

Short Communication

# Mechanistic studies on the decomposition of carbon suboxide in a cometary ice analog

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Received 15 March 2008; received in revised form 2 May 2008; accepted 5 May 2008

Available online 17 May 2008

## Abstract

A cometary ice analog sample consisting primarily of carbon suboxide ice ( $C_3O_2$ ) was produced from the irradiation of its precursor, carbon monoxide. This carbon suboxide sample was subjected to irradiation with energetic electrons at 10 K to simulate the interaction of carbon suboxide-rich cometary analog ices with ionizing radiation. The destruction of carbon suboxide as well as the production of the primary degradation products, dicarbon monoxide ( $C_2O$ ), and carbon monoxide (CO), were monitored quantitatively by infrared spectroscopy in situ; the gas phase was simultaneously sampled via quadrupole mass spectrometry. A kinetic model was produced to help explain the decomposition kinetics of carbon suboxide in cometary ices and to infer the underlying reaction mechanisms. Published by Elsevier Ltd.

*Keywords:* Radiation chemistry; Comets; Composition; Spectroscopy; Ices; Kinetics

## 1. Introduction

Carbon suboxide ( $C_3O_2$ ) is one of the most stable polycarbon oxides of the series  $C_nO_2$  where typically, odd numbered  $n$  values within the series are found to be more stable (Wang et al., 2002). It is readily formed when carbon monoxide is subjected to irradiation by UV photolysis (Gerakines et al., 1996; Gerakines and Moore, 2001; Loeffler et al., 2005), energetic ions (Baird, 1972; Haring et al., 1984; Chrisey et al., 1986; Gerakines and Moore, 2001; Trottier and Brooks, 2004; Loeffler et al., 2005), and keV electrons (Jamieson et al., 2006). Upon further radiation, carbon suboxide is found to polymerize (Smith et al., 1966; Blake and Hodgson, 1966; Bruns et al., 1967; Baird, 1972; Barkalov et al., 1980; Gerakines and Moore, 2001); this process may also be initiated thermally by warming carbon suboxide (Smith et al., 1963; Blake et al., 1964), producing a pink/reddish-brown solid.

These characteristics, as well its low vapor pressure (Gerakines and Moore, 2001), make carbon suboxide and its polymers good candidates as constituents of the nucleus

of comet Halley as proposed by Huntress et al. (1991), which is found to have a very low albedo ( $<4\%$ ) consistent with the proposed polymers (Keller et al., 1986). They proposed that a production rate of only 0.03–0.04 times that of water in the coma would be required to explain the Giotto spacecraft neutral-gas mass spectrometer and Earth-orbit measurements of carbon monoxide and carbon atoms detected (Krankowsky et al., 1986; Woods et al., 1987). Eberhardt (1999) suggested that formaldehyde ( $H_2CO$ ) could serve as a possible parent molecule able to explain extended CO sources in comets. However, DiSanti et al. (2001) determined that the abundance of formaldehyde was found to be at least an order of magnitude too low to account for the extended carbon monoxide source from comet Hale-Bopp and suggested carbon suboxide as an alternative. Fomenkova (1997, 1999) and Fomenkova et al. (1994) analyzed mass spectra of dust particles from comet Halley and have shown that up to 5% of the cometary nuclei could be made up of carbon suboxide polymers. However, there has still yet to be a direct detection of carbon suboxide in comets via either infrared (e.g., Brooke et al., 2003) or radio wave spectroscopy (e.g., Crovisier et al., 2004). Carbon suboxide carries several strong infrared features (Smith and Leroi, 1966; Gerakines

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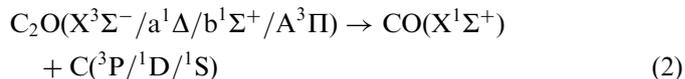
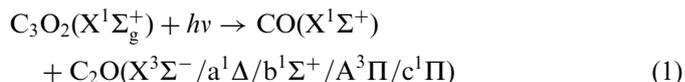
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and Moore, 2001); however, attempts to confirm its presence from its most intense band ( $\nu_3$ , which in the gas phase occurs at  $4.43 \mu\text{m}$ , or  $2258 \text{ cm}^{-1}$ ) within the coma of comet Halley using the infrared spectrometer onboard the VEGA 1 probe were discouraging (Crovisier et al., 1991). Allen (1991) suggested that the signal may be masked by the much stronger signal from carbon dioxide and is weak because of its comparatively wide distribution area within the coma. Regarding the detection of carbon suboxide by radio wave spectroscopy, it is important to note it is a common misconception is that this molecule is linear; in which case it would possess no permanent dipole moment and this in turn would cause the transition probability of any rovibrational excitation to be near zero. In fact, carbon suboxide has a W-shaped  $C_{2v}$  structure, and features a very low lying bending mode to linearity of only  $18.2 \text{ cm}^{-1}$  (Karyakin et al., 1982), which complicates experimental determination of its geometry (Winnewisser, 1985). It is currently described as a quasi-linear molecule (Winnewisser et al., 2006), and in fact has a rich rovibrational spectrum (Burenin et al., 1979; Karyakin et al., 1982) which could be used for its detection by radio wave spectroscopy.

