CARBONIC ACID AS A RESERVE OF CARBON DIOXIDE ON ICY MOONS: THE FORMATION OF CARBON DIOXIDE (CO_2) IN A POLAR ENVIRONMENT

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ABSTRACT

Carbon dioxide (CO_2) has been detected on the surface of several icy moons of Jupiter and Saturn via observation of the ν_3 band with the Near-Infrared Mapping Spectrometer on board the *Galileo* spacecraft and the Visible-Infrared Mapping Spectrometer on board the *Cassini* spacecraft. Interestingly, the CO_2 band for several of these moons exhibits a blueshift along with a broader profile than that seen in laboratory studies and other astrophysical environments. As such, numerous attempts have been made in order to clarify this abnormal behavior; however, it currently lacks an acceptable physical or chemical explanation. We present a rather surprising result pertaining to the synthesis of carbon dioxide in a polar environment. Here, carbonic acid was synthesized in a water (H_2O)–carbon dioxide (CO_2) (1:5) ice mixture exposed to ionizing radiation in the form of 5 keV electrons. The irradiated ice mixture was then annealed, producing pure carbonic acid which was then subsequently irradiated, recycling water and carbon dioxide. However, the observed carbon dioxide ν_3 band matches almost exactly with that observed on Callisto; subsequent temperature program desorption studies reveal that carbon dioxide synthesized under these conditions remains in solid form until 160 K, i.e., the sublimation temperature of water. Consequently, our results suggest that carbon dioxide on Callisto as well as other icy moons is indeed complexed with water rationalizing the shift in peak frequency, broad profile, and the solid state existence on these relatively warm moons.

Key words: methods: laboratory: solid state – planets and satellites: composition – planets and satellites: surfaces – planet–star interactions – solid state: volatile

Online-only material: color figures

1. INTRODUCTION

The surfaces of Jupiter's and Saturn's satellites are well known to be dominated by water ice, along with salts, hydrated minerals, and traces of frozen gases (Dalton 2010). Carbon dioxide (CO_2) was detected via the ν_3 band on the surfaces of Ganymede and Callisto by reflectance spectra obtained with the Near-Infrared Mapping Spectrometer (NIMS) on board the *Galileo* spacecraft (Hibbitts et al. 2000, 2002, 2003; McCord et al. 1997). On both moons, the CO_2 ν_3 absorption band is symmetric and centered at 2349 ± 2 cm^{-1} ($4.257\,\mu m \pm 0.004\,\mu m$), which is slightly blueshifted with respect to pure carbon dioxide (2343 cm^{-1}; Sandford & Allamandola 1990). Furthermore, the observed CO_2 band profile was consistent in both peak position and band width in all physical areas probed by the spectrometer. An example of the CO_2 spectrum on Callisto, courtesy of Robert Carlson (McCord et al. 1997), is given in Figure 1.

In addition, the Visible-Infrared Mapping Spectrometer on board the *Cassini* spacecraft discovered carbon dioxide via the same ν_3 band on Phoebe, Iapetus, Hyperion, and Dione (Brown et al. 2004; Buratti et al. 2005; Clark et al. 2005, 2008). While on Phoebe, carbon dioxide exhibits similar spectral behavior to that of pure CO_2 or type II clathrates, the other moons (Iapetus, Hyperion, and Dione) all display a blueshifted peak at about 2950 cm^{-1} and a broad symmetric CO_2 ν_3 band profile similar to that observed at Ganymede and Callisto (Cruikshank et al. 2010). Also of note is the surface temperature (110–160 K) where carbon dioxide was observed on these icy bodies is beyond the sublimation point (90 K); however, significant amounts of carbon dioxide can be trapped in a water ice matrix and may

therefore remain observable at warmer temperatures (Gerakines et al. 2005, 1995; Jones et al. 2014; White et al. 2009). As such, the noticeable difference of the observed band on these satellites with respect to pure carbon dioxide has prompted great interest in the scientific community. Accordingly, many hypotheses have been put forth in order to explain the odd CO_2 ν_3 band profile on these icy satellites, from carbon dioxide clathrates (Cruikshank et al. 2010; Dartois & Schmitt 2009; Oancea et al. 2012), carbon dioxide physisorbed to minerals (Hibbitts & Szanyi 2007), molecular complexes with water (Chaban et al. 2007), and trapped within one or more non-ice host material (Hibbitts et al. 2002, 2003; McCord et al. 1998). Furthermore, spectral modeling of carbon dioxide and admixtures with other volatiles at various temperatures based on numerous laboratory investigations (Cruikshank et al. 2010; Dartois et al. 1999; Ehrenfreund et al. 1996; Gerakines et al. 2005, 1995; Hodyss et al. 2008; Öberg et al. 2007; Palumbo & Baratta 2000; Sandford & Allamandola 1990; Sandford et al. 1988; White et al. 2009, 2012) have failed to adequately reproduce the profile observed on the icy moons of Jupiter and Saturn (Chaban et al. 2007; Cruikshank et al. 2010; Oancea et al. 2012). Thus far, the best apparent fit to the observed ν_3 CO_2 band profile has been carbon dioxide physisorbed onto Ca-montmorillonite at 125 K (Hibbitts & Szanyi 2007); however, the band profile was asymmetric and failed to match the longer wavelength portion.

Carbon dioxide is well produced by bombardment of ions and UV photons in simple ices containing some form of carbon and oxygen (Allamandola et al. 1988; Bennett et al. 2010; Gomis & Strazzulla 2005; Hudson & Moore 1999; Loeffler et al. 2005). This is relevant here, as the icy moons in the outer solar system are exposed to high fluxes of energetic charged particles, mostly
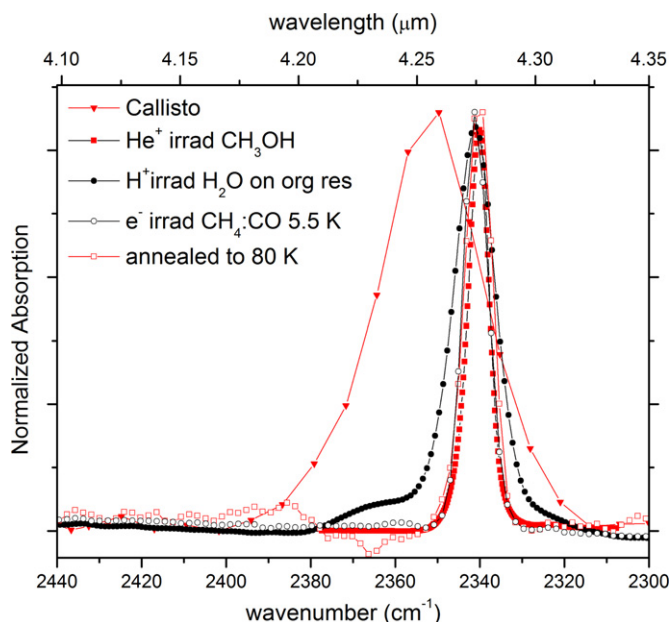
Figure 1. Comparison of the ν_3 carbon dioxide (CO_2) band as observed on Callisto with carbon dioxide synthesized following irradiation of methanol (CH_3OH) ice at 10 K with 3 keV He^+, of water (H_2O) on amorphous carbon residue at 80 K with 200 keV He^+, and of methane–carbon monoxide (CH_4–CO; 1:1) ice at 5.5 K and subsequent annealing at 80 K with 5 keV electrons. The abnormal profile of carbon dioxide on Callisto is clearly seen and has yet to have an acceptable explanation. Note that the band profile of carbon dioxide for this moon is very similar to other icy moons (see main text for details and references).

