            | 1039            | O\textsubscript{3} | Sicilia et al. (2012) |

Figure 7. Ratio of the \textsuperscript{13}CO: \textsuperscript{13}CO\textsubscript{2} column densities during irradiation obtained from integration of the IR bands using Formula 1.

Table 5. IR bands (cm\textsuperscript{-1}) detected after 90 min irradiations for different \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} mixtures, experiments 7-11.

\textsuperscript{13}CO\textsubscript{2} and N\textsubscript{2} photodesorption. Their photodesorption rates increase during irradiation, what implies an energy transfer from \textsuperscript{13}CO to the UV low-absorbing N\textsubscript{2} molecules in the ice (Bertin et al. 2013). Although no photodissociation in pure N\textsubscript{2} ice, using the MDHL, was observed (Cruz-Diaz et al. 2014a), irradiation of the \textsuperscript{13}CO\textsubscript{2}:N\textsubscript{2} mixtures lead to formation of NO, N\textsubscript{2}, NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4}, detected by FTIR, (see Fig. 5 and Table 5). Figure 8 shows the photodesorption rate of the molecules of interest regarding \textsuperscript{13}CO\textsubscript{2}: N\textsubscript{2} mixtures. The \textsuperscript{13}CO photodesorption rate is higher than that of \textsuperscript{13}CO\textsubscript{2}, even in the pure \textsuperscript{13}CO\textsubscript{2} ice. Photon-induced desorption of a specific nitrogen oxide molecule could not be confirmed in our experiments. The ion current of fragment NO\textsuperscript{+} (m/z = 30) showed a significant increase upon irradiation, indicative of a photon-induced desorption. However, this fragment is common to various species (NO, NO\textsubscript{2}, N\textsubscript{2}O and N\textsubscript{2}O\textsubscript{4}).

Reaction to form \textsuperscript{13}CO from \textsuperscript{13}CO\textsubscript{2} is not unidirectional (see Schemes 3 and 4), leading to a constant \textsuperscript{13}CO/\textsuperscript{13}CO\textsubscript{2} ice abundance ratio during irradiation. However, adding N\textsubscript{2} to \textsuperscript{13}CO\textsubscript{2} ices changes the equilibrium state. When a photon induces dissociation of a \textsuperscript{13}CO\textsubscript{2} molecule, the remaining photofragments will be placed further away from each other if more N\textsubscript{2} is present. Consequently, it becomes more difficult for two \textsuperscript{13}CO molecules to reform \textsuperscript{13}CO\textsubscript{2}. The more N\textsubscript{2} in the sample, the larger amount of \textsuperscript{13}CO is present in the ice at the end of the irradiation period, as it is shown in Figure 7. As the amount of \textsuperscript{13}CO in the original \textsuperscript{13}CO\textsubscript{2} ice increases, the VUV absorption of the ice is shifted to longer wavelengths, which means that the emission spectrum of the MDHL lamp, in particular the Ly-\alpha to molecular lines ratio, influences the outcome of these experiments. Therefore, in terms of UV absorption, upon irradiation, these ice mixtures can no longer be considered as binary \textsuperscript{13}CO\textsubscript{2}: N\textsubscript{2} mixtures, but ternary \textsuperscript{13}CO\textsubscript{2}: \textsuperscript{13}CO: N\textsubscript{2} mixtures, with variable ratios along the irradiation periods.

Pure N\textsubscript{2} ice photodesorption rate was below the QMS detection limit, as expected, due to its low VUV absorbance (Cruz-Diaz et al. 2014b). However, when N\textsubscript{2} is mixed with \textsuperscript{13}CO\textsubscript{2}, N\textsubscript{2} photodesorption is observed. Thus, photon energy is transferred from the ice molecules with a significant absorbance in the VUV, mainly \textsuperscript{13}CO\textsubscript{2} and \textsuperscript{13}CO. Due to the cut off of the MgF\textsubscript{2} window at 114 nm, the main absorption bands of \textsuperscript{13}CO\textsubscript{2} play only a minor role, since only the tail of this band overlaps with the photon emission spectrum of the MDHL. On the other hand, the "A-X" absorption bands of \textsuperscript{13}CO match the emission range.
Photodesorption obtained for $^{13}\text{CO}_2$ experiments as a function of the fraction of N$_2$.

