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The electronic structure of carbonate ion in aqueous solution studied by soft X-ray emission spectroscopy

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ABSTRACT

X-ray absorption and emission spectra of carbonate ions in aqueous solution were measured at two concentrations. The signals from the ion were extracted via selective excitation and background subtraction. The obtained spectral shape for the emission of the ion was well explained by DFT calculations.

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1. Introduction

Information concerning the electronic states of materials is valuable because valence electrons play an important role in determining material properties. It is of great interest to observe the electronic structure of molecules in solution to determine how they are affected by dissolution. However technical development is required to enable these observations. Carbonate ions were investigated in this study. It is known that there are four carbonate forms when carbon dioxide dissolves in water: CO_2 (aq.), H_2CO_3 , HCO_3^- , and CO_3^{2-} . When CO_2 molecules dissolve in water, carbonic acid forms according to the following equilibrium: $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$. Carbonic acid is a polyprotic acid and can take three forms: carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). Since the global carbon cycle includes the absorption of carbon dioxides into oceans [1], the study of carbon dioxide and its protonated forms in an aqueous solution is important for understanding climate change and ocean acidification [2]. In addition, the chemical state of carbon dioxide and its protonated forms in aqueous solution is required fundamental knowledge for improved understanding of photosynthesis and the development of artificial

photosynthesis. Therefore, it is important to identify the electronic structure of these ions under ambient conditions.

Herein, we report the first observation of the electronic structure of carbonate ions in aqueous Na_2CO_3 solution under ambient conditions using X-ray absorption and emission spectroscopy (XAS and XES, respectively). XAS and XES are direct methods for observing the valence electronic states of molecules. Over the last decade, XAS and XES have become applicable to liquid systems through newly developed instrumentation including liquid cells [3–5] and liquid jet techniques [6–9]. We developed a soft X-ray emission spectrometer combined with a liquid cell at BL17 at SPring-8 [10,11] and have studied various liquid systems using these instruments. For example, the C=O oxygen atoms in the carboxyl groups of liquid acetic acid were selectively observed by resonant excitation [12]; this technique was also used to observe the pH-dependent variation of the occupied valence state in aqueous solution [13].

In this study, we investigated the valence electronic structure of carbonate ions in aqueous solution using XAS and XES. The resonance peak of the carbonate ion was identified via the concentration dependence of the peak intensity. XES spectra were measured by tuning energy of the incident light at the resonance peak. In contrast to our previous reports on aqueous acetic acid [13], the peak is not well separated from the absorption structure of liquid water; hence, signal extraction was performed. The obtained XES spectra were compared with the XES spectrum calculated using StoBe-deMon DFT code, and the molecular orbitals of the measured XES peaks were assigned.

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2. Experimental

XAS and XES spectra were recorded at the SPring-8 synchrotron radiation facility using circularly polarized soft X-rays at beamline BL17SU [14]. A liquid flow cell with a 150 nm thick Au-coated thin-film SiC window was used to measure XES spectra of the samples under ambient conditions. Although a SiC window is more difficult to oxidize than SiN windows, the signal from the oxide that formed on the window was not negligible in this study. Therefore, we also measured background spectra using acetonitrile, which does not contain oxygen. The XES spectra were recorded using a slitless emission spectrometer, i.e., HEPA2.5. Details of the emission spectrometer and liquid flow cell used for these measurements are described elsewhere [11,12]. The XAS spectra were recorded as total fluorescence yield (TFY) using a standard 100 mm² Si photodiode (AXUV-100, IRD Inc.) that faced the window. The photoelectrons emitted from the window were eliminated using an electrically biased mesh screen placed in front of the photodiode. The shape of the XAS spectrum is affected by the saturation effect of the TFY method. The energy resolutions of the XAS and XES spectra were 0.1 eV and 0.27 eV, respectively. The obtained XAS and XES spectra were normalized to the intensity of the incident light detected by the photodiode located downstream of an M42 mirror, which is the optic used to focus the soft X-rays onto the liquid flow cell. Sample solutions were prepared by mixing ultra-pure water (Millipore Simpli Lab UV purification system) and Na₂CO₃ (Wako Pure Chemical Industries, Ltd., Japan). The concentrations of the aqueous solutions were 1.0 and 2.0 M; the pH values of these solutions were 11.6 and 11.7, respectively. All chemicals were used without further purification. Before and after the measurements, the pH values of the sample solutions were confirmed to be within ±0.1 of the reported values using a pH meter (Horiba F-54).

3. Results and discussion

It is known that carbonate can take four forms when carbon oxide dissolves in water: CO₂ (aq.), H₂CO₃, HCO₃⁻ and CO₃²⁻. Considering the equilibria between the three different carbonate forms (H₂CO₃, HCO₃⁻ and CO₃²⁻) and the hydration equilibrium between dissolved CO₂ and H₂CO₃, two dissociation constants exist: H₂CO₃^{*} ↔ HCO₃⁻ + H⁺; pK_{a1}(app) = 6.3 and HCO₃⁻ ↔ CO₃²⁻ + H⁺; pK_{a2} = 10.3 (H₂CO₃^{*} includes dissolved CO₂ and H₂CO₃). Since most H₂CO₃^{*} is present as dissolved CO₂, the mole fractions of the carbonate forms are represented by the curves shown in Fig. 1. We confirmed that more than 96% of the carbonate ions are in the CO₃²⁻ form in the prepared Na₂CO₃ aqueous solutions.

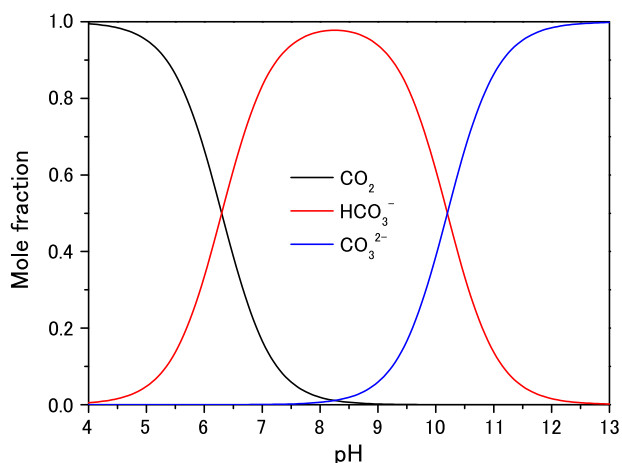


Fig. 1. Mole fractions of the three different carbonate forms, i.e., carbon dioxide, carbonate ion, and bicarbonate ion, as a function of pH.

Fig. 2 shows O 1s XAS spectra of the Na₂CO₃ aqueous solutions and of water and oxide on the membrane. In the XAS spectra of the aqueous solutions, shoulder peaks around 533 eV are evident and increase with the increasing sample concentration; this is considered to be the signal that corresponds to the carbonate ion. Background subtraction was performed on the spectrum of the more concentrated solution using the water spectrum; the resultant spectrum is shown in the bottom of Fig. 2. Since oxide is present on the window, the signal intensity of the oxide is free from the saturation effect and is constant for all the spectra in Fig. 2 except for the bottom spectrum, which had the oxide signals subtracted. An isolated peak is observed at 533.2 eV, which corresponds to the resonance peak of the carbonate ion. We chose 533.2 eV as the excitation energy for the XES measurements because the absorption intensity of the carbonate ion is strong while that of water is lower; this enables selective excitation of the carbonate ion.

Fig. 3 shows the XES spectra of Na₂CO₃ aqueous solutions and of water and oxide on the window of the liquid cell. All spectra were normalized to the intensity of incident light and contain oxide signals of the same intensity. The water spectrum does not resemble the spectra published in the literature [15]; this is because the excitation energy is much lower than that of reported spectra. The intensity of the XES spectrum increases with increasing sample concentration, which suggests that the signal from the carbonate ion is dominant. However, water is also excited by 533.2 eV incident light during XES measurement. Therefore, the obtained XES spectra contain emission signals from water in addition to those of the carbonate ions. In fact, there are three intersections at 520, 522, and 524 eV that indicate that these spectra consist of overlapping signals of two components, i.e., carbonate ions and water. These intersections can be observed because the intensities and shapes of the oxide signals are constant for all the XES spectra. In order to remove the water background signal from the XES spectra, we focused on the signal intensity between 511 and 515 eV. In this region, the spectral intensity of water is the highest and the intensity decreases when the concentration of carbonate ion increases. Therefore, the signal from water is considered to be dominant in this region. Thus, we subtracted the water background from the solution spectra by estimating the amount of water based on the intensity of the measured spectra between 511 and 514 eV. The water signal is subtracted from the spectra that have undergone oxide-background subtraction. The results are shown in the bottom of Fig. 3. The shapes of these spectra

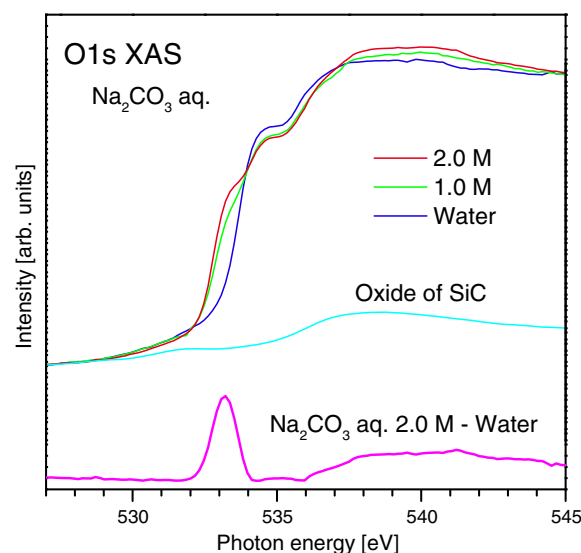


Fig. 2. O 1s XAS spectra of the Na₂CO₃ aqueous solutions. XAS spectra of pure water and oxide on the thin-film window are also plotted for reference. Bottom: Background-subtracted spectrum for the 2.0 M Na₂CO₃ solution. The resonance peak of the carbonate ion is at 533.2 eV.

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