From these considerations, it is clear that it is important to understand from a mechanistic viewpoint, the destruction of carbon suboxide when it is subjected to irradiation with ionizing particles in our Solar System. There has been a lot of research done in attempts to determine the decomposition products of carbon suboxide and attempts to characterize the nature of the polymers formed. We would now like to give a brief compilation of some these findings. To help clarify these results, Table 1 shows a summary of the minimum energies (or maximum wavelengths) for which each dissociation pathway should be accessible using values obtained from standard references and the latest experimental results.

Bayes (1961, 1962, 1963) carried out a series of experiments to determine the primary products formed under photolysis of carbon suboxide (in the presence of ethylene, and later also oxygen) by subjecting a gaseous sample to wavelengths greater than  $220 \text{ nm}$ . They found evidence for carbon monoxide, the dicarbon monoxide

radical ( $C_2O$ ; also referred to as ketenylidene) and carbon atoms produced via the following pathway:



Although all the possible electronic excited states are given here, from Table 1 we can determine that only the three lowest energy states of dicarbon monoxide are accessible at these wavelengths. They found evidence for two different pathways based on the interactions the products with ethylene in the presence of ‘triplet scavengers’. At wavelengths above  $302 \text{ nm}$ , it was determined that only the ground state ( $X^3\Sigma^-$ ) dicarbon monoxide radical was produced, whereas at wavelengths under  $254 \text{ nm}$ , another channel becomes accessible, generating the radical most probably in the ( $a^1\Delta$ ) electronically excited state. Additional photolysis experiments carried out at  $248 \text{ nm}$  (Becker et al., 1992) and  $266 \text{ nm}$  (Pitts et al., 1981) were shown to give identical products, indicating the lack of involvement of the ( $b^1\Sigma^+$ ) excited state at  $248 \text{ nm}$ , although the involvement of an entrance barrier for this pathway cannot be ruled out. A number of investigations have been carried out to determine the branching ratios of the electronic states of the dicarbon monoxide radical based on the distributions of the remaining energy into the vibrational, rotational, and translational energy of the carbon monoxide fragments (McFarlane et al., 1986; Weiner and Rosenfeld, 1986; Anderson and Rosenfeld, 1991). These models can be based on either a statistical or impulsive model; in the latter, the distribution of energy into these states is dependant upon the lifetime of an excited carbon suboxide intermediate. Anderson and Rosenfeld (1991) concluded that the primary products at  $248 \text{ nm}$  involve the ground state dicarbon monoxide radical, whereas at the higher energy of  $193 \text{ nm}$ , the primary product is the ( $a^1\Delta$ ) electronically excited state, but acknowledge that neither

Table 1  
Required energy for pathways (1–3) depending on the electronic state of the product species (based on information from Chase, 1998; Choi et al., 1998)

Reactant	Products	Energy ( $\text{kJ mol}^{-1}$ )	Energy (eV)	Wavelength (nm)
$C_3O_2(X^1\Sigma_g^+)$	$2CO(X^1\Sigma^+) + C(^3P)$	589 (577 <sup>a,b</sup> )	6.11 (5.98)	203 (207)
	$2CO(X^1\Sigma^+) + C(^1D)$	711 (700 <sup>a</sup> )	7.37 (7.25)	168 (171)
	$2CO(X^1\Sigma^+) + C(^1S)$	848 (837 <sup>a</sup> )	8.79 (8.67)	141 (143)
	$CO(X^1\Sigma^+) + C_2O(X^3\Sigma^-)$	373 (360 <sup>b</sup> )	3.86 (3.73)	321 (332)
	$CO(X^1\Sigma^+) + C_2O(a^1\Delta)$	436 (444 <sup>b</sup> )	4.52 (4.60)	274 (270)
	$CO(X^1\Sigma^+) + C_2O(b^1\Sigma^+)$	472 (510 <sup>b</sup> )	4.89 (5.29)	254 (234)
	$CO(X^1\Sigma^+) + C_2O(A^3\Pi)$	512 (498 <sup>b</sup> )	5.31 (5.16)	233 (240)
	$CO(X^1\Sigma^+) + C_2O(c^1\Pi)$	641	6.64	187

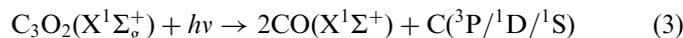
For ease of comparison to different experimental information, the energies are given in  $\text{kJ mol}^{-1}$ , eV, and the equivalent photon energy in nm.

<sup>a</sup>Experimentally determined values from Okabe (1978).

<sup>b</sup>Previous estimates based on experimental and theoretical evidence from Anderson and Rosenfeld (1991).

model could adequately explain the observed energy partitions.

When using higher energy photons (below 207 nm) to dissociate carbon suboxide, another dissociation channel becomes accessible:



Indeed, when Braun et al. (1969) exposed carbon suboxide to photons of the wavelength range 140–170 nm, they reported the production of atomic carbon in the ground state ( $^3\text{P}$ ) and first two excited states ( $^1\text{D}$  and  $^1\text{S}$ ). The percentage of carbon atoms produced depends strongly upon wavelength; at a wavelength of 193 nm, only 6% of ground state carbon ( $^3\text{P}$ ) was generated via reaction (3) (McFarlane et al., 1986), whereas using the higher photon energy of 158 nm gives almost exclusively carbon atoms (<2% dicarbon monoxide produced) being produced predominantly in the ground state,  $^3\text{P}$ (97%) with a small amount formed in the first excited state,  $^1\text{D}$ (3%) (Strauss et al., 1991).

