



PENTACARBON DIOXIDE (C₅O₂) FORMATION AND ITS ROLE AS A TRACER OF SOLAR SYSTEM EVOLUTION

MARKO FÖRSTEL^{1,2}, PAVLO MAKSYUTENKO^{1,2}, ALEXANDER M. MEBEL³, AND RALF I. KAISER^{1,2}

¹ W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii, HI 96822, USA; ralfk@hawaii.edu

² Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii, HI 96822, USA

³ Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, FL 33193, USA

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ABSTRACT

Carbon monoxide is the second most abundant molecule on icy grains in the interstellar medium. These grains are under the influence of ionizing radiation, which induces the chemical reaction within the ice. Here we report the first observation of subliming pentacarbon dioxide (C₅O₂) after irradiation of pure carbon monoxide ice with energetic electrons. Our results show that pentacarbon dioxide is a stable reaction product in a carbon monoxide matrix that survives the sublimation in star-forming regions at sublimation temperatures of 175 K. Along with carbon suboxide (C₃O₂), this molecule can serve as a powerful tracer of the temperature history of formerly carbon monoxide rich ices in molecular clouds and star-forming regions.

Key words: astrochemistry – comets: general – cosmic rays – infrared: ISM – methods: laboratory: molecular – molecular processes

1. INTRODUCTION

Carbon monoxide (CO) represents the second most abundant molecule on icy grains in the interstellar medium (ISM) with water (H₂O) being dominant (Whittet et al. 1985; Salyk et al. 2011; Boogert et al. 2015). In its solid form, carbon monoxide has been detected toward a wide range of interstellar environments, among them, the Taurus Molecular Cloud (Whittet et al. 1985), the Serpens dark cloud (Chiar et al. 1994), and young stellar objects (YSOs; Chiar et al. 1998; Pontoppidan et al. 2008). The abundance of carbon monoxide reaches up to 90% in some of the YSOs such as NGC 7538:IRS9 and W33A (Chiar et al. 1998; Boogert et al. 2002; Pontoppidan et al. 2008). Due to the low sublimation temperature of carbon monoxide of around 18 K (Nakagawa 1980), the temperature of interstellar clouds has a critical effect on the ratio of gas phase to solid state carbon monoxide, as demonstrated for W3 IRS5, NGC 7538:IRS1, NGC 7538:IRS9, W33A, and RCrA:IRS2 (Whittet et al. 1985; Mitchell et al. 1990; Chiar et al. 1998). Of the higher mass carbon oxides, carbon dioxide (CO₂) is the most abundant species and has been detected in its solid form toward, for example, YSOs like W33A and NGC 7538:IRS1, AFGL 961, AFGL 989, and AFGL 890 (d’Hendecourt & Jourdain de Muizon 1989; De Graauw et al. 1996; Guertler et al. 1996; Strazzulla et al. 1998) mostly in combination with carbon monoxide (CO) and water (H₂O). More complex carbon-rich oxides have only been detected in the gas phase. In TMC-1, dicarbon monoxide (C₂O) was observed at fractional abundances of about 6×10^{-11} with respect to molecular hydrogen (H₂; Brown et al. 1991; Ohishi et al. 1991). More abundant than dicarbon monoxide (C₂O), and probed earlier, was the linear carbon chain molecule tricarbon monoxide (C₃O) with relative abundances of 1.4×10^{-11} to 1×10^{-7} with respect to molecular hydrogen (H₂; Brown et al. 1985; Kaifu et al. 2004; Tenenbaum et al. 2006; Agúndez et al. 2008). The observation of interstellar pentacarbon monoxide (C₅O) has been referred to in the literature (Ohishi et al. 1991; Trottier & Brooks 2004), however, the sources cited therein are unavailable and no further confirmation is reported. Carbon

suboxide (C₃O₂) has not been confirmed in the ISM, but was suggested as a potential source of carbon and carbon monoxide in the coma of comet Halley (Huntress et al. 1991).

