Carbonic Acid Stability in Solar Systems Ices

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Introduction

Carbonic acid (H_2CO_3) is a major product of energetically processed ices containing H_2O and CO_2. It is thermally stable at 200 K, higher than the sublimation temperature of H_2O. Ices containing both H_2O and CO_2 have been found on a variety of surfaces such as those of Europa, Callisto, Iapetus, and Mars, where processing by magnetospheric ions or the solar wind may lead to the formation of H_2CO_3. A tentative detection was made by Johnson et al. [1], who compared the infrared geometric albedo spectrum of Callisto with laboratory carbonic acid spectra. We have investigated spectral properties and the stability of carbonic acid at different temperatures upon irradiation with 0.8 MeV protons. The energy deposited into the ice by the incident proton beam not only destroys H_2CO_3, but also amorphizes the crystalline phase of the solid. The radiation destruction and amorphization processes will be discussed along with an estimate for the expected lifetimes of H_2CO_3 on surfaces in the outer solar system.

Formation

The system used for this experiment was previously described in Hudson and Moore [2]. H_2CO_3 was produced by irradiating an ice mixture of H_2O:CO_2=1 at 14 K with 0.8 MeV protons to a total dose of 13.2 eV molecule^{-1}. The resulting ice mixture was warmed to 240 K to drive off excess H_2O and CO_2, followed by a cooling to the required temperature. All experiments were done at 14 K, unless stated otherwise. Once the desired temperature was reached a spectrum was recorded to mark the start of the experiment.

Spectral properties

A layer of carbonic acid was formed as described above. After warming to 240 K, the carbonic acid was slowly cooled in 20 K steps to 14 K. At each step an infrared spectrum was recorded. Then, the process was reversed and the temperature was raised in 20 K steps to 200 K. From the spectra, the peak position and full width at half max (FWHM) of the most prominent band at 2618 cm^{-1} were determined. The results are shown in figure 1. Between 14 K and 140 K, the peak position does not change. Above 140 K, the peak position shifts to lower wavenumbers and reaches 2612 cm^{-1} at 240 K. The FWHM remains unchanged at temperatures below 40 K. From 40 K to 240 K the band widens almost linearly with temperature. The results for the first leg of the experiment (decreasing temperature, denoted by solid circles in figure 1) and the second leg of the experiment (increasing temperature, crosses) are very similar, which means that the change in peak position and FWHM at different temperatures is reversible.

Dissociation rate

A layer of H_2CO_3 was irradiated with 0.8 MeV protons at increasing doses. After each dose, an infrared spectrum was recorded. The rate of dissociation was determined from the decrease in integrated absorbance of spectral features. The carbonic acid dissociation rate was measured at 14 K, 100 K, and 200 K and the results are shown in table 1. However, the carbonic acid spectra differed not only in absorbance after each irradiation dose, but also showed a change in peak shape and peak position. The energy deposited in the ice by the incident proton beam, not only dissociated the carbonic acid, as evidenced by the formation of water and CO_2, but also amorphized the crystalline H_2CO_3 ice. In order to disentangle the two processes, we performed an additional experiment, in which the temperature was raised to 200 K after each irradiation step, to recrystallize the ice layer and to drive off any water and CO_2 produced by the dissociation of carbonic acid. Then, the temperature was lowered to the experiment temperature and an infrared spectrum was recorded. Again, the rate of dissociation was determined from the difference in integrated absorbance, but now from the spectra after the annealing step. The results, summarized in table 1, show that the proton irradiation dissociation rate does not depend on temperature.

The dissociation rate was extrapolated to a half life – the dose at which 50 % of the starting material is dissociated – at the surface of Callisto. The solar wind delivers MeV protons to the surface of Callisto with a flux of 6 eV year^{-1}. At a depth of 50 μm, the maximum penetration depth for the near and mid infrared, the solar wind flux is 0.002 eV year^{-1}.

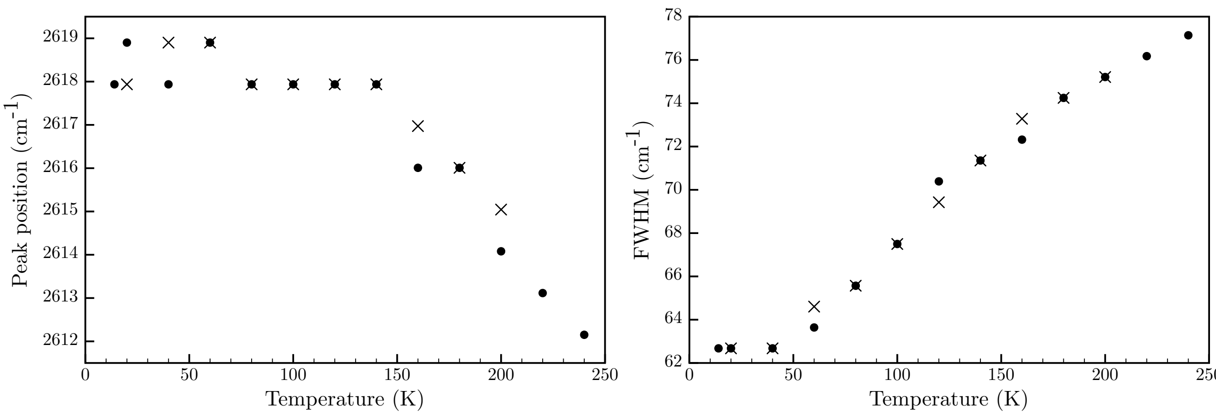

Figure 1: Peak position (left) and full width at half max (FWHM, right) of a prominent band of carbonic acid in the OH-stretch region of the mid-IR. The circles represent the data at decreasing temperature (240 K → 14 K), while the crosses mark the data at increasing temperature (14 K → 200 K). This distinction shows that the change in peak position and FWHM at different temperatures is repeatable and reversible.

The dissociation rates and half lives are shown in table 1.

Conclusion

We have measured infrared properties (peak position and FWHM) of layers of carbonic acid ice at different temperatures. Upon irradiation with MeV protons, the carbonic acid ice amorphized, while at the same time carbonic acid may dissociate. We measured the dissociation rate for carbonic acid at 14 K, 100 K, and 200 K, with correction for amorphization. The results show that the dissociation rate is not dependent on temperature. On Callisto, carbonic acid would have a half life of 1×10^4 year at a depth of 50 μm.

Table 1: H_2CO_3 dissociation rate at three temperatures. The uncorrected dissociation rate was measured from the direct irradiation of H_2CO_3. The third column shows the dissociation rate after correction for amorphization, see text. The dissociation rate was extrapolated to the surface of Callisto where the solar wind delivers 0.002 eV year^{-1} at a depth of 50 μm [3].

T (K)	dissociation rate (molec (100 eV)$^{-1}$) uncorrected	corrected	$t_{1/2}$ at Callisto ($\times 10^3$ year)
14	19	3.7	9.4
100	11	3.1	11
200	4.6	4.6	7.5

Acknowledgement

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References

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