

Identification of Valence Electronic States of Aqueous Acetic Acid in Acid-Base Equilibrium Using Site-Selective X-Ray Emission Spectroscopy

The electronic structure of a material is important for many fields of science, because valence electrons play important roles in properties of many systems including molecules in liquids and solutions. Due to its importance in chemistry and biology, recent studies have applied direct methods to observe electronic states of aqueous solutions. One characteristic phenomenon in the solution is deprotonation. Deprotonation plays an important role in many biological and chemical reactions. The pH dependence of chemical reactivity and property is known to be directly associated with geometric/steric and electronic changes accompanying deprotonation. Well-known examples include those of sulphuric acid, phenol, the helix structure of poly-L-glutamine, pH dependence of micellization, and pH-sensitive fluorescence of proteins. It is expected that the valence electrons contributing to the chemical bonding of hydrogen will undergo changes upon deprotonation. Hence, it is extremely important to study the occupied valence electronic structure of solutions in acid-base equilibrium.

The method we applied for the study of aqueous acetic acid solutions is X-ray emission spectroscopy (XES). In recent studies, XES was successfully used as a powerful element-selective tool to elucidate the electronic states of liquid water [1]. We have recently reported the site-selective observation of two oxygens in different chemical environments, namely, C=O and

OH, using resonant XES at the oxygen 1s edge for liquid acetic acid (CH_3COOH) under ambient conditions [2]. Using the site selectivity of resonant X-ray emission spectroscopy, we report here chemical-state-selective observations of the valence electronic states for acetic acid molecules in an aqueous solution. Furthermore, we report the systematic pH dependence of the occupied valence electronic structure of aqueous acetic acid solutions under ambient conditions. Acetic acid is a simple and common acid containing a single carboxyl group ($-\text{COOH}$) and has been well studied in terms of acid-base equilibrium. It represents a model case used to discuss deprotonation inducing the neutral to anionic transition.

X-ray absorption spectroscopy (XAS) and XES spectra were recorded using circularly polarized soft X-rays at beamline **BL17SU** [3]. Details of the emission spectrometer were reported elsewhere [4]. To perform a selective excitation XES of acetic acid molecules in solvent water, we have tuned the incident energy to the $\text{O}_{\text{C=O}} 1s \rightarrow \pi^*$ resonance excitation, which is absent in water (Fig. 1(a)). Figure 1(b) shows the XES spectra obtained for the samples at pH 0.29 and pH 11.44 [5]. The origin of the difference in spectral feature at pH 11.44 and pH 0.29 are readily explained by chemical equilibrium considerations. According to the well-known Henderson-Hasselbalch equation, more than 99.9% of acetic acid at pH 11.44

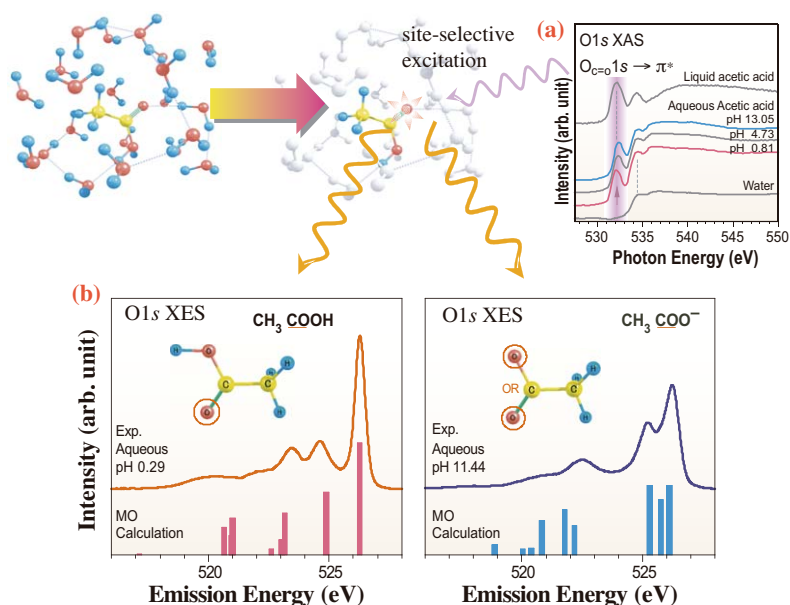


Fig. 1. Illustration showing site-selective excitation. Under non-resonant conditions, one cannot distinguish the oxygen atom of an acetic acid from that of water. Using resonant site-selective excitation, we can selectively excite the oxygen in the C=O structure of acetic acid molecule. (a) XAS spectra of liquid acetic acid, aqueous acetic acid and water. Excitation energy was tuned to the resonance peak structure indicated by an arrow. (b) Measured and calculated XES spectra of neutral (left) and ionic (right) acetic acid in aqueous solutions. Red circles indicate selectively excited oxygen atoms.

exists in the anionic form, while the neutral form predominates (more than 99.9%) at pH 0.29. The calculated energy levels for the XES spectra of neutral and anionic acetic acid, by performing density functional (DFT) calculations of XES spectra for both forms of the molecule using the ground state wave functions by the StoBe-deMon code, are also shown in Fig. 1(b). All peak structures in the experiment are well reproduced in the calculation with a small difference in energy position. From the XES spectra obtained at O_{C=O} 1s site-selective resonant excitation and comparison with the DFT calculation of XES spectra, it is confirmed that we could successfully extract the occupied valence electronic structure of the acetic acid molecules in aqueous solutions.

So far, valence electronic structures of anionic and neutral acetic acid under extreme pH conditions (strongly acidic and strongly basic) have been determined. It is interesting to examine the electronic structures under intermediate pH conditions, especially at a pH value of the acid dissociation constant, where the molar fraction of anionic and neutral acetic acid varies drastically and is therefore suspected to cause a spectral change through the interaction between the two species. In Fig. 2, we plot the area-normalized O 1s XES spectra of 2M acetic acid solutions obtained using an excitation energy of 532.1 eV. The spectra show systematic changes as a function of pH. Importantly, five isoemissive points are clearly observed (arrows in Fig. 2), indicating that the spectra consist of

the overlapping signals of neutral and anionic forms. In fact, the obtained XES spectra of intermediate pH values can be accurately reproduced by summing the spectra of the two forms. The reconstructed spectra show a residual error for an area under the curve of less than 6% for all the intermediate pH values. If the interaction between solute molecules is strong, the molecular electronic states can be perturbed by the interaction, and isoemissive points cannot be observed owing to the interaction between the two species. Thus, we conclude that the anionic and neutral forms of acetic acid in aqueous solutions do not interact with each other to form new states, and only the population of the two components changes depending on solution pH. As shown on the left side of Fig. 2, ratio analysis leads to a successful matching of molar fractions derived from XES spectra and the Henderson-Hasselbalch equation. This result shows the validity of quantitative analysis using XES and the non-interactive nature in terms of the electronic structure between the anionic and neutral forms of acetic acid molecules in an aqueous solution at a low concentration.

Since it is the first observation of the valence occupied electronic state of solute molecules in a solution using XES, we need to study other liquid and solution systems to establish this method as a tool for observing valence electronic states. However, we believe that this method will be a powerful tool for biological and chemical systems.

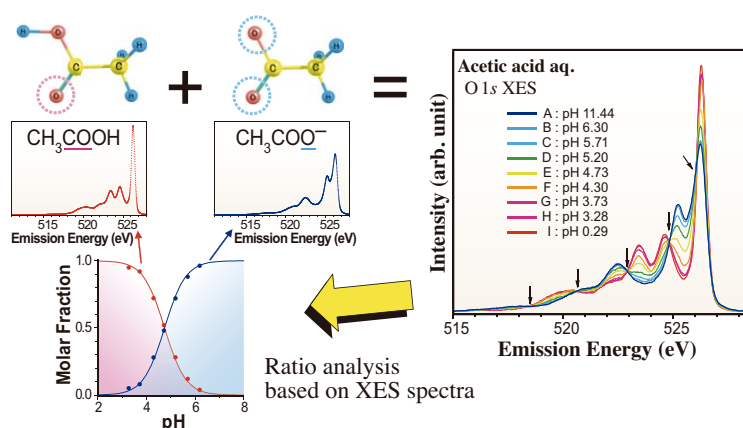


Fig. 2. pH dependence of XES spectra and molar fraction analysis. Each spectrum consists of two states and their molar fraction matches well with the values derived from the Henderson-Hasselbalch equation.

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