

CO₂ SYNTHESIS BY ION BOMBARDMENT

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Abstract

Here we present laboratory studies where we measure, using infrared spectroscopy, the production of CO₂ from amorphous carbon grains with a water ice cap that have been irradiated with 100 keV H⁺ ions. We find that CO₂ is produced in both thin films where the ions hit the substrate and in thicker films where the ions stop in the ice film. Furthermore, we have found that we produce more CO₂ at 16 K than we do at 120 K. Also after we warm the film and the water ice desorbs, we detect semi-stable carbonaceous species on the substrate. One of the species identified appears to be carbonic acid, H₂CO₃, which shows that even with two of the most basic substances present in outer space, more complex molecules can be produced by radiation processing.

Introduction

Identifying possible mechanisms for CO₂ synthesis is of interest, because it has been observed in a variety of interstellar environments, ranging from ISM to the satellites of Jupiter. D'Hendecourt and Jourdain de Mazon (1989) first discovered CO₂ in the interstellar media by identifying its 15.2 μm band. This confirmed expectations that CO₂ should be present as it could result from accretion of interstellar grains of CO parent molecule. The ratio of the column densities of CO and CO₂ (Gerakines et al. 1995) showed that oxidation of CO may be an important mechanism for forming CO₂. This process may be enhanced by destruction of neighboring molecules, such as O₂, H₂O, etc., by incoming radiation, such as cosmic rays, interstellar winds, or magnetic ions. Studies of whether radiation may greatly increase CO₂ concentration in CO ices have been done previously (Gerakines et al 2001, Loeffler et al. 2005). In both cases, CO₂ was produced but in smaller amounts than what has been observed in the interstellar media. Thus, it was concluded that while CO₂ could be produced efficiently by Lyman-α radiation and H⁺ bombardment, neither were dominant mechanisms in interstellar media.

Recently the Galileo NIMS instrument identified the presence of solid CO₂ on Callisto and Ganymede (McCord et al. 1997), two main satellites of Jupiter, where temperatures are much higher than in the interstellar media (80-160 K). The existence of CO₂ in these conditions is of interest, because its likely parent molecule in the ISM (CO) has not been detected

(McCord et al 1997) and thus another mechanism of CO₂ formation is likely active. Furthermore its presence at high temperatures where it can sublime indicates that it may be trapped or bound in some other matrix material (Hibbitts 1998). In this environment, the peak position of CO₂ shifts from 4.27 to 4.25 microns, which supports that is in a more restricted environment (McCord 1998). However, the origin and location of the CO₂ on the satellites is not completely understood. Hypotheses include that CO₂ may exist in clathrates - which generally form higher than 120 K - but be unable to rotate, may be trapped in amorphous water ice that condenses below 120 K, which has been observed in comets and interstellar grains (Whittet et al, 1996), may be trapped in hydroxide bearing minerals as fluid inclusions present in the darker regions of the satellites, or possibly even by some impact induced synthesis between a carbon bearing species and water ice, which may be subsequently trapped in the host material.

Here we present experimental studies that are of interest to CO₂ formation in both ISM and in the icy satellites of Jupiter. In both cases, some type of carbon - PAH, graphite, carbonaceous materials, etc - and water ice have been detected. We have studied the synthesis of CO₂ from films of H₂O grown on a thin amorphous ¹³C layer 100 keV H⁺ at 16 K and 120 K. We have used isotopic labeling to discriminate against CO₂ condensation.

Experimental Setup

All experiments were performed in a stainless steel vacuum chamber (figure 1) at a base pressure of $5\text{-}10 \times 10^{-10}$ Torr. Water ice films were grown by vapor deposition on the carbon substrate, which was deposited on an optically flat gold mirror. The average size of the grains were $\sim 5 \mu\text{m}$ (figure 1). The water vapor was sent through a micro capillary array at normal incidence. The thin films ($< 2 \mu\text{m}$) were grown at irradiation temperatures, while the thicker films were grown at 120 K to prevent cracking. In the thin film experiments, we implanted the 100 keV protons in the carbon grains, while the ions stopped in the thick films (Zeigler 2003). The mass-analyzed ion beams were produced by an ion accelerator and scanned uniformly over the target. A calibrated thin wire collector placed in the beam path before the target chamber was used to monitor the beam current density in real time.