The formation of interstellar dicarbon monoxide (C₂O) and tricarbon monoxide (C₃O) is speculated to occur in the gas phase. Ohishi et al. (1991) suggest a formation pathway of C₂O, including ion-molecule reactions of the methyl cation (CH₃⁺) and carbon monoxide (CO) and of the ethylene ion (C₂H₄⁺) with atomic oxygen (O) toward CH₃CO⁺, which then undergoes dissociative recombination with an electron to form the ethynyl radical (HC₂O). HC₂O can then react with atomic oxygen to form dicarbon monoxide (C₂O) and the hydroxyl radical (OH). Another suggestion was the formation via the reaction of the ethynyl radical (C₂H) with atomic oxygen (O). A theoretical review on possible pathways is given by Loison et al. (2014). Some of these reaction pathways were also studied in the gas phase (Peeters et al. 1995; Devriendt & Peeters 1997); however, a prediction of the observed relative abundances of dicarbon monoxide (C₂O) to tricarbon monoxide (C₃O) could not yet be made. With regard to tricarbon monoxide (C₃O), Tenenbaum et al. (2006) discuss that the observed tricarbon monoxide (C₃O) in IRC +10216 formed via ion-molecule reactions with atomic oxygen (O) or via radiative association of carbon monoxide (CO) and H_nC_m. The possibility of an icy grain origin of O-bearing species in IRC +10216 is suggested by Agúndez et al.; however, they do not explicitly discuss dicarbon monoxide (C₂O) or tricarbon monoxide (C₃O; Agúndez & Cernicharo 2006). The formation of higher mass carbon oxides is discussed based on gas-phase experiments (Adams et al. 1989). The authors calculated relatively high abundances of C_nO ($n = 4-7$), with respect to tricarbon monoxide (C₃O), and predicted that an observation of these species should be possible in the ISM. Due to elusive gas-phase production routes, the condensed phase of carbon monoxide (CO) in the form of interstellar ices in cold molecular clouds has been discussed as a strong alternative “synthetic resource” toward oxygen-terminated carbon clusters. Several studies analyzed the radiation induced chemistry of carbon monoxide (CO) ices. Radiation sources employed were

energetic protons and photons (Haring et al. 1984; Gerakines & Moore 2001; Cottin et al. 2003; Trottier & Brooks 2004) as well as electrons (Jamieson et al. 2006). Using infrared spectroscopy, these studies identified the following species in the ice matrix: tricarbon (C_3) and hexacarbon (C_6), dicarbon monoxide (C_2O), tricarbon monoxide (C_3O), tetracarbon monoxide (C_4O), pentacarbon monoxide (C_5O), carbon dioxide (CO_2), tricarbon dioxide (C_3O_2), tetracarbon dioxide (C_4O_2), pentacarbon dioxide (C_5O_2), and heptacarbon dioxide (C_7O_2). Carbon monoxide (CO), carbon dioxide (CO_2), and tricarbon dioxide (C_3O_2) were identified in the gas phase using mass spectroscopy (Jamieson et al. 2006).

We recently established a new experimental technique that allows us to detect subliming molecules with unprecedented sensitivity, exploiting vacuum ultraviolet single photon ionization coupled with a reflectron time of flight mass spectrometer (PI-ReTOF-MS; Jones & Kaiser 2013; Kaiser et al. 2014; Maity et al. 2014). By using photon energies close to the ionization threshold of the molecules, ions are generally detected without fragmentation. On the other hand, a traditional residual gas analyzer such as a quadrupole mass spectrometer (QMS) exploits electron impact ionization to generate the ions suffering from significant fragmentation of the molecules under investigation. In this article, we exploit PI-ReTOF-MS to monitor the reaction products of electron irradiated carbon monoxide (CO) ices, which could not be detected earlier in the gas phase via QMS. In detail, we observe for the first time pentacarbon dioxide (C_5O_2) in the gas phase after it sublimes from the substrate at a temperature of around 175 K, thus paving its way for a prospective infrared spectroscopic observation in the ISM.

2. EXPERIMENTAL

The experiments were carried out in an ultra-high vacuum chamber with a base pressure of $(1.1 \pm 0.2) \times 10^{-10}$ torr. A rhodium coated silver wafer (1 cm^2) is mounted on a coldhead and cooled down to a temperature of 5.5 ± 0.1 K. Carbon monoxide (Matheson Gas Research Grade 99.999%) was deposited onto the wafer via a glass capillary array. Deposition of the ice took 10 minutes at a background pressure of $(2 \pm 1) \times 10^{-8}$ torr yielding an ice thickness of 800 ± 50 nm as monitored in situ using He-Ne laser (CVI Melles-Griot, 25-LHP-213) interferometry at 632.8 nm and calculated using a refractive index of carbon monoxide (CO) of 1.25 (Baratta & Palumbo 1998). After deposition, the ice was irradiated with 5 keV electrons with a current of 15 ± 2 nA for 1 hr. Using the Monte Carlo simulation program CASINO (Drouin et al. 2007), we determined the average electron penetration depth to be 310 ± 80 nm, the fraction of transmitted and backscattered electrons to be 0.03 ± 0.02 and 0.4 ± 0.1 , respectively, and the average kinetic energy of transmitted and backscattered electrons to be 0.03 ± 0.01 keV and 1.3 ± 0.4 keV, respectively. Using these values, we calculated the average dose per irradiated carbon monoxide (CO) molecule to be 2.2 ± 0.2 eV (Förstel et al. 2016).