(A color version of this figure is available in the online journal.)

keV to MeV H^+, O^{n+}, S^{n+}, and electrons, that populate the magnetospheres of the giant planets (Johnson et al. 2004). The effects of such processing range from ion sputtering (Baragiola 2005; Brown et al. 1978; Johnson 1990; Johnson et al. 2008), physical modification of the structure (Baratta et al. 1991; Famà et al. 2010; Leto & Baratta 2003; Moore & Hudson 1992), and induced non-thermal chemical reactions resulting in the formation of a wide variety of molecules and refractory organic residues (Jones et al. 2011; Kaiser et al. 1997, 2013; Kaiser & Roessler 1997; Moore et al. 2001; Strazzulla 1998; Strazzulla et al. 2001). Unfortunately, the profile of the ν_3 band of CO_2 on Ganymede and Callisto is also drastically different from that observed in icy mixtures where carbon dioxide is synthesized as an endogenous product upon exposure to ionizing radiation. This is made clear in Figure 1 as well, where the spectra of the CO_2 ν_3 band obtained after ion-processing methanol ice (Palumbo et al. 1999) and a water ice layer on top of a carbon-rich organic material (Gomis & Strazzulla 2008) as well from the electron bombardment of a simple binary mixture composed of methane and carbon monoxide (Kaiser et al. 2014) are given as examples.

Also relevant are those ice mixtures containing water and carbon dioxide that have been irradiated in laboratory settings as water is a primary component of the icy moons as well (Clark et al. 2013; Dalton 2010). Several experimental studies have been conducted with a large variety of ions at several energies, temperatures, and water to carbon dioxide ratios (Boduch et al. 2011; Brucato et al. 1997; DelloRusso et al. 1993; Gerakines et al. 2000; Jones et al. 2014; Moore et al. 1991; Moore & Khanna 1991; Peeters et al. 2010; Pilling et al. 2010; Strazzulla et al. 2005; Zheng & Kaiser 2007). Despite the differences in experimental parameters, all agree

in that the products, carbon monoxide (CO), carbon trioxide (CO_3), and carbonic acid (H_2CO_3), are primarily formed. As such, carbonic acid has been suggested to be present in the surfaces of these icy moons (Johnson et al. 2004; McCord et al. 1997), comets (Hage et al. 1998; Moore et al. 1991), and Mars (Zheng & Kaiser 2007). Evidence for the existence of carbonic acid on icy moons (Europa and Callisto) is supported by the similarities in the 2577 cm^{-1} (3.880 μm) feature of the NIMS IR reflectance spectrum as it matches well with carbonic acid mixed in water–carbon dioxide ice (Carlson et al. 2002, 2005; Johnson et al. 2004; Peeters et al. 2010). Furthermore, as carbonic acid has an extremely low vapor pressure under vacuum at relatively warm temperatures ($\sim 10^{-12}$ torr at 240 K (Peeters et al. 2010)), H_2CO_3 can easily be isolated on a warm solar system body, remaining as the dominant species susceptible to bombardment of ions and subsequent energetic processing. Here we present experimental results concerning electron (5 keV) irradiation of carbonic acid at a temperature of 80 K; of particular note is the band position and width of carbon dioxide formed in the irradiation of carbonic acid.