More recently, Gerakines and Moore (2001) have carried out an analysis of the formation of carbon suboxide in carbon monoxide ices and destruction of carbon suboxide ices after subjecting them to ion irradiation (0.8 MeV protons) as well as broadband UV photolysis (110–250 nm). In the energetic processing of carbon suboxide, they used infrared spectroscopy to identify carbon monoxide and dicarbon monoxide, as well as other products such as the cyclic form of carbon trioxide ( $\text{c-CO}_3$ ;  $\text{C}_{2v}$ ) and evidence of  $\text{C}_3\text{O}_2$  polymers. It is anticipated that the dicarbon monoxide radical may be easier to detect in the solid state as the surrounding matrix is able to stabilize highly excited molecules through phonon interactions.

From these previous studies, we can see that the dissociation products depend strongly on the radiation source and energy. Here, we expand these investigations and carry out electron irradiation experiments on low temperature carbon suboxide ice. Several experiments have been carried out irradiating carbon suboxide with ions, but to the best of our knowledge, they have always used energies in the keV energy range (<1 MeV). The electrons used in our experiment, however, can also simulate the irradiation effects resulting from MeV cosmic ray ion bombardment, similar to those that affect extraterrestrial ices. This is justified more thoroughly in some of our previous works (e.g., Bennett et al., 2005; Jamieson et al., 2006). We will quantify the development of the dissociation products which will allow us to kinetically interpret the carbon suboxide destruction. Our results should aid in a more complete and quantitative understanding of the radiation-induced dissociation of carbon suboxide as it occurs on comets. This should give clues to the mechanisms of polymerization and will help reveal the potential for carbon suboxide to act as an extended source of carbon monoxide and carbon atoms in the coma of comet Halley.

## 2. Experimental

Details of our experimental set-up can be found elsewhere (Bennett et al., 2004; Jamieson et al., 2006). In order to prepare a carbon suboxide sample, we irradiated a carbon monoxide ice at 10 K with 5 keV electrons (similarly described in Jamieson et al., 2006) then annealed the sample to sublime the less volatile species. The procedure is described as follows and the purity of the sample will be justified in Section 3. Carbon monoxide gas was condensed for 8 min at a background pressure of  $1.0 \times 10^{-7}$  Torr in the main chamber onto a highly polished silver mirror surface at 10 K. The unirradiated spectrum was recorded using a Nicolet 510 DX Fourier transform infrared spectrometer (FTIR) operating in absorption–reflection–absorption mode with a reflection angle of  $75^\circ$  from the normal relative to the mirror surface. Throughout the experiment, infrared spectra of the ice were recorded online and in situ at an integrated time of 2.5 min and at a resolution of  $2 \text{ cm}^{-1}$  over the spectral range of  $6000\text{--}500 \text{ cm}^{-1}$ . Details of how the column densities can be derived can be found in Bennett et al. (2004). Using an integrated band strength of  $1.1 \times 10^{-17} \text{ cm molecule}^{-1}$  (Jiang et al., 1975), gives a column density of carbon monoxide prior to irradiation as  $4.4 \times 10^{17} \text{ molecules cm}^{-2}$ . Using the column density, the molecular weight,  $28 \text{ g mol}^{-1}$ , and the density,  $1.0288 \text{ g cm}^{-3}$  (Jiang et al., 1975), the thickness for the carbon monoxide ice was calculated to be  $200 \pm 30 \text{ nm}$ .

The ice was then irradiated isothermally for 1 h with 5 keV electrons at a pressure of  $10^{-10}$  Torr in our effort to synthesize carbon suboxide starting material. The electron beam was operated at a nominal current of 100 nA with an extraction efficiency of 78.8% and scanned over the sample area ( $3.0 \pm 0.4 \text{ cm}^2$ ) to avoid heating the ice. The 1 h of irradiation exposed the target to  $1.8 \times 10^{15}$  electrons; higher beam currents were avoided to eliminate overlapping electron trajectories and heating the ice surface. Afterwards, the sample was warmed at a rate of  $0.5 \text{ K min}^{-1}$  to a temperature of 100 K. At this temperature, nearly all of the products from the carbon monoxide irradiation (e.g.,  $\text{CO}_2$ ,  $\text{C}_n\text{O}$ ,  $n = 1\text{--}5$ ,  $\text{C}_3$ ,  $\text{C}_4\text{O}_2$ ; see Jamieson et al., 2006) had either sublimed into the gas phase or been destroyed by reactions within the ice, leaving carbon suboxide as the primary component left in the solid sample. The ice was then immediately cooled back down to 10 K and then the sample was allowed to thermally equilibrate for another 15 min. The carbon suboxide sample was then irradiated for an hour using the same conditions as previously used to irradiate the original carbon monoxide sample (5 keV electron energy at 100 nA current) while the sample was continuously monitored by the infrared spectrometer. After irradiation, the sample was again left at 10 K for 1 h before being warmed at a rate of  $0.5 \text{ K min}^{-1}$ . During this stage, the gas phase was monitored utilizing a quadrupole mass spectrometer (Balzer QMG 420) operating in the residual gas analyzer mode.