After the irradiation, the ices were kept at 5.5 K for one hour. FTIR spectra (Nicolet 6700, MCT-A) were recorded during the irradiation in the wavelength range of 6000–600 cm^{-1} with a 4 cm^{-1} resolution. UV-VIS spectra of the ice were collected during the irradiation from 190 to 750 nm with a 2 nm resolution and 60 nm minute⁻¹ scan time (Nicolet Evolution 300). The ice was then heated with a constant rate of

0.5 K minute⁻¹ to 300 K (TPD). During the TPD process we recorded the subliming molecules using a residual gas analyzer (RGA, Extrel, Model 5221) operated with electrons of 70 eV ionization energy and 2 mA emission current. The subliming molecules were also ionized by 10.49 eV photons generated using frequency tripling of the third harmonic of a Nd:YAG (Spectra Physics, PRO-250-30) laser in xenon (Xe) gas (Specialty Gases, 99.999%). The VUV beam had a diameter of 2.0 ± 0.5 mm above the substrate and a flux of $(1.5 \pm 1) \times 10^{10}$ photons per pulse operating at a frequency of 30 Hz. The ionized molecules were then recorded using a reflectron time of flight spectrometer (ReTOF, Jordan TOF products, Inc.). For time-to-mass conversion, we used a calibration curve generated by the measured times of flight of a set of ions with known masses (Jones & Kaiser 2013; Kaiser et al. 2014; Maity et al. 2014).

3. THEORETICAL

In order to be able to interpret our PI-ReTOF-MS spectra in detail, we calculated the ionization energies of several carbon oxides. Ground electronic state structures, term symbols, and ionization energies are compiled in Figure 1. Geometries of various C_nO_m molecules and their cations were optimized using the hybrid density functional B3LYP method (Lee et al. 1988; Becke 1992) with the 6-311G(d) basis set employing the GAUSSIAN 09 program (Frisch et al. 2010). Vibrational frequencies were computed at the same B3LYP/6-311G(d) level of theory. Ionization energies were refined by single-point coupled cluster CCSD(T) calculations (Purvis & Bartlett 1982), with Dunning’s correlation-consistent cc-pVQZ basis set (Dunning 1989), that were performed with the MOLPRO 2010 program (Werner et al. 2012). These calculations are accurate within ± 0.1 eV (Kaiser et al. 2010). Some of the calculated structures are also investigated by Woon & Herbst (2009) and our results agree with their findings.

4. RESULTS

The FTIR spectra before and after the irradiation are shown in Figure 2. The top panel shows the region between 4500 and 600 cm^{-1} . The bottom panels magnify regions labeled “A” and “B.” The observed peaks and their identifications are summarized in Table 1. Before the irradiation, only carbon monoxide (CO) and its isotopomers (^{13}CO , $C^{17}O$) are observed. The main irradiation products are carbon dioxide (CO_2), carbon suboxide (C_3O_2), and pentacarbon dioxide (C_5O_2). The first two account to more than 99% of the observed infrared intensity of the irradiation products. Using previously reported absorption coefficients of these species (Jamieson et al. 2006) we determined the relative abundances of CO_2 : C_3O_2 : C_5O_2 after the irradiation to be $1:0.4 \pm 0.1:0.04 \pm 0.02$. Also, heptacarbon dioxide (C_7O_2), tricarbon (C_3), dicarbon monoxide (C_2O), and tetracarbon monoxide (C_4O) were monitored via their absorptions at 2183 cm^{-1} , 2020 cm^{-1} , 1988 cm^{-1} , and 1919 cm^{-1} , respectively (Table 1).

