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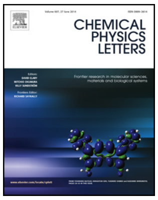

The hydration structure of aqueous carbonic acid from X-ray absorption spectroscopy

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ABSTRACT

Despite much effort, aqueous carbonic acid (H_2CO_3) remains poorly characterized because it is very short-lived. We describe the detection and characterization of aqueous H_2CO_3 by X-ray absorption spectroscopy, wherein protonation of a bicarbonate solution continuously generates the acid under ambient conditions. Accompanying first principles calculations of the carbon K-edge transitions facilitate spectral assignment and interpretation in terms of the H_2CO_3 π^* orbital, which exhibits a small (0.2 eV), systematic blueshift relative to that of bicarbonate. These results establish the detailed hydration properties of this short-lived molecule and will thereby facilitate future studies of carbonate chemistry in biological and geological system.

1. Introduction

Aqueous carbonic acid (H_2CO_3) is the centerpiece of both the global carbon cycle [1–3] and physiological buffer and respiration systems [4–6], yet it remains incompletely characterized despite enormous effort. As described in a very recent review [7], carbonic acid has been well studied in both the gas phase [8–10] and in cryogenic matrixes [11–15], but there have been very few successful spectroscopic studies of the *aqueous* acid, and none of its electronic structure [16–18]. Carbonic acid is intrinsically unstable upon contact with even a single water molecule, reacting via a proton chain mechanism to rapidly form aqueous bicarbonate, carbonate, and hydrated protons [19–21], which comprises the reversible mechanism for dissolution of CO_2 gas. Here we report the first measurement of X-ray absorption spectra for aqueous carbonic acid, enabled by the use of rapid-flow liquid microjet technology [22–24], wherein protonation of a bicarbonate solution continuously generates the acid as a function of pH under ambient conditions. We combine molecular dynamics (MD) simulations with a first principles density functional theory (DFT) method [25] to model and interpret the small (0.2 eV) measured blueshift of the carbonic acid π^* orbital in the C K-edge spectrum relative to that of bicarbonate [22], thereby gaining new and detailed insights into the nature of aqueous carbonic acid. We find that the two most stable isomers donate two strong hydrogen (H—) bonds to water oxygens and accept a stronger H-bond at the carbonyl and weaker H-bonds at the acidic oxygens, exhibiting an average hydration number of 3.17 as torsional motions rearrange the solvation structures. Because both gas phase and solid phase carbonic acid have been well studied, this work will facilitate the development of detailed models for the reversible gas-liquid chemistry of carbon dioxide.

Near edge X-ray absorption fine structure spectroscopy (NEXAFS), is an atom-specific probe of both the electronic structure of a molecule and its local chemical environment, making it a method of choice for detailed characterization of hydration interactions. Until very recently, NEXAFS studies of the carbonate system were restricted to gaseous CO_2 [26], and to carbonates adsorbed to a surface [27] or in various solid mineral forms [28] by the difficulties then inherent in addressing liquid samples by this high vacuum technology. In 2011, we reported the first NEXAFS study of *aqueous* carbonate and bicarbonate ions [22], which was followed by an X-ray emission study in 2014 [29]. In the present experiment, we follow an approach similar to that employed by Eberle et al. [16] in observing Raman spectra of aqueous H_2CO_3, enabled by the slow dehydration of carbonic acid ($k = 26.3\ s^{-1}$, $t_{1/2} = 26\ ms$) relative to the very rapid protonation rate of the

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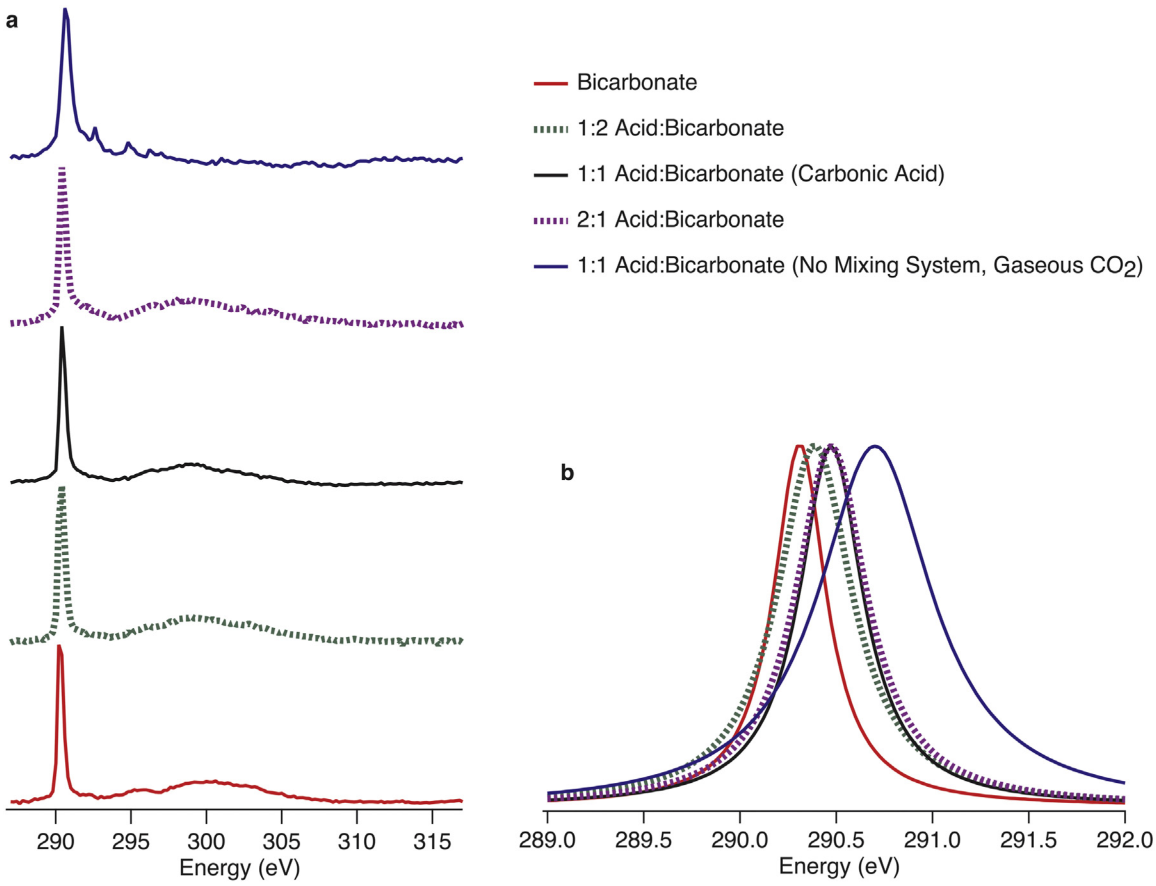

Figure 1. Peak-normalized experimental carbon K-edge X-ray absorption spectra. (a) Overview of measured spectra for bicarbonate (red), and the mixtures 1:2 HCl:$NaHCO_3$ (green), 1:1 HCl:$NaHCO_3$ (black), 2:1 HCl:$NaHCO_3$ (purple), and 1:1 HCl:$NaHCO_3$ without the mixing system (blue). (b) Lorentzian-fit experimental X-ray absorption spectra of the C(1s) → π^* transition in bicarbonate (red), 1:2 HCl:$NaHCO_3$ (green), 1:1 HCl:$NaHCO_3$ (black), 2:1 HCl:$NaHCO_3$ (purple), and 1:1 HCl:$NaHCO_3$ without the mixing system (blue). The maximum absorptions are at 288.31, 288.41, 288.49, 288.49, and 288.71 eV, respectively. All other spectra were measured using a sample introduced by the rapid-flow microjet mixing system.

bicarbonate anion ($k_{on} = 4.7 \times 10^{10}\ M^{-1}\ s^{-1}$, $t_{1/2} = 21.3$ ps) [17,30], which facilitates accumulation of carbonic acid. We combine a 0.5 M solution of $NaHCO_3$ with 1 M HCl in a high velocity liquid microjet mixing system to generate the acid at 25 °C.

2. Materials and methods

2.1. Sample preparation

Samples (0.5 M $NaHCO_3$ and 1 M HCl) were prepared using 18.2 MΩ cm resistivity water obtained from a Millipore purification system. Concentrated HCl (12.1 M) was obtained from J.T. Baker. $NaHCO_3$ with stated purity of at least 99.7% was commercially obtained from Sigma–Aldrich. Samples were used without further purification.

2.2. Experimental design

Carbon K-edge total electron yield (TEY) spectra were collected at Beamline 8.0.1. A detailed description of the experimental setup has been published previously [31]. Briefly, an intense (>10^{11} photons/s), high resolution ($E/\Delta E = 7000$), tunable soft X-ray beam is generated from an undulator at the ALS. The beam is focused (100 × 35 μm spot size) onto the liquid microjet. A dual syringe pump system (Teledyne-ISCO 260D) drives the solution through 30–50 μm inner diameter fused silica tubing to generate the liquid microjet with high linear flow velocities (1–200 m/s) that is intersected with the X-ray beam in the high vacuum (~2×10^{-4} Torr) chamber.

Solutions are typically mixed shortly after the pump. The mixed solution then travels through several meters of PEEK tubing (~7.5 min mixing time) before reaching the silica capillary. The long mixing time associated with this 'standard' experimental setup precluded studies of short-lived intermediate species such as carbonic acid. To transcend this limitation, a new fast-flow microjet mixing system was designed to mix the two solutions immediately prior to the generation of the fast-flowing liquid jet. A Hastelloy Microvolume Y-Connector was mounted inside the vacuum chamber and used to generate the liquid jet. To introduce the sample, two of the openings in the connector were attached directly to the syringe pumps with PEEK tubing. The third was used to hold the silica capillary and generate the liquid jet. The mixing time in this scheme was shortened to ~0.5 ms, thereby facilitating the observation of short-lived species in solution. This time is shorter than the previously measured half-life of carbonic acid (~26 ms) [16] but significantly longer than the measured rate for the proton transfer to bicarbonate ($k_{on} = 4.7 \times 10^{10}\ M^{-1}\ s^{-1}$) [17,30]. The liquid jet then passes through a skimmer and freezes onto a cryogenic (liquid nitrogen) trap. A TEY signal is then collected as a function of photon energy (0.2 eV step size), with a positively biased (2.1 kV) copper electrode. Vapor phase TEY spectra were measured by positioning the microjet a few microns above or below the incident X-ray beam.