The specular infrared reflectance of the films on the thin carbon substrate was measured at an incident angle of 35° with a Thermo-Nicolet Nexus 670 Fourier Transform infrared spectrometer at 2-cm^{-1} resolution. The spectra were divided by the spectrum from the carbon covered gold mirror before ice deposition. The ratios R were then converted to optical depth units: $-\ln(R)$, and the band area was quantified after subtraction of a fitted, non-linear baseline. We multiplied the band area by the ratio of the film thickness and the path length of the infrared beam, which normalizes our calculated value to the thickness of the sample and divided by the relative band strength

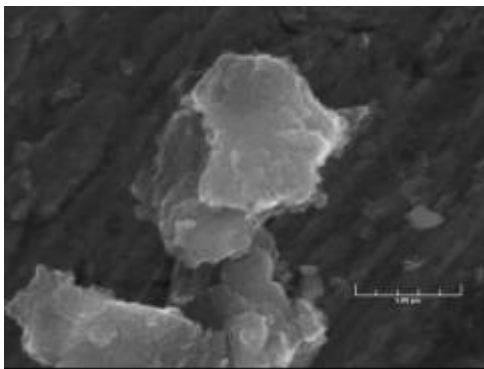


Figure 1. An SEM micrograph of a carbon grain, typical size was $\sim 5 \mu\text{m}$.

Results

Production in Thin Films

In our study of thin films, we determined that we could produce CO_2 at both 16 K and 120 K, and at 16 K we always produced more CO_2 . Figure 2 shows the production of CO_2 for different thicknesses at 16 K.

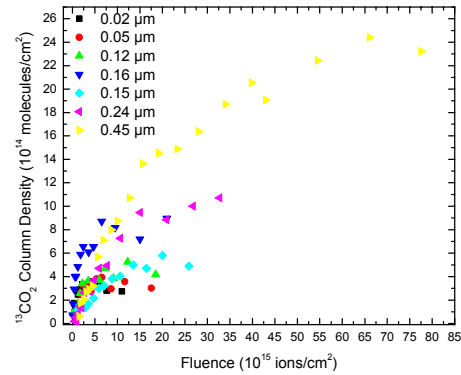


Figure 2. The production of CO_2 from an amorphous carbon substrate with a water ice cap as a function of 100 keV H^+ ion fluence for different thicknesses.

Figure 3 shows that the saturation values of CO_2 produced at the higher fluence as a function of film thickness. It appears that at 16 K, the saturation value increases with thickness, while at 120 K it does not.

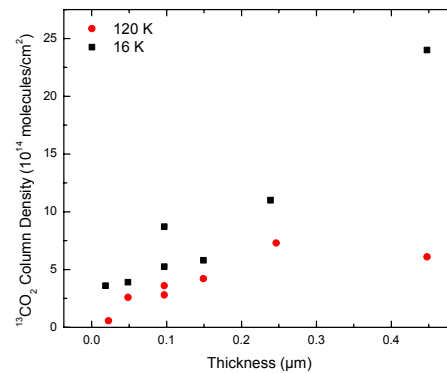


Figure 3. Thickness dependence of CO_2 production in films irradiated at 16 K and 120 K with 100 keV protons.

Thick Films

In an attempt to understand whether the direct interaction of the ion and the substrate was critical, we performed experiments, where the film were $\sim 2.7 \mu\text{m}$, which was much larger than the expected range of the protons ($1.6 \mu\text{m}$). We measure a different trend than in the thin film experiments. Figure 4 shows that temperature dependence of the CO_2 production. It is interesting to note that in these thicker films, negligible CO_2 is produced at temperatures greater than 80 K, while below 80 K the CO_2 is produced in the film linearly, after a long incubation period: 1×10^{16} ions/ cm^2 . To study the stability in the film, we step ramped a film from 20 K to 120 K, holding the temperature constant intermittently to see if the CO_2 column density changed (figure 5). It appears that the film is relatively stable at temperatures as higher as 120 K.

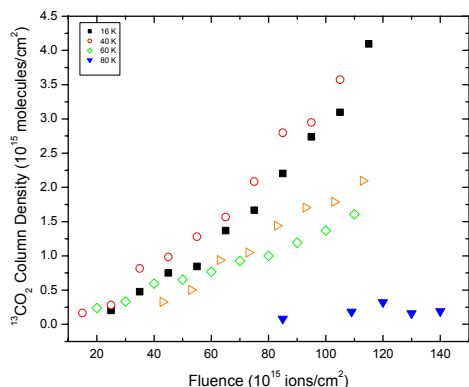


Figure 4. The production of CO_2 in films thicker than the range of the incident ions.