The development of the UV/VIS absorption spectra during irradiation are visualized in Figure 3. The irradiated ice shows an increase in absorption in the region from 190 to 300 nm as evident from the emergence of a broad absorption feature in the range from 190 to 300 nm. Also seen is a sharper feature at 230 nm with a width at half maximum of 12 nm. The unspecific increase in absorption in the 190–300 nm region with a

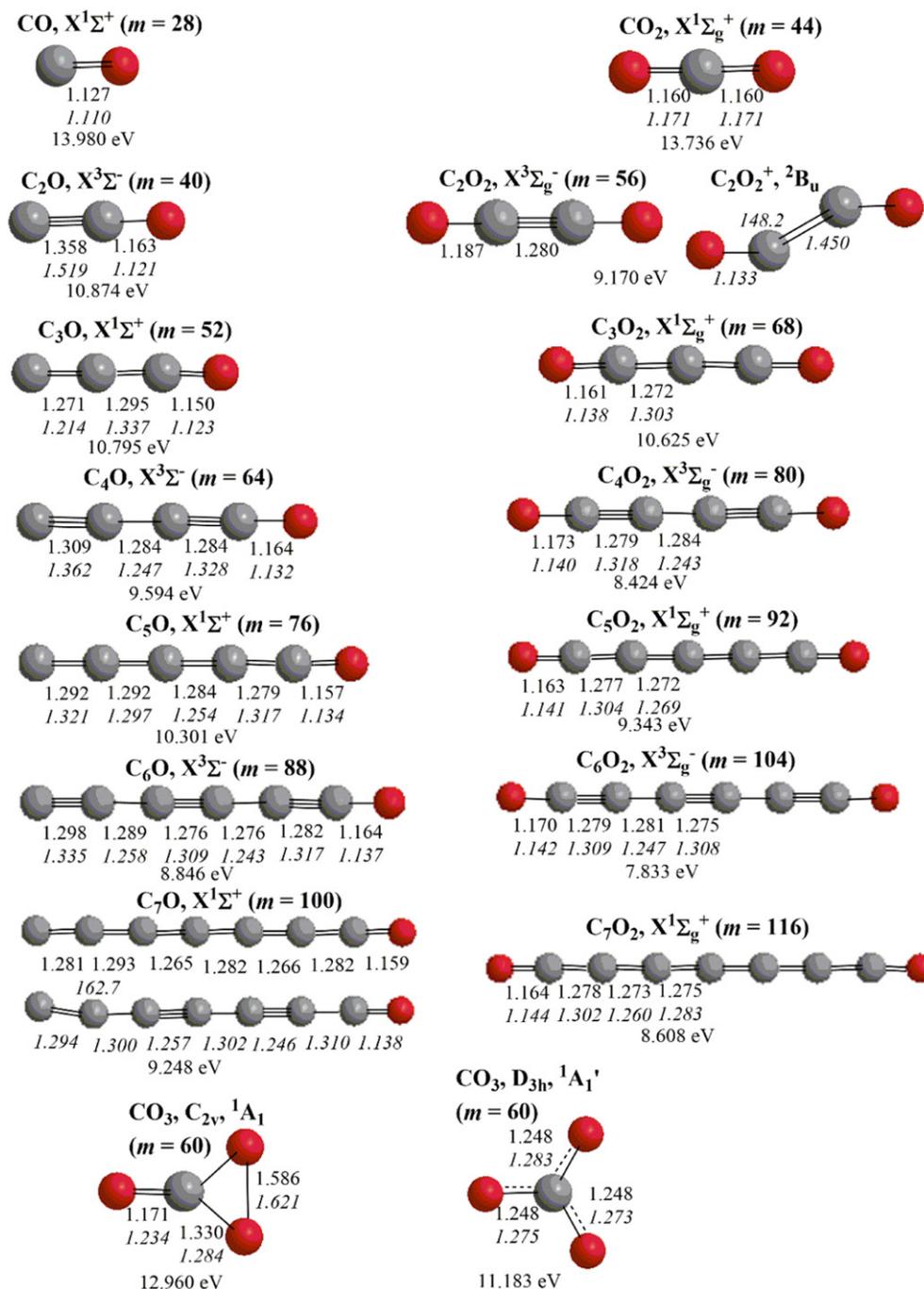


Figure 1. Geometries (bond lengths in Å and bond angles in degrees are given in plain and italic numbers for neutral molecules and cations, respectively), masses, term symbols, and calculated ionization energies of the molecules under discussion.

maximum at 190 nm during irradiation originates from $\pi \rightarrow \pi^*$ transitions of conjugated/cumulenic carbon–carbon double bonds and from $n \rightarrow \pi^*$ transitions of the carbon–oxygen double bonds (Hesse et al. 1987).

During the sublimation of carbon monoxide (35–60 K), RE-TOF-MS observed several species co-subliming from the irradiated sample, including $m/z = 60, 64, 76, 80, 92,$ and 104 . Within the temperature range from 150 K to about 200 K, signal could be monitored at $m/z = 92$ (Figure 4). The QMS showed signal at $m/z = 12, 16, 28, 44,$ and 68 with the traces of the last ions visualized in Figure 4. The species at $m/z = 44$ and 68 sublime around 75 K and 100 K,

respectively. No signal is observed in the QMS at $m/z = 92$ (Figure 4).

