pH Dependence of Aