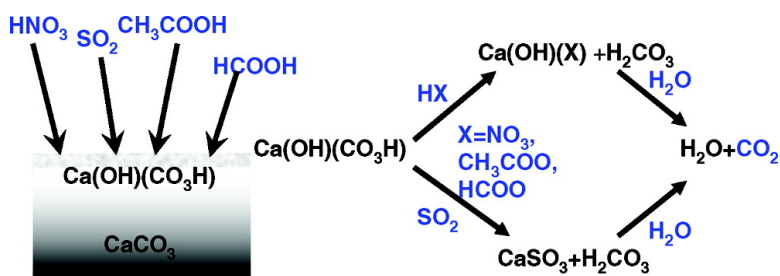


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## Carbonic Acid: An Important Intermediate in the Surface Chemistry of Calcium Carbonate

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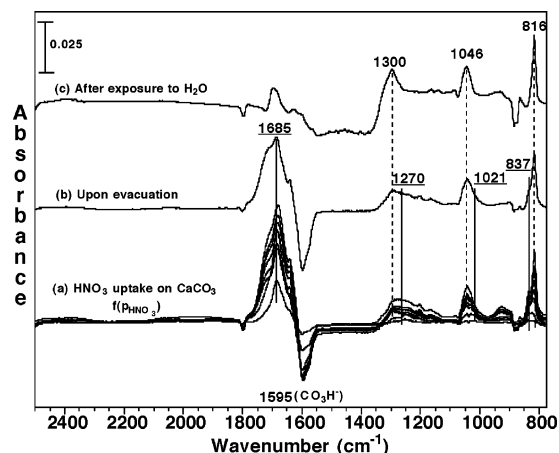
Calcium carbonate is an important and ubiquitous mineral in biological and geochemical systems. In the Earth's atmosphere, carbonate minerals are important in global CO<sub>2</sub> exchange<sup>1</sup> and energy storage,<sup>2</sup> and they represent a reactive component of the mineral aerosol present in the troposphere.<sup>3,4</sup> Calcium carbonate is also a major structural component of many natural and engineered systems. In biological systems, carbonate minerals are the building blocks of shells and skeletons.<sup>5</sup>

From experimental and theoretical surface science studies,<sup>6–13</sup> there is clear evidence that under ambient conditions of pressure, temperature, and relative humidity, the surface chemistry of calcium carbonate will terminate with OH groups that persist even under ultrahigh vacuum conditions. The OH-terminated surface is a result of the dissociative adsorption of water according to the reaction  $\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})(\text{CO}_3\text{H})$ . As shown here, it is the reaction chemistry of this layer that is important in the surface chemistry of calcium carbonate.

In this study, the surface chemistry of calcite, the most common and stable phase of calcium carbonate, is investigated using infrared spectroscopy. In particular, the chemistry of several trace atmospheric gases including HNO<sub>3</sub>, SO<sub>2</sub>, HCOOH, and CH<sub>3</sub>COOH with calcium carbonate particles is studied. A major finding of this study is that carbonic acid, H<sub>2</sub>CO<sub>3</sub>, is found to be an intermediate in these reactions. This is the first study to identify adsorbed H<sub>2</sub>CO<sub>3</sub> in the surface chemistry of calcium carbonate. As shown here, in the absence of adsorbed water, carbonic acid is stable on the surface.

Carbonic acid is an intermediate in the surface chemistry of carbonate minerals in aqueous solution, although in solution it quickly dissociates into CO<sub>2</sub> and H<sub>2</sub>O. It has also been postulated to be of astrophysical importance.<sup>14–16</sup> Cryogenic techniques have been used to synthesize carbonic acid.<sup>14–21</sup> Characteristic infrared absorptions, along with theoretical calculations of the frequency of the vibrational modes, have been used to identify carbonic acid in these low temperature experiments. As discussed by Moore and Khanna, the vibrational spectrum of carbonic acid is distinctly different from that of carbonate, CO<sub>3</sub><sup>2-</sup>, and bicarbonate, HCO<sub>3</sub><sup>-</sup>.<sup>17</sup> In the case of carbonic acid, the C=O stretching frequency near 1700 cm<sup>-1</sup> is at a much higher frequency than any of the carbon–oxygen stretching motions found in CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>. This is because the bond order for the C=O bond in carbonic acid is two, whereas it is lower in both carbonate and bicarbonate ions. Thus, this characteristic band is particularly useful in distinguishing H<sub>2</sub>CO<sub>3</sub> from CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>.