5. DISCUSSION

The infrared results confirm previous studies of high energy electron exposure of carbon monoxide ices verifying the formation of three groups (Trottier & Brooks 2004; Jamieson et al. 2006): $C_n\text{O}$ ($n = 2, 4$), $C_n\text{O}_2$ ($n = 1, 3, 5, 7$) and C_3 . To our knowledge, we are presenting the first UV/VIS absorption spectra of irradiated carbon monoxide ices. Gerakines and Moore describe a “dark reddish brown” residue after irradiating

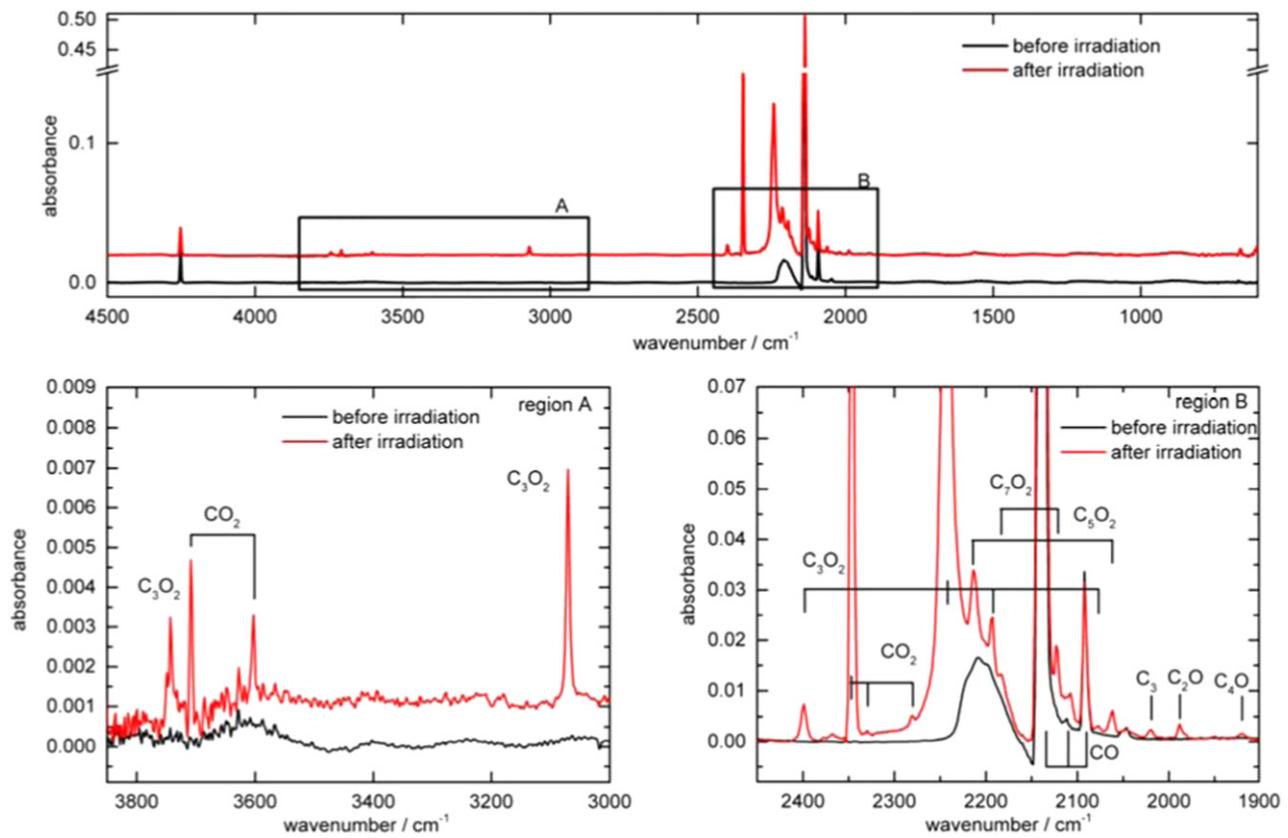


Figure 2. Infrared spectra of the carbon monoxide ice before (black) and after irradiation (red) is shown on top. The bottom panels show details of the spectrum in regions A and B. For better representation, the infrared trace after irradiation was offset by a constant factor of 0.02 in the top panel and by a constant factor of 0.001 in the bottom left. Included in the bottom panels are the assignments of the peaks.