2. EXPERIMENTAL APPARATUS

The experiments were conducted at the W. M. Keck Research Laboratory in Astrochemistry (Bennett et al. 2013; Jones & Kaiser 2013; Jones et al. 2014; Kaiser et al. 2014). Typical operating pressures within the main chamber of a few 10^{-11} torr are reached utilizing using oil-free magnetically suspended turbo-molecular pumps and dry scroll backing pumps. Housed within the main chamber is a rhodium-coated silver mirror coupled to cryostat (Sumitomo, RDK-415E) that cools the substrate to an ultimate temperature of 5.5 ± 0.1 K. Upon reaching this temperature, the water–carbon dioxide ice was deposited onto the substrate via gas phase deposition with a thickness of 500 ± 20 nm as determined from in situ laser interferometry (Fulvio et al. 2009; Hudgins et al. 1993; Kaiser et al. 2014; Westley et al. 1998) utilizing a HeNe laser (CVI Melles-Griot, 25-LHP-213) at 632.8 nm with an incident angle of $4°$ and a refractive index (n_f) of 1.3 (Hudgins et al. 1993). After condensation, a Fourier infrared transform spectrometer (Nicolet 6700) monitored the ice sample throughout the extent of the experiment with an IR spectrum collected every 2 minutes (average of 230 scans) in the range of 6000–400 cm^{-1} at a resolution of 4 cm^{-1}. Additionally, a quadrupole mass spectrometer (Extrel, Model 5221) operating in residual-gas analyzer mode (mass range of 1–500 amu) allowed for the detection of species evolving into the gas phase during temperature program desorption studies post irradiation. The solid state ratio of the water–carbon dioxide ice mixture was found to be 1 H_2O:5 CO_2 determined by integration and subsequent calculation of the column density using a modified Beers–Lambert law (Bennett et al. 2004; Hudson & Moore 2001; Wada et al. 2006) of the $^{13}CO_2$ at 2280 cm^{-1} with an A value of 7.6×10^{-17} (Gerakines et al. 1995) and subtraction of the shoulder area (determined from deconvolution) due the $H_2O \cdot CO_2$ complex at 1610 cm^{-1}, yielding the H_2O band area at 1660 cm^{-1} with an A value of 1.2×10^{-17} (Gerakines et al. 1995).

The ice mixture was subsequently irradiated with 5 keV electrons (beam current of 100 nA) isothermally (5.5 ± 0.1 K) at an angle of $70°$ relative to the surface normal for 2 hr over an area of 1.0 ± 0.1 cm^2. The dose deposited into the ice sample was determined utilizing a Monte Carlo electron simulation (CASINO) software package (Hovington et al. 1997) assuming the density of the sample is a weighted average (1:5 from the
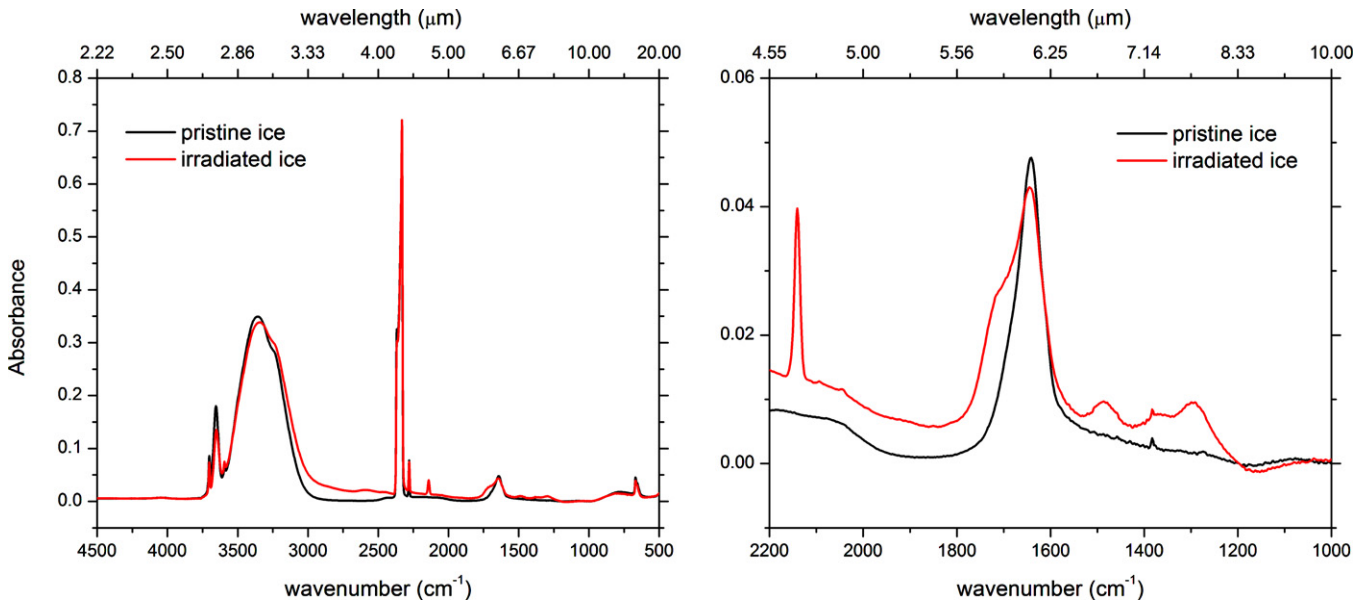
Figure 2. Infrared spectra of the H_2O–CO_2 ice mixture (1:5) as deposited at 5.5 K (black) and post irradiation (red). The main products identified in the post irradiation include carbon monoxide (CO), carbon trioxide (CO_3), and carbonic acid (H_2CO_3) corresponding well with previous experimental studies as discussed in the text. (A color version of this figure is available in the online journal.)