### 3. Results

The analyses of the ice samples were carried out using the FTIR spectrometer. By comparing the peak positions in the spectra with published experimental and theoretical studies, the carrier to each absorption feature was assigned. A discussion of the features present in the pure carbon monoxide ice sample and the bands resulting from its irradiation (Fig. 1a) will not be made since this is thoroughly discussed in a previous paper (Jamieson et al., 2006). Instead we will limit our discussion to assignments in our carbon suboxide sample at 10 K before and after its irradiation (Fig. 1b and c). In addition, a brief discussion of the species observed in the gas phase by the quadrupole mass spectrometry will also be presented.

#### 3.1. C<sub>3</sub>O<sub>2</sub> sample

Briefly recapping, a pure carbon monoxide sample was irradiated for 1 h and then annealed to 100 K. At this

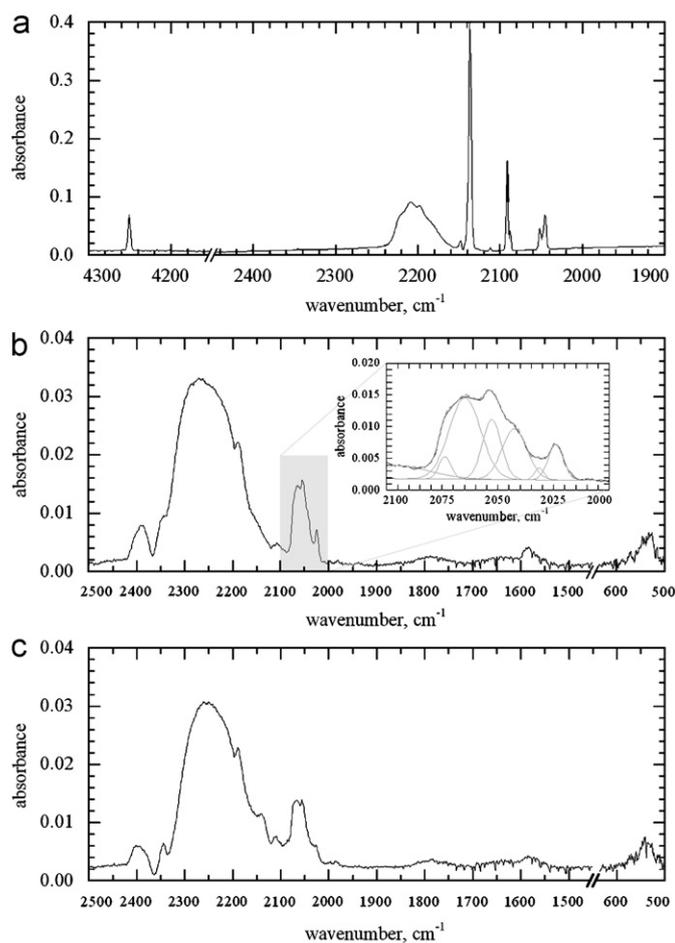


Fig. 1. Infrared spectrum of (a) the carbon monoxide ice at 10 K after 1 h of irradiation with 5 keV electrons at 100 nA, (b) the carbon suboxide ice prior to irradiation after the original irradiated carbon monoxide ice was heated to 100 K and re-cooled to 10 K after being equilibrated for 15 min, and (c) the carbon suboxide ice after a further 1 h of irradiation by 5 keV electrons at 100 nA. The inset in (b) shows the deconvolution of the peaks within the range of 2000–2100 cm<sup>-1</sup>.

temperature, the majority of the products resulting from the irradiation had either sublimed or been destroyed through reaction leaving carbon suboxide as the primary component in the sample. The ice was then cooled down to 10 K. An infrared analysis of this ice reveals several absorptions, most of which are assigned to carbon suboxide. Their assignments are listed and compared to those from previous works in Table 2. The column density of carbon suboxide was determined by integration of the band at 2390 cm<sup>-1</sup> ( $\nu_2 + \nu_4$ ); using an experimentally determined band strength of  $8.0 \times 10^{-18}$  cm molecule<sup>-1</sup> (Gerakines and Moore, 2001), the column density was calculated to be  $7.5 \times 10^{15}$  molecules cm<sup>-2</sup>. At this point, we shall address the purity of the carbon suboxide sample that we have synthesized in the irradiation experiment. An infrared analysis of the pre-irradiated carbon suboxide ice reveals several bands (Fig. 1b). All but a few of the observed bands belong to the carbon suboxide molecule; other than remaining carbon monoxide at 2137 cm<sup>-1</sup>, the only obvious bands that may constitute impurity in our sample come in the 2100–2200 cm<sup>-1</sup> region. In order to attempt to identify and quantify these impurities, this region was deconvoluted using the least number of Gaussians possible to achieve an acceptable fit. The results of this procedure are shown in the inset of Fig. 1b, the region was found to contain at least six underlying absorption features centered at 2024, 2031, 2042, 2053, 2065, and 2074 cm<sup>-1</sup>; the last of which has previously been assigned to the  $\nu_4 + \nu_6$  combination band of the carbon suboxide molecule based on the correlated disappearance of this band with the other carbon suboxide bands during the warm-up phase of experiments on the irradiation of carbon monoxide (Jamieson et al., 2006). The band at 2024 cm<sup>-1</sup> is identified as an absorption from tricarbon (C<sub>3</sub>) based on prior irradiation experiments on pure carbon monoxide where it was found to absorb around 2028 cm<sup>-1</sup> (e.g., Gerakines et al., 1996). Using an integrated band strength of  $1.3 \times 10^{-16}$  cm molecule<sup>-1</sup> (Jamieson et al., 2006), the calculated column density is  $1.1 \times 10^{14}$  molecules cm<sup>-2</sup>.