Table 1

Observed Infrared Peaks before and after Irradiation and Their Assignments (Gerakines & Moore 2001; Trottier & Brooks 2004; Jamieson et al. 2006)

	Wavenumber	Species
Before irradiation	4251	CO ($2\nu_1$)
	2208	CO ($\nu_1 + \nu_L$)
	2137	CO (ν_1)
	2111	C ¹⁷ O (ν_1)
	2090	¹³ CO (ν_1) and C ¹⁸ O (ν_1)
New peaks after irradiation	3743	C ₃ O ₂ ($\nu_1 + \nu_4$)
	3708	CO ₂ ($\nu_1 + \nu_3$)
	3602	CO ₂ ($2\nu_2 + \nu_3$)
	3070	C ₃ O ₂ ($\nu_2 + \nu_3$)
	2399	C ₃ O ₂ ($\nu_2 + \nu_4$)
	2347	CO ₂ (ν_3)
	2329	OC ¹⁸ O (ν_3)
	2281	¹³ CO ₂ (ν_3)
	2242	C ₃ O ₂ (ν_3)
	2213	C ₅ O ₂ (ν_4)
	2192	C ¹³ C ₂ O ₂ (ν_1) and/or C ₃ O ₂ (ν_1)
	2183	C ₇ O ₂ (ν_5)
	2121	C ₇ O ₂ (ν_6) and / or C ₄ O ₂ (ν_2)
	2077	C ₃ O ₂ ($\nu_2 + \nu_6$)
	2062	C ₅ O ₂ (ν_5)
	2020	C ₃ (ν_3)
	1988	C ₂ O
	1919	C ₄ O
1564	C ₃ O ₂ (ν_4)	
660	CO ₂ (ν_2)	

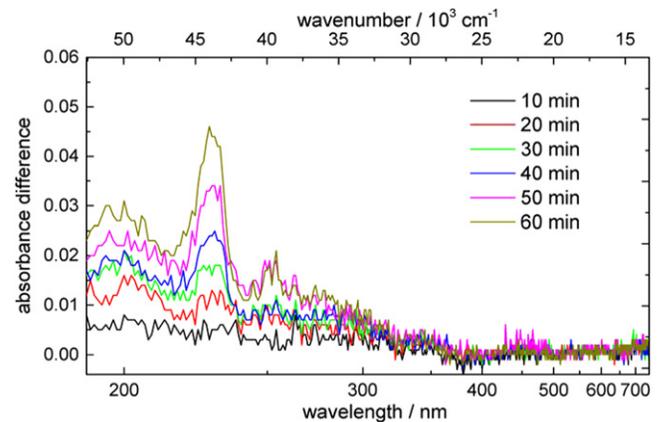


Figure 3. Time dependent difference of the UV-VIS absorption spectra during irradiation.

carbon monoxide with 0.8 MeV protons (Gerakines & Moore 2001). However, we did not observe any absorption above 300 nm; likewise, no residue was formed in our experiments. The average dose per irradiated molecule are comparable in both experiments with 2.2 ± 0.2 eV (present study) and 1.0 ± 0.1 eV per molecule (Gerakines and Moore). However, the actual number of processed molecules is roughly a factor of 100 lower in our experiment considering the distinct penetration depths of the charged particles likely leading to the formation of a refractory residue in the proton irradiation experiments. Also, carbon suboxide and its polymers depict absorptions in the 190–300 nm region and could contribute to