$^{13}\text{CO} : N_2$ and $^{13}\text{CO}_2 : N_2$ ice mixtures

$^{13}\text{CO} : N_2$ and $^{13}\text{CO}_2$ photodesorption rates in $^{13}\text{CO}_2 : N_2$ ice mixtures.

Concerning $^{13}\text{CO}_2 : N_2$ mixtures, the efficient formation of $^{13}\text{CO}$ (Fig. 7), led to a higher VUV absorption cross section than pure $^{13}\text{CO}_2$ ice (Cruz-Díaz et al. 2014a). VUV absorbance shifts to longer wavelengths as the ice is irradiated, contributing to N$_2$ photodesorption, as it occurs in the $^{13}\text{CO} : N_2$ mixtures. MDHL emitted VUV photons are absorbed in a broader wavelength range, while $^{13}\text{CO}_2$ in the ice absorbs from 114 nm to 140 nm, $^{13}\text{CO}$ molecules absorb mainly from 140 nm to 162 nm. The addition of N$_2$ in the $^{13}\text{CO}_2$ ice obviously increases N$_2$ photodesorption, since more N$_2$ molecules are available at the ice surface, but the maximum does not occur at a fraction of N$_2$ of 0.5. Instead, it corresponds to a fraction of 0.64. The presence of N$_2$ molecules promotes $^{13}\text{CO}$ formation from $^{13}\text{CO}_2$ (Fig. 7), and, as explained above, the combined absorption of both $^{13}\text{CO}$ and $^{13}\text{CO}_2$ on the ice surface covers a broader photon energy range, thus enhancing photodesorption.

$^{13}\text{CO}_2$ ice photodissociates readily to form $^{13}\text{CO}$ molecules. On the other hand, $^{13}\text{CO}$ irradiation using T-type MDHL only produces a small amount of $^{13}\text{CO}_2$ (e. g. Muñoz Caro et al. (2010); Chen et al. (2014)). This low conversion of $^{13}\text{CO}_2$ diminishes when $^{13}\text{CO}$ is mixed with N$_2$. $^{13}\text{CO}$ molecules absorb photons that induce mainly photodesorption rather than photochemistry. This is due to weak intermolecular forces and the low efficiency of $^{13}\text{CO}$ dissociation. In these experiments, on the contrary, $^{13}\text{CO}_2$ absorbed photons are employed mainly in photochemistry, promoting the formation of photoproducts, such as $^{13}\text{CO}_3$, O$_2$, O$_3$, or nitrogen oxides.
different composition for ice mantles. During low luminosity periods, different molecules will be incorporated onto dust grains (e. g. CO). Then, secondary UV radiation induces chemical changes (e. g. formation of CO\textsubscript{2} from CO). High luminosity results in a higher temperature, when volatile species will thermally desorb. For instance, CO would thermally desorb, leaving CO\textsubscript{2} behind (Kim et al. 2012; Dunham et al. 2010).

CO : N\textsubscript{2} mixtures are present within the first scenario and low luminosity periods from the second scenario, while pure CO\textsubscript{2} : N\textsubscript{2} mixtures will not be present in astrophysical environments. However, CO : CO\textsubscript{2} : N\textsubscript{2} mixtures will be present within the episode accretion scenario. The ratio between the three components will vary depending on the luminosity period. As luminosity and temperature start to raise up, CO and N\textsubscript{2} will thermally desorb at a different rate depending on the environment.

This work is focused on scenarios at low temperatures, where CO and N\textsubscript{2} will form the top MLs of the ice. Thus, studying the photochemistry of ice mixtures including CO, CO\textsubscript{2} and N\textsubscript{2} turns out to be relevant to understand the behaviour of the dense clouds interior. Photodesorption rates of 13CO : N\textsubscript{2} and 13CO\textsubscript{2} : N\textsubscript{2} ice mixtures have been studied, as well as their dependence on the amount of N\textsubscript{2}. 13CO absorbs photons and release energy to the surrounding molecules via indirect DIET. Therefore, the presence of N\textsubscript{2} diminishes the 13CO photodesorption rate. Fig 4 shows that the ice composition determines the ratio between CO and N\textsubscript{2} photodesorption rates, while the absolute value of photodesorption depends on the absorbed photons. Concerning 13CO\textsubscript{2} : N\textsubscript{2} ice mixtures, direct energy transfer also plays a role, as 13CO\textsubscript{2} VUV absorption bands overlap with those of N\textsubscript{2}. In both cases, N\textsubscript{2} photodesorption rate increases up to a maximum, as a consequence of the energy received from surrounding 13CO and, at a lesser extent, 13CO\textsubscript{2} molecules. For 13CO and 13CO\textsubscript{2} ice mixtures, fractions of N\textsubscript{2} above 0.5 and 0.64, respectively, imply a decrease in the photodesorption rate. This reduction is a result of the lower VUV absorbance in the top MLs.

In relation to photochemistry, pure 13CO and 13CO\textsubscript{2} ices have been extensively studied (Martín-Doménech et al. 2015; Ciaravella et al. 2016, and references therein). However, a more realistic scenario including N\textsubscript{2} was not sufficiently explored regarding product formation and desorption. Nitrogen oxides have been detected in dense molecular clouds (Ziurys et al. 1994; Halfen et al. 2001), which may appear after dissociation of N\textsubscript{2} molecules and subsequent chemical reactions (see Schemes 8 and 9). A reaction pathway for the formation of nitrogen oxides is proposed. 13CO\textsubscript{2} dissociation produces C and O radicals, which may react with N atoms or N\textsubscript{2} molecules to form NO, N\textsubscript{2}O, NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} in the ice. Molecules carrying CN groups are also expected from reactions involving carbon radicals, although they have not been detected in this work.

CO, CO\textsubscript{2}, N\textsubscript{2} or O\textsubscript{2} gas phase abundances at low temperatures in dense clouds can be estimated from the photodesorption rates calculated in this work. Photodesorption of photoproducts, such as 13CO\textsubscript{3}, O\textsubscript{3}, NO, N\textsubscript{2}O, NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} was negligible at this low temperature. However, as the temperature is increased, nitrogen oxides co-desorb thermally with N\textsubscript{2}, contributing to the gas phase abundance in dense clouds. Gas phase abundances can be explained, to a certain extent, based on the column density found in our IR spectra in agreement with the work of Elsila et al. (1997). To look further, different formation pathways must be considered. Regarding nitrogen oxides, NO\textsubscript{2} was the most abundant species, followed by NO and N\textsubscript{2}O. Observational measurements reported by Halfen et al. (2001) calculated the abundance of these molecules in Sagittarius B2 complex. They found NO column density (1.32 × 10\textsuperscript{16} cm\textsuperscript{-2}) to be larger than that of NO\textsubscript{2} (1.50 × 10\textsuperscript{15} cm\textsuperscript{-2}) and N\textsubscript{2}O (< 3.3 × 10\textsuperscript{15} cm\textsuperscript{-2}), suggesting that NO must be formed by other synthetic routes (e. g. involving H\textsubscript{2}O molecules as a source of oxygen atoms). Halfen et al. (2001) suggested chemical reactions which may formed N\textsubscript{2}O from NO or NO\textsubscript{2}, which will be negligible in our experiments, due to the low temperature, but may change the ratio between the components in dense clouds.

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