Table 2

Infrared band features observed for carbon suboxide in the prepared sample at 10 K before irradiation

Assignment	Band position (cm <sup>-1</sup> )		
	This work	Smith and Leroi (1966)	Gerakines and Moore (2001)
$\nu_1 + \nu_4$	3740	3766	3744
$\nu_2 + \nu_4$	2390	2400	2396
$\nu_3$	2269	2320–2199	2200, 2177
$\nu_1$	2188	2184	
$\nu_1 - \nu_L$	2109	2125–2112	2109
$\nu_4 + \nu_6$	2071	2076 <sup>a</sup>	–
$\nu_4$	1583	1589–1576	1581
$\nu_5$	572	577–570.5	–
$\nu_6$	544, 533	545–514.5	540

<sup>a</sup>Observed in the gas phase.

The band at  $2053\text{ cm}^{-1}$  is identified as the  $\nu_3$  vibration of  $\text{C}_3\text{O}_2$  previously identified at  $2059\text{ cm}^{-1}$  (Maier et al., 1988). Using a calculated band strength of  $7.4 \times 10^{-17}\text{ cm molecule}^{-1}$ , the calculated column density for this species is  $4.0 \times 10^{14}\text{ molecules cm}^{-2}$  (Jamieson et al., 2006). The carrier of the  $2065\text{ cm}^{-1}$  absorption band is tentatively assigned to the  $\text{C}_6\text{O}/\text{C}_7\text{O}$  species in accordance with calculated frequencies for these species (Moazzen-Ahmadi and Zerbetto, 1995); using a calculated band strength of  $4.3 \times 10^{-17}\text{ cm molecule}^{-1}$  we estimate the upper limit of the column density to  $1.6 \times 10^{15}\text{ molecules cm}^{-2}$  (Jamieson et al., 2006). Both bands at  $2031$  and  $2042\text{ cm}^{-1}$  remain undetermined at this time. Possible carriers of the bands include Ag–CO complexes and carbon trioxide ( $\text{CO}_3$ ;  $\text{C}_{2v}$ ), respectively (Wang, 1990; Bennett et al., 2004). Tentatively assigning these bands to these carriers and using band strengths of  $1.1 \times 10^{-17}$  and  $1.3 \times 10^{-16}\text{ cm molecule}^{-1}$ , we determine upper limits for their column densities of  $2.7 \times 10^{14}$  and  $3.8 \times 10^{14}\text{ molecules cm}^{-2}$ , respectively (Jiang et al., 1975; Bennett et al., 2004). Any other unidentified species are likely to be minor components which may include some amount of carbon suboxide polymer already produced in the initial irradiation on carbon monoxide. Considering the remaining carbon monoxide, we find the column density to be  $3.2 \times 10^{15}\text{ molecules cm}^{-2}$ . A quick ratio of the abundance of carbon suboxide relative to the identified impurities shows that the composition is at least 56% carbon suboxide.

### 3.2. Products formed after irradiation

Due to the complexity of the region upon irradiation, we have focused primarily on the generation of carbon monoxide and dicarbon monoxide. Here, the fundamental band from carbon monoxide was identified at  $2137\text{ cm}^{-1}$  in accordance with previous studies (e.g., Gerakines and Moore, 2001). Dicarbon monoxide was identified through its  $\nu_1$  absorption at  $1987\text{ cm}^{-1}$  in good agreement with previous matrix isolation experiments where it was found to absorb at  $1987\text{ cm}^{-1}$  in a molecular nitrogen matrix and  $1978\text{ cm}^{-1}$  in an argon matrix (Jacox et al., 1965), as well as previous experiments on the irradiation of pure carbon suboxide where it was found to absorb at  $1994\text{ cm}^{-1}$  (Gerakines and Moore, 2001). In contrast to the experiments carried out by Gerakines and Moore (2001), we did not find evidence for the further production of cyclic carbon trioxide which was present in our sample as an impurity; however, detectable amounts of carbon dioxide were produced, but we could not monitor its production via its strongest band due to overlapping absorptions from carbon suboxide. An upper limit of  $9.5 \times 10^{13}\text{ molecules cm}^{-2}$  was calculated from the  $\nu_2$  bending mode of  $\text{CO}_2$  which occurs at  $668\text{ cm}^{-1}$  using an experimentally determined band strength of  $1.1 \times 10^{-17}\text{ cm molecule}^{-1}$  (Gerakines et al., 1995). It is likely that the cyclic carbon trioxide observed by Gerakines and Moore (2001) is a product from the irradiation of the observed carbon dioxide (see Bennett et al., 2004), which is in turn produced

from the carbon monoxide (see Jamieson et al., 2006) and is therefore not directly associated with the irradiation of carbon suboxide. Note that the column densities of the impurities mentioned in Section 3.1 were all found to decrease slightly; however, the amount of these species destroyed is not thought to have a large influence on the results reported. Moreover, these species are therefore not expected as initially produced products from the degradation of carbon suboxide.