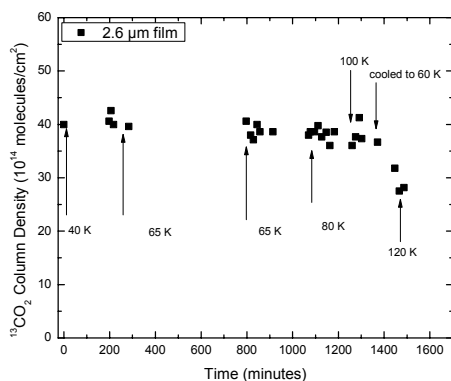


Figure 5. The stability of CO_2 produced in an ice at 16 K, as we increase the temperature.

Residue

Thin Films

After warming these films, we find that in some cases there is a residue left on the substrate that is semi-stable even above 200 K. The amount left on the substrate varies. The most prominent finding for thin films is when we grew films that were approximately as thick as the range of the ion beam. Thus, it is not entirely clear whether the ions hit the substrate. Regardless, after warming the film and desorbing the water ice, we find an absorption feature that was previously covered up by water ice absorptions (figure 6).

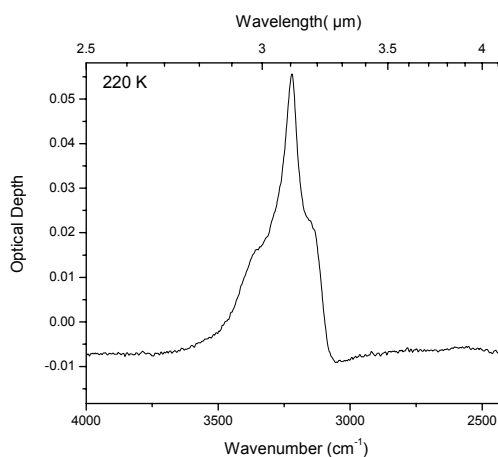


Figure 6. A residue left on the substrate at 220 K after using 100 keV protons to irradiate a water ice film on a carbon substrate.

This residue has been identified tentatively as H_2CO_3 by comparing with other findings of carbonic acid in literature (Moore & Khanna, 1990; Brucato, Palumbo, & Strazzulla 1996).

Thick Films

In thick films, we also saw residues left over after we desorbed the film (figure 7). However, we also saw drastic changes in infrared spectra at 16 K, while relatively little changed occurred at 120 K (figure 8). This suggests that CO_2 is only a minor component in all that is produced at 16 K for thick films.

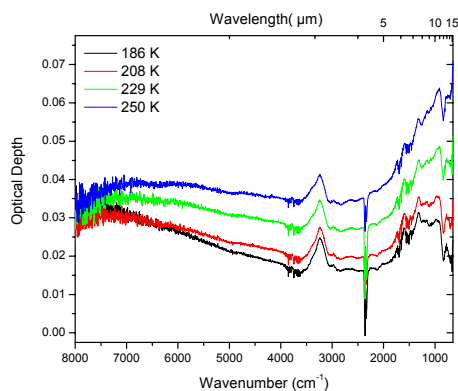


Figure 7. Residue left after water has desorbed from a 2.7 μm film of water ice irradiated at 16 K.

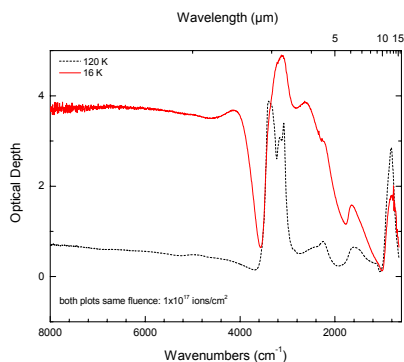


Figure 8. Comparison of spectra of a 2.6 μm water ice film irradiated at 16 K and 120 K, both were grown at 120 K. The one at 120 K closely resembles water ice before irradiation

Astrophysical Implications

Recently many radiation studies have focused on making complex molecules from other complex molecules in mixtures. However, these studies never have addressed how the first complex molecules may have formed. Recently two studies have produced CO and CO₂ by deposited water on hydrogenated carbon grains or carbonaceous minerals, which is a good simulation of conditions in outer space with fundamental components (Mennella, Palumbo, & Baratta 2004, Gomis, Strazzulla, Leto, in press). Our experiments are different in that we start from perhaps more basic components of the solar system: amorphous carbon and water ice. Water ice is essentially omnipresent in outer space, and carbon grains are fundamental components of

most bodies. Thus, these experiments show that with the most basic components in space, more complex molecules, like CO₂ and possibly other carbonaceous species (e.g. H₂CO₃) can form by the common radiation processing that occurs.

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