calculated column densities) of their respective pure volumetric mass densities supposing volume additivity (Luna et al. 2012). From this, the H_2O–CO_2 mixture has an estimated density of 0.97 g cm^{-3} utilizing a density of amorphous solid water of 0.94 g cm^{-3} (Angell 2004; Floriano et al. 1989; Jenniskens et al. 1998) and 0.98 g cm^{-3} for CO_2 ice (Satorre et al. 2008; Schulze & Abe 1980). From the CASINO simulations, total energy deposited into the ice was estimated at 7.0 $\pm$ 0.8 eV per 16 amu ($\sim$9.2 eV per molecule CO_2 and $\sim$12.2 eV per molecule H_2O). Upon irradiation, the sample was then warmed up to 220 K at a rate of 1 K minute^{-1}, allowing all other volatiles to completely sublimate, leaving a pure sample of carbonic acid and then cooled to a final temperature of 80 K. The temperature has been chosen to adequately simulate those determined on several icy moons in the external solar system. For example, the surface temperature of Europa has been measured between 50 and 125 K, Enceladus is between 30 and 145 K, and on Rhea between 50 and 100 K (Collins & Johnson 2006; Spencer et al. 2006). From here, pure carbonic acid was then irradiated with 5 keV electrons, the results of which are discussed below.

3. RESULTS

Carbonic acid (H_2CO_3) was synthesized following the irradiation of the 500 nm thick water–carbon dioxide mixture at 5.5 K with 5.2 $\times$ 10^{15} (5 keV electrons cm^{-2}) as shown in Figure 2. Additional products identified included carbon monoxide (CO) and carbon trioxide (c-CO_3), in agreement with previous studies (Boduch et al. 2011; Brucato et al. 1997; DelloRusso et al. 1993; Gerakines et al. 2000; Jones et al. 2014; Moore et al. 1991; Moore & Khanna 1991; Peeters et al. 2010; Pilling et al. 2010; Strazzulla et al. 2005; Zheng & Kaiser 2007). The irradiated ice mixture was subsequently warmed to a temperature of 220 K allowing all other volatiles to sublimate, leaving pure carbonic acid which then re-cooled to 80 K, as shown in Figure 3. Upon reaching a temperature of 80 K, H_2CO_3 was further irradiated with additional 5 keV electrons. Before irradiation, a new background was acquired; accordingly, bands that appear as having a negative absorbance are due to species that have been destroyed
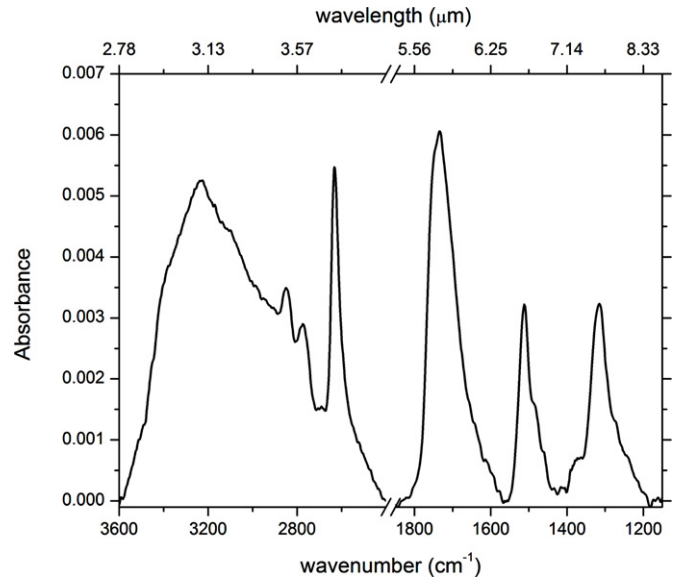

Figure 3. Infrared spectrum of pure carbonic acid synthesized from warming the irradiated H_2O–CO_2 ice mixture (Figure 2) to 220 K and then re-cooling to a final temperature of 80 K.

and those with positive absorbance are newly synthesized, as shown in Figure 4.

Immediately following irradiation, two distinctive absorbance features emerged (Figure 4) and were assigned to water (3400 cm^{-1}) and carbon dioxide (2350 cm^{-1}) in agreement with previous studies on the UV photolysis and 0.8 MeV H$^+$ irradiation of carbonic acid at temperatures of 14–20 K (Gerakines et al. 2000; Moore et al. 2001; Peeters et al. 2010). However, we saw no evidence for irradiation-induced amorphization (broadening and shift in peak positions of H_2CO_3) as noted in the 0.8 MeV irradiation experiment of crystalline carbonic acid (Peeters et al. 2010). After irradiation, the sample was then warmed to 300 K at a moderate rate of 1 K minute^{-1} while monitoring the sublimating molecules via a residual gas analyzer as described above. As
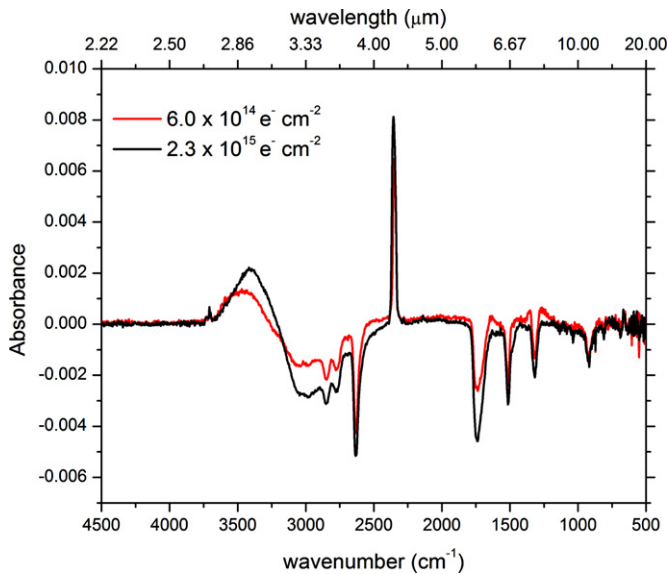
Figure 4. Irradiated carbonic acid at different electron fluences showing the appearance of water and carbon dioxide along with the destruction of carbon acid. Note that the IR spectrum of pure H_2CO_3 (see Figure 3) was used as the background, hence the negative peak areas following irradiation.

(A color version of this figure is available in the online journal.)

shown in Figure 5, carbon dioxide starts to sublimate at about 100 K; however, it does not completely sublimate until water finally evolves into the gas phase at 160 K. This observation alone indicates that carbon dioxide is formed as a molecular complex of water and not a matrix isolated in water. A comparison of the sublimation profile derived from the integrated ν_3 band area for carbon dioxide co-condensed with water and subsequently irradiated is also shown for comparison; note that when mixed with water, CO_2 completely dissipates from the solid state in this system well below 160 K.

4. DISCUSSION AND CONCLUSION

One of the most interesting results from this experiment is the band profile of carbon dioxide synthesized in carbonic acid upon exposure to ionizing radiation. Here, the peak position is slightly blueshifted from typical values by about 8 cm^{-1} and displays a much broader band width (34 cm^{-1}) as well. Displayed in Figure 6 is the CO_2 ν_3 band observed in the spectrum of Callisto (same as in Figure 1) compared with that obtained after electron bombardment of carbonic acid. From this figure, we can see that the bands overlap and match surprisingly well. Also shown in the same figure is spectra of carbon dioxide synthesized by 5 keV electron irradiation of a methane–carbon monoxide (1 CH$_4$:1 CO) ice at 5.5 K (Kaiser et al. 2014) and subsequent thermal annealing to 80 K (as shown in Figure 1), presented to confirm that, to the best of our knowledge, CO_2 produced after energetic processing of carbonic acid is a very plausible process that reproduces well the observed band on several icy moons of Jupiter and Saturn.

The results presented here can be put in the context of the so-called "carbon cycle" in which different species such as condensed volatiles like H_2O and CO_2 and refractory material (e.g., amorphous carbon, carbonates) are continuously altered and recycled by energetic processes. In such a scenario carbon dioxide has been demonstrated (Gomis & Strazzulla 2005) to be produced by ion bombardment at the interface between water ice and refractory carbon (Figure 1), possibly delivered from
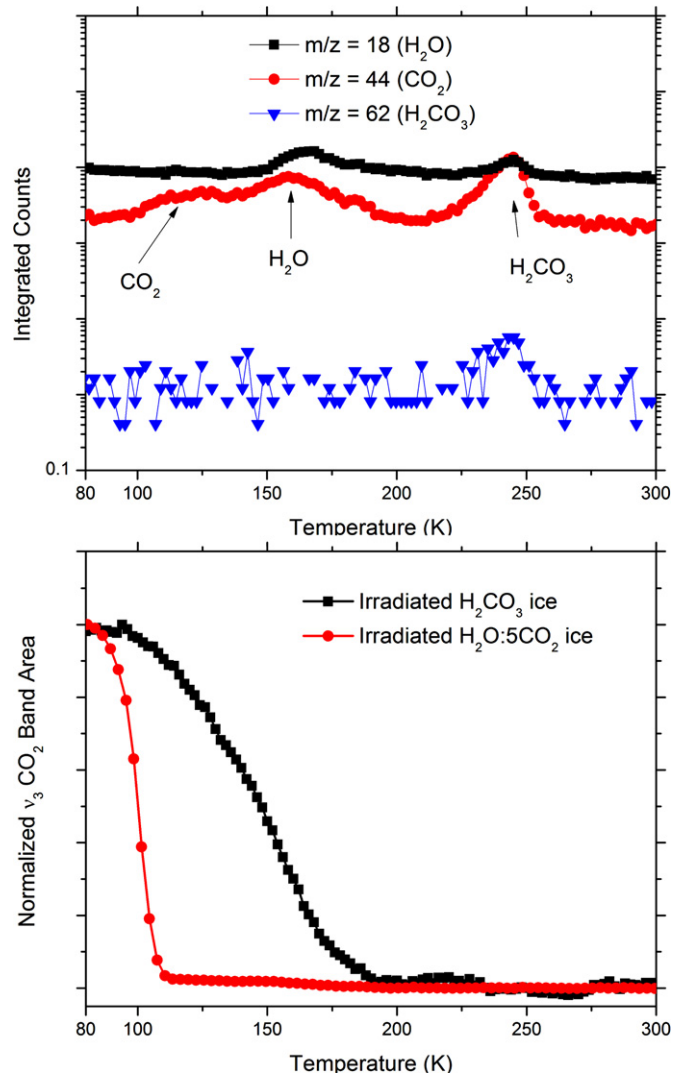