Evidence for the formation of adsorbed carbonic acid is seen in the infrared difference spectra of calcium carbonate particles following reaction with HNO<sub>3</sub>. FT-IR difference spectra of calcium carbonate particles following increasing exposure of HNO<sub>3</sub> are plotted in Figure 1. The spectra shown in Figure 1a as a function of HNO<sub>3</sub> uptake are plotted in the presence of gas-phase nitric acid but with the nitric acid gas-phase absorptions subtracted from each of the spectra. As shown in the spectrum labeled upon evacuation

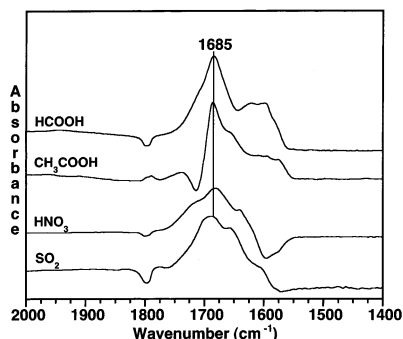


**Figure 1.** FT-IR difference spectra are shown for CaCO<sub>3</sub> particles (a) as a function of nitric acid vapor ( $p = 5$  to 150 mTorr), (b) following evacuation of nitric acid vapor, and (c) after exposure of the same surface to water at 80% RH. Absorption bands due to adsorbed nitrate and adsorbed carbonic acid are seen in the spectra. Frequencies of the vibrational bands of adsorbed carbonic acid are underlined, and the bands are marked with a solid line. The vibrational bands of adsorbed nitrate are marked with a dashed line. The negative band at 1598 cm<sup>-1</sup> is due to the loss of CO<sub>3</sub>H<sup>-</sup> from the surface.

**Table 1.** Vibrational Assignment of Adsorbed Carbonic Acid<sup>14,18,23,24</sup>

vibrational mode	Frequency (cm <sup>-1</sup> )	
	condensed phase H <sub>2</sub> CO <sub>3</sub> (D <sub>2</sub> CO <sub>3</sub> ) <sup>14,18,23</sup>	adsorbed H <sub>2</sub> CO <sub>3</sub> (D <sub>2</sub> CO <sub>3</sub> )
$\nu(\text{C}=\text{O})$	1705 (1617)	1685 (1659)
$\delta_{\text{ip}}(\text{COH})$	1296 (1021)	1270 (971)
$\nu_s(\text{C}(\text{OH})_2)$	1034 (997)	1021 (971)
$\delta_{\text{oop}}(\text{CO}_3)$	812 (812)	837 (834)

in Figure 1b, there is little change in the spectrum upon evacuation of gas-phase HNO<sub>3</sub>. Absorption bands due to new surface species are seen in the spectra of calcium carbonate following reaction of HNO<sub>3</sub>. As discussed in detail below, it is proposed that these absorption bands can be assigned to two products: adsorbed nitrate ion and adsorbed carbonic acid. Adsorbed nitrate is characterized by infrared absorptions at 1300, 1046, and 816 cm<sup>-1</sup>, consistent with the frequencies previously observed for nitrate absorptions.<sup>22</sup> The band near 1685 cm<sup>-1</sup> is assigned to the C=O stretch of adsorbed carbonic acid. The frequency of this band is shifted by approximately 20 cm<sup>-1</sup> from that found for carbonic acid in the condensed phase. Other absorptions near 1270, 1021, and 837 cm<sup>-1</sup> are also due to the presence of adsorbed carbonic acid. An assignment of the bands associated with adsorbed carbonic acid is given in Table 1 and is based on infrared studies of carbonic acid in the condensed phase.<sup>14,18,23,24</sup>



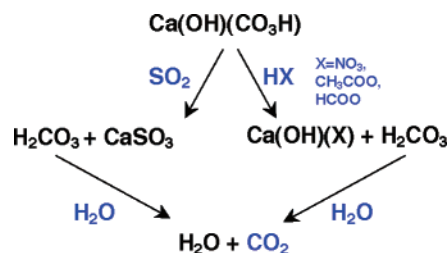
**Figure 2.** FT-IR difference spectra of calcium carbonate particles following reaction of approximately 100 mTorr of  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HCOOH}$ .