### 3.3. Isolation period and warm-up

The column density of carbon suboxide was found to remain constant throughout the isolation period (within error limits), and up until a temperature of  $97\text{ K}$ , where it quickly began to sublime as noted by both decrease in the FTIR peaks and the QMS signal (see Fig. 2), whereby signals corresponding to carbon suboxide ( $m/z = 68$ ;  $\text{C}_3\text{O}_2^+$ ) and the fragmentation product dicarbon monoxide ( $m/z = 40$ ;  $\text{C}_2\text{O}^+$ ) could be seen up to  $141\text{ K}$ . Note that the FTIR showed that there were in fact no detectable traces of carbon suboxide after  $110\text{ K}$ , this is consistent with the sharp rise in vapor pressure measured for this species around this temperature (Gerakines and Moore, 2001). The dicarbon monoxide radical itself also remained at a constant column density (again, within the error limits) during the isolation period. Monitoring of this species via FTIR showed that the column density steadily decreased between a temperature of  $60$ – $110\text{ K}$ ; this is expected to be from its decomposition/reaction within the ice as no signal for this species ( $m/z = 40$ ;  $\text{C}_2\text{O}^+$ ), nor of the expected fragmentation products ( $m/z = 12$ ;  $\text{C}^+$ ,  $m/z = 28$ ;  $\text{CO}^+$ ) could be observed in the gas phase at these times. Carbon monoxide was also found to be steady during the isolation

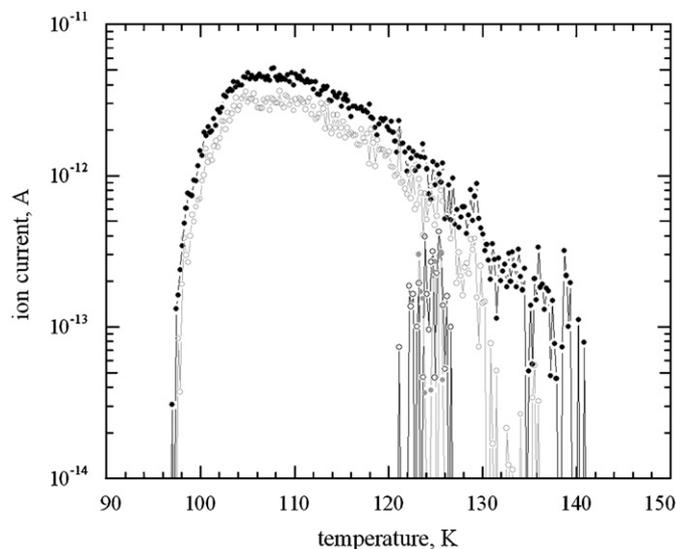


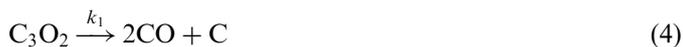
Fig. 2. Temporal development of the ion current versus the corresponding temperature for  $m/z = 68$  ( $\text{C}_3\text{O}_2^+$ , black line, filled circles),  $m/z = 40$  ( $\text{C}_2\text{O}^+$ , gray line, open circles),  $m/z = 88$  ( $\text{C}_6\text{O}^+$ , gray line, filled circles), and  $m/z = 60$  ( $\text{C}_5^+$ , black line, open circles).

period. As the warm-up period begins, as verified through both FTIR and QMS, it sublimates in two episodes; a minor amount (<10%) is released from 13 to 25 K, and then the remaining carbon monoxide appears to come off between 32 and 64 K. Although no signal could be determined for the sublimation of the carbon suboxide polymers, we were also able to detect two additional signals which have been assigned to the sublimation of the C<sub>6</sub>O species occurring between 121 and 127 K (see Fig. 2;  $m/z = 60$ ; C<sub>5</sub><sup>+</sup>,  $m/z = 88$ ; C<sub>6</sub>O<sup>+</sup>). Support that the signal at  $m/z = 60$  is a daughter fragment of a larger molecule comes from the simultaneous increase in the signal at  $m/z = 28$  (CO<sup>+</sup>) at this time, indicating loss of the carbon monoxide fragment is also likely. Although other species with similar  $m/z$  ratios could account for these peaks (e.g., CO<sub>3</sub><sup>+</sup> and C<sub>2</sub>O<sub>4</sub><sup>+</sup>), we see a decrease in the FTIR signal from the peak at 2065 cm<sup>-1</sup> previously assigned to the C<sub>6</sub>O species at exactly the same time. After carbon suboxide has sublimed, the only remaining feature in the infrared are two bands at 2180 and 2056 cm<sup>-1</sup>, which are expected to be from carbon suboxide polymers similar to those reported by Gerakines and Moore (2001). These bands slowly disappear over the temperature range 130–201 K, yet we were unable to detect any signal in the QMS associated with the polymer species.

## 4. Discussion

### 4.1. Reaction model

In order to effectively model, the degradation of carbon suboxide, we considered three primary reaction channels in order to determine their relative importance:



We included two additional pathways to account for alternative loss processes of the carbon suboxide and dicarbon monoxide species. A further pathway for carbon monoxide was not needed as it is a fairly inert species once generated:



Thus, reactions (7) and (8) were included to account for any other possible species which may be formed in these experiments, but which could not be incorporated into the model. The system of coupled differential equations given by reactions (4)–(8) was solved numerically (Frenklach et al., 1992). The results of the resulting kinetic fits to the column densities of each species are shown in Fig. 3. The values for the underlying rate constants were found to be  $k_1 = 2.94 \times 10^{-5} \text{ s}^{-1}$ ,  $k_2 = 2.28 \times 10^{-6} \text{ s}^{-1}$ ,  $k_3 = 1.14 \times$

$10^{-4} \text{ s}^{-1}$ ,  $k_4 = 8.56 \times 10^{-6} \text{ s}^{-1}$ , and  $k_5 = 1.22 \times 10^{-4} \text{ s}^{-1}$ . Comparison of  $k_1$  and  $k_2$  indicates that the relative branching ratio of reactions leading to dissociation via the dicarbon monoxide radical (4) and directly into two carbon monoxide species and a carbon atom (5) indicates that 93% of the reaction proceeds via reaction (4). In fact, reaction (4) can account for 73% of the total loss of carbon suboxide throughout the irradiation. However, it is seen that both destruction pathways for dicarbon monoxide,  $k_3$  and  $k_5$ , are found to be almost two orders of magnitude faster than its production rate. Because the value of  $k_4$  (destruction of carbon suboxide by any other pathway than reactions (4) and (5)) is larger than  $k_2$ , the production rate of dicarbon monoxide, we can conclude that there are additional loss pathways for carbon suboxide other than the generation of polymers by direct reaction with dicarbon monoxide. At this time, we cannot elucidate on the relative importance of the electronic states of the products formed.

### 4.2. Energetics and carbon/oxygen budget

We would now briefly like to comment on the carbon/oxygen budget for the observed products and reactants. During the irradiation, the column density of the carbon suboxide sample decreased by 38%, meaning a destruction of  $2.82 \times 10^{15} \text{ molecules cm}^{-2}$  ( $8.47 \times 10^{15} \text{ C atoms cm}^{-2}$ ,  $5.64 \times 10^{15} \text{ O atoms cm}^{-2}$ ). The observed column density of dicarbon monoxide after irradiation was found to be  $4.16 \times 10^{13} \text{ molecules cm}^{-2}$  ( $8.32 \times 10^{13} \text{ C atoms cm}^{-2}$ ,  $4.16 \times 10^{13} \text{ O atoms cm}^{-2}$ ). The observed column density of carbon monoxide was found to be  $1.18 \times 10^{15} \text{ molecules cm}^{-2}$  ( $1.18 \times 10^{15} \text{ C atoms cm}^{-2}$ ,  $1.18 \times 10^{15} \text{ O atoms cm}^{-2}$ ). Thus, the carbon/oxygen budgets hold for this experiment, where the majority of unaccounted carbon atoms ( $7.21 \times 10^{15} \text{ C atoms cm}^{-2}$ ) and oxygen atoms ( $4.42 \times 10^{15} \text{ O atoms cm}^{-2}$ ) expected to be locked up within the carbon suboxide polymer formed. From an energetic viewpoint, the minimum required energy for reactions (1)–(3) are 3.86, 2.24, and 6.11 eV, respectively (Table 1; Choi et al., 1998). Note that formation of carbon monoxide through Eqs. (1) and (2) or (3) are energetically equivalent. Here, we find that the required energy to account for the column densities of the observed products is  $9.32 \times 10^{13} \text{ eV}$  for dicarbon monoxide  $7.21 \times 10^{15} \text{ eV}$  for carbon monoxide. If we take into account that  $6 \times 10^{14} \text{ electrons cm}^{-2}$  hit our target during irradiation, this translates to the formation of 0.1 and 2.0 molecules of dicarbon monoxide and carbon monoxide, respectively, per electron. This translates to a linear energy transfer of roughly 12 eV per impinging electron, in good agreement with values from previous studies on electron irradiation using 5 keV electrons (e.g., Bennett et al., 2006).

## 5. Astrophysical implications and conclusion

Here, we have reported on the dissociation mechanisms of carbon suboxide produced in a cometary ice analog via