Figure 5. Quadrupole Mass Spectrometer sublimation profiles (top) for H_2O (18 amu), CO_2 (44 amu), and H_2CO_3 (62 amu) with normalized infrared band areas of carbon dioxide as a function of temperature (bottom) of the irradiated carbonic acid and the H_2O–CO_2 ice mixture. Here, carbon dioxide does not completely sublime at the typical temperature of 100 K for pure carbon dioxide. However, it remains complexed with water as displayed, finally sublimating water at 160 K.

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carbonaceous grains via micrometeorite bombardment. The next step, reported many times in the literature, is the formation of carbonic acid by the energetic processing of a mixed ice consisting of adequate amounts of carbon dioxide and water. In a recent paper (Jones et al. 2014) we have shown that the irradiation of a water–carbon dioxide ice mixture exhibits a "red" continuum in the UV region that corresponds well with some observations of Europa, Ganymede, and Callisto (Hendrix et al. 2011; Hendrix & Johnson 2008). Further, H_2CO_3 has an extremely low vapor pressure and can easily be segregated as a consequence of temperature variations on the surfaces of the icy moons. Consequently, patches of pure carbonic acid are formed and irradiated by the intense fluxes of ions and electrons from the parent planet's magnetosphere, ultimately resulting in the reformation of carbon dioxide and water. Our results suggest that carbon dioxide band observed on Ganymede and Callisto is attributed in part to those molecules produced by the energetic processing of carbonic acid. At the very least
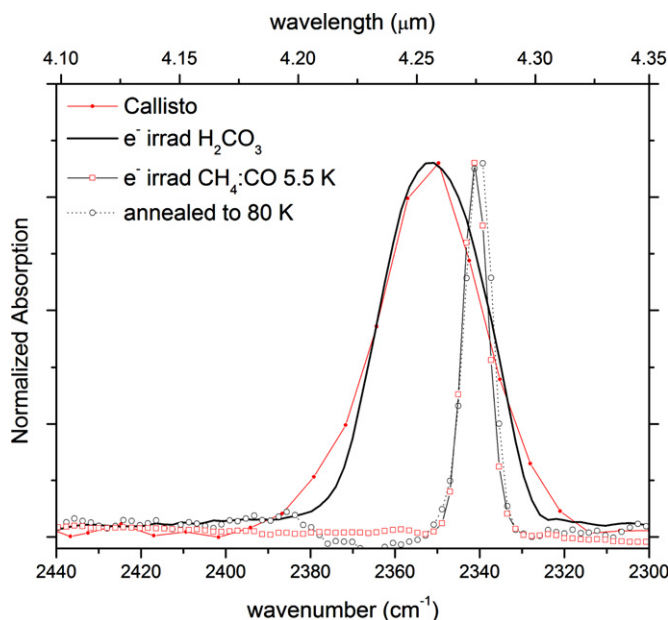
Figure 6. Comparison of the ν_3 carbon dioxide band as observed on Callisto with carbon dioxide synthesized with that observed from the irradiation of carbonic acid. The apparent match between both systems suggests that carbon dioxide on Callisto (as well as other moons) may be formed from the subsequent in situ energetic processing of carbonic acid. Also reported, for comparison are the spectra obtained after 5 keV electron irradiation of methane–carbon monoxide binary ice at 5.5 and subsequent annealing at 80 K (Figure 1).

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propose that carbon dioxide is present as a molecular complex with water in agreement with previous explanations for this band (Chaban et al. 2007). In addition, we have shown under these circumstances that carbon dioxide can remain condensed at temperatures near 160 K, well above the typical sublimation point, thereby also explaining the observation of solid carbon dioxide on these moons.

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