Besides the close agreement in frequency of the absorption bands associated with condensed carbonic acid and that for adsorbed carbonic acid, the reaction chemistry of this surface species is also consistent with that expected for carbonic acid. Carbonic acid is stable on the surface in the absence of water at 298 K. However, theoretical calculations have shown that carbonic acid is significantly destabilized even in the presence of only one water molecule and rapidly dissociates to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .<sup>23</sup> From these theoretical results, it is reasonable to expect that adsorbed carbonic acid would dissociate on the surface in the presence of adsorbed water. The infrared data after water vapor (80% RH) was introduced into the infrared cell for several hours and then evacuated show that the absorption bands associated with adsorbed carbonic acid have nearly disappeared, whereas absorptions due to adsorbed nitrate have not (Figure 1c). The evolution of gas-phase  $\text{CO}_2$  is evident in the spectrum recorded in the presence of the gas phase (not shown), consistent with the decomposition chemistry of carbonic acid.

Additional confirmation of the assignment presented in Table 1 comes from results obtained from the adsorption of  $\text{DNO}_3$  on a calcium carbonate sample whose surface was repeatedly exposed to gas-phase  $\text{D}_2\text{O}$ . This pretreatment of the surface results in the exchange of surface-adsorbed hydrogen for deuterium, resulting in a  $\text{Ca}(\text{OD})(\text{CO}_3\text{D})$  surface. Following reaction of  $\text{DNO}_3$  on a  $\text{Ca}(\text{OD})(\text{CO}_3\text{D})$ , two products form: adsorbed  $\text{D}_2\text{CO}_3$  and adsorbed nitrate. The frequencies observed for adsorbed  $\text{D}_2\text{CO}_3$  are also listed in Table 1. On the basis of the condensed phase assignments, the frequencies of the vibrational bands of adsorbed  $\text{D}_2\text{CO}_3$  are found to be in good agreement with that expected upon deuteration of the molecule.

Further evidence that carbonic acid is an important intermediate in the surface chemistry of calcium carbonate is seen in the difference spectra shown in Figure 2. The characteristic/signature absorption band due to the  $\text{C}=\text{O}$  stretching motion of adsorbed carbonic acid is seen in the difference infrared spectra following reaction with  $\text{SO}_2$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HCOOH}$  as well as  $\text{HNO}_3$  (see Figure 2). There are absorption bands associated with sulfite, acetate, and formate in the respective spectra as well, additional products of the reaction with calcium carbonate surface. Upon adsorption of water on the surface following each of these adsorption experiments, the band at  $1685\text{ cm}^{-1}$  disappears, concomitant with the production of gas-phase  $\text{CO}_2$ , again consistent with the expected reaction chemistry of adsorbed carbonic acid. These data show that the reaction chemistry of the  $\text{Ca}(\text{OH})(\text{CO}_3\text{H})$  surface layer with several atmospheric gases, including  $\text{SO}_2$ , a molecule that contains no source of hydrogen atoms, results in the

### Scheme 1



formation of adsorbed carbonic acid. The surface chemistry of  $\text{CaCO}_3$  is found to be distinctly different from  $\text{CaO}$ .<sup>25</sup> The formation of carbonic acid from reaction of  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HCOOH}$  is shown in Scheme 1. Only under dry conditions is carbonic acid stable. In the presence of adsorbed water, carbonic acid dissociates into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Thus, carbonic acid may be an important, albeit short-lived, intermediate in the surface chemistry of calcium carbonate.

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**Supporting Information Available:** Difference FT-IR spectra following reaction of  $\text{DNO}_3$  on  $\text{Ca}(\text{OD})(\text{CO}_3\text{D})$  and  $\text{HNO}_3$  on  $\text{CaO}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (25) Infrared absorptions due to adsorbed carbonic acid are not observed following reaction of  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HCOOH}$  on  $\text{CaO}$ . This is consistent with the observation that the surface of calcium oxide is terminated by  $\text{Ca}(\text{OH})_2$ . See Liu, P.; Kendelewicz, T.; Brown, G. E.; Parks, G. A.; Pianetta, P. *Surf. Sci.* **1998**, *416*, 326.

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