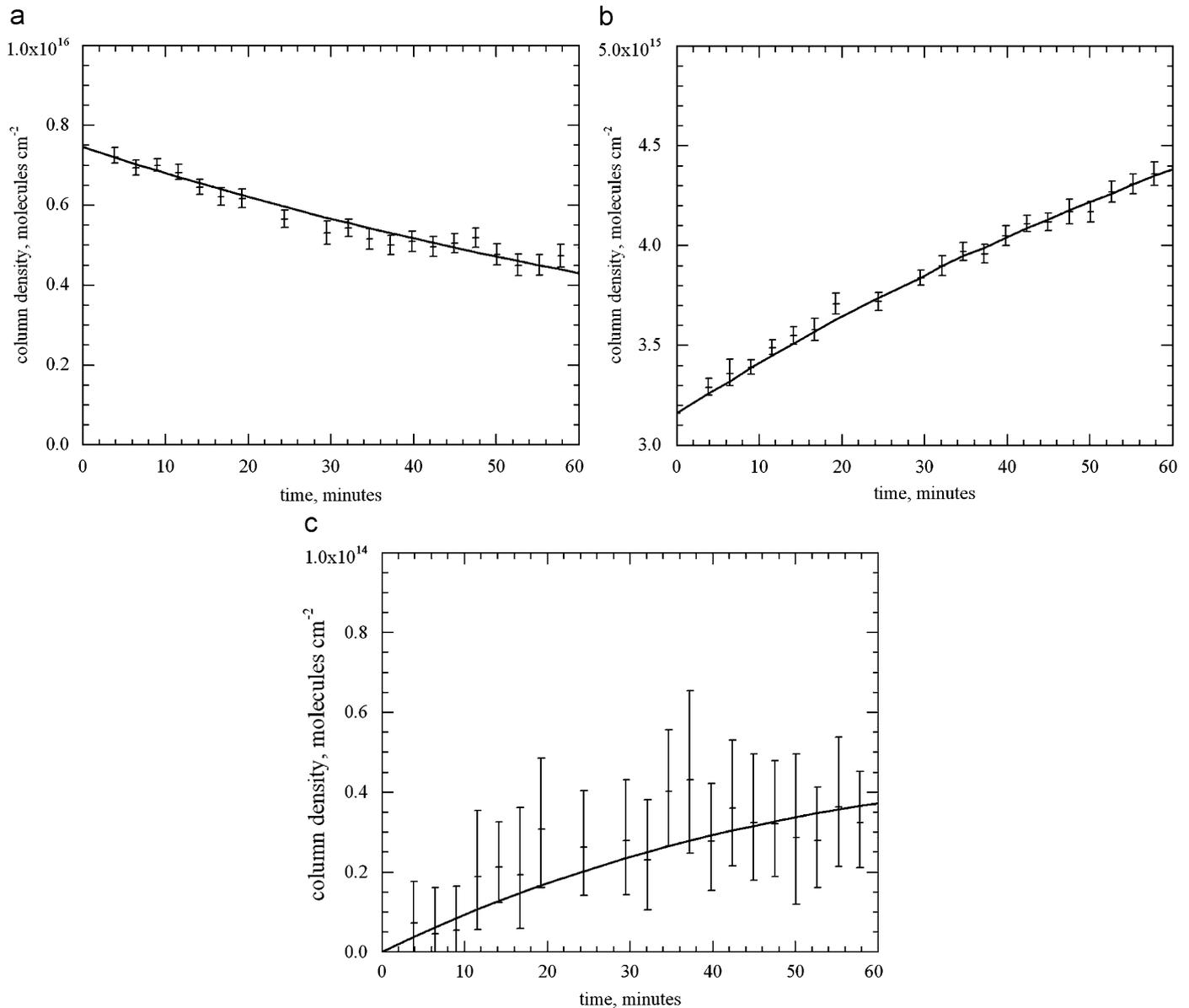


Fig. 3. Kinetic fits of the data for (a) carbon suboxide, (b) carbon monoxide, and (c) dicarbon monoxide. Error bars shown are  $1\sigma$  values for the area arising from the deconvolution procedure used to fit Gaussians to the observed peak positions.

its production from carbon monoxide. Carbon monoxide itself is a known constituent of both cometary ices (e.g., Mumma et al., 2003) as well as their precursors, interstellar ices (e.g., Gibb et al., 2004) where its abundance can be found up to 15% and 50% relative to water, respectively. Since both of these sources are exposed to irradiation from solar and/or galactic sources the production of carbon suboxide and its polymers is anticipated, and hence the detection of this species through (for example) infrared spectroscopy should be feasible. The fact that carbon monoxide is found in comets, while the similarly volatile molecular nitrogen has posed a problem, which could be solved through clathrates trapping carbon monoxide (Iro et al., 2003). An alternative view can be presented in terms of carbon suboxide serving as a carbon monoxide reservoir; whereby carbon monoxide under irradiation can

form carbon suboxide and other polymers which are substantially less volatile and can then re-form carbon monoxide upon further irradiation, the same is not true of molecular nitrogen which only forms N<sub>3</sub> which itself is unstable (Hudson and Moore, 2002; Jamieson and Kaiser, 2007) and hence could explain this discrepancy. Additional work needs to be done on the characterization of the polymers formed. While thermal polymers are thought to have some kind of a cross-linked structure (e.g., Ballauff et al., 2004; Schmedt auf der Günne et al., 2005), it has been determined that the dicarbon monoxide radical itself initiates the polymerization reaction in the radiolysis-induced process (Smith et al., 1966; Bruns et al., 1967).

The kinetics presented here should aid in future models based on the destruction of carbon suboxide, or formation of polymers within these environments. Studying the

reaction dynamics of carbon oxides and carbon atoms is essential as they are key players in a number of other different areas of active research which include, but are not limited to: (i) hydrocarbon combustion (e.g., Agafonov et al., 2002), (ii) interstellar chemistry (e.g., Smith et al., 2004), and (iii) high energy density materials (e.g., Fridman et al., 2006).

## Acknowledgments

This material is based upon work supported by the National Aeronautics and Space Administration (NASA Astrobiology Institute under Cooperative Agreement no. NNA04CC08A issued through the Office of Space Science). We would like to thank Prof. M. Winnewisser for his discussions regarding the quasi-linear nature of carbon suboxide.

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