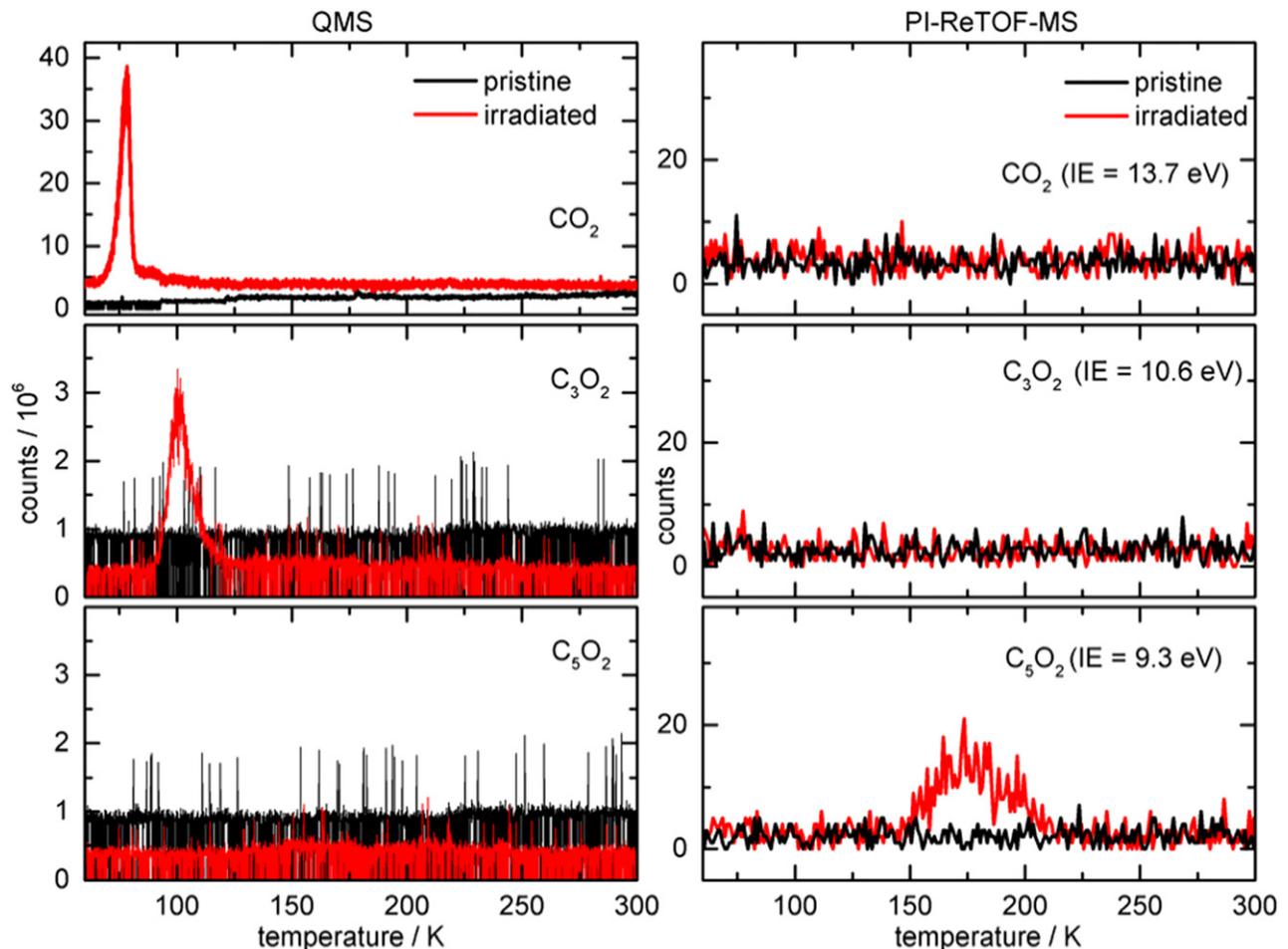


Figure 4. Comparison of selected TPD profiles recorded with the two complimentary techniques of electron ionization quadrupole mass analysis (QMS, left) and the PI-ReTOF-MS (right). While the QMS analyzer can detect CO, CO₂, and C₃O₂, due to its high ionization energy, with the PI-ReTOF-MS we can detect C₅O₂ at very low concentrations due to the high detection efficiency.

the UV–VIS features observed in the present study (Smith et al. 1963). Here, the pronounced peak with a maximum at 230 nm may originate from carbon suboxide monomers; the broad feature in the 190–300 nm range can originate from $\pi \rightarrow \pi^*$ transitions of carbon–carbon double bonds and from $n \rightarrow \pi^*$ transitions of carbon oxide double bonds of higher molecular weight carbon oxides (Hesse et al. 1987). This is in agreement with the FTIR observation of OC_{*n*} and OC_{*n*}O species, which all carry cumulenlic carbon–carbon double bonds as well as the carbonyl functional group.

Let us now shift to the PI-ReTOF-MS data. The observed signal in the unirradiated sample (blank experiment) depicts a surprisingly large number of species. The observed masses match those of (CO)_{*n*} clusters with $n = 1–7$. The ionization energy of carbon monoxide is 14.0 eV (Lias 2016), and thus is significantly higher than the energy of the ionizing photons (10.49 eV). Unfortunately, literature data on ionization energies of carbon monoxide clusters are unavailable. However, a shift in ionization energy of more than 3.5 eV due to final state polarization effects in the carbon monoxide dimer or trimer or even the hexamer would be exceptionally large. We therefore suggest that it is more likely that the ionization of the carbon monoxide clusters is possible due to multiphoton absorption processes, which could be resonantly enhanced in the cluster. One factor supporting this theory is that we observe (CO)C₂⁺.

In order to break two carbon–oxygen triple bonds (11.2 eV), we need at least three photons (Tilford & Simmons 1972). Another possible formation route of some of the observed ionic species is a resonant excitation of carbon monoxide, and subsequent ionization by the absorption of a second photon followed by gas-phase ion–molecule reactions. The difference here to the first scenario is that the observed clusters form in the gas phase after carbon monoxide is ionized as opposed to already existing gas-phase clusters being directly ionized. With an energy of 10.45 eV, the $X^1\Sigma^+(n=0) \rightarrow A^1\Pi(n=16)$ transition in the carbon monoxide molecule is very close to the photon energy of 10.49 eV (Tilford & Simmons 1972) and could allow for such a resonantly enhanced two photon ionization process. Note that the pristine sample shows no signal at temperatures above 60 K, while the irradiated sample shows a clear signal at $m/z = 92$ (Figure 4). This signal can be attributed to subliming C₅O₂. This molecule holds an ionization energy of 9.4 eV, which is well below the energy of our photons (10.49 eV). Carbon dioxide (CO₂) and carbon suboxide (C₃O₂) have ionization energies of 13.7 eV and 10.6 eV, respectively, and hence cannot be ionized and are therefore not observable via PI-ReTOF-MS. However, both are detected via QMS with CO₂ and C₃O₂ subliming around 75 K and in the range from 90 to 115 K, respectively. These results are in agreement with earlier observations (Gerakines & Moore 2001; Jamieson et al. 2006).

The increase in desorption temperature from 75 K via 100 K to 175 K for CO₂, C₃O₂, and C₅O₂ is in line with an enhanced molecular weight of the products.

Since we have established that pentacarbon dioxide (C₅O₂) forms in carbon monoxide irradiated ices and also sublimates into the gas phase at temperatures of 150–200 K, let us summarize possible formation pathways. The formation pathway toward C₅O₂ in irradiated carbon monoxide ices was elucidated in Trottier & Brooks (2004) and Jamieson et al. (2006). Both articles suggest that the reaction C₄O + CO → C₅O₂ is the most likely formation pathway of C₅O₂. Jamieson et al. extracted a second pathway via C₄O₂ + C → C₅O₂. Trottier et al. speculated on a reaction via C₃O + C₂O → C₅O₂ but pointed out that it is less likely than the C₄O + CO → C₅O₂ pathway due to the lower concentration of C₂O compared to CO.

6. CONCLUSION

Low temperature carbon monoxide ice was irradiated and several new molecules formed that can be classified into three main groups: oxygen-terminated carbon clusters, C_nO (*n* = 2, 4), dioxygen terminated carbon clusters, C_nO₂ (*n* = 1, 3, 5, 7), and carbon clusters, (C₃). Upon heating the sample and after the host matrix of carbon monoxide sublimed, only species of the second group with *n* = 1, 3, and 5 survive sublimation into the gas phase. These molecules were detected with two complimentary techniques upon their sublimation (QMS-EI and PI-ReTOF-MS) to determine their sublimation temperatures. The key novel finding of this work is the very first observation of gas phase C₅O₂ and the determination of its sublimation profile. This was made possible by a strong enhancement in the detection efficiency exploiting the PI-ReTOF-MS approach.

The central astrophysical relevance of our findings lies in the use of C₅O₂ as a tracer on the nascent composition and temperature history of interstellar grains and comets. In earlier experiments with polar CO containing ices, no C₅O₂ was synthesized (Bennett et al. 2011). Also, irradiation of CO₂ ices yields no C₅O₂ (Bennett et al. 2009). This means that an observation of C₅O₂ toward distinct interstellar sources indicates that a low temperature (<30 K) carbon monoxide rich ice was present in these environments. It is also possible that a separation of H₂O and CO occurs in short-periodic comets' fractionated sublimation and that C₅O₂ can form when those comets are under the influence of cosmic rays. Apart from the ice composition, we can also infer the temperature history of interstellar environments. If neither CO nor C₃O₂ is observed in an interstellar environment, but C₅O₂ can be detected, then we have to conclude that a once carbon monoxide rich object must have been warmed up beyond 125 K. It can also be concluded that a detection of C₅O₂ in the gas phase points toward a once carbon monoxide rich object approaching a Sun and/or a central star. In the case of our solar system, these temperatures can be reached at distances in the range from 2 to 4 au. With the availability of *Rosetta* and the *James Webb Space Telescope*, molecules like C₅O₂ can prove to be very precise tools to elucidate the history of our solar system and the evolution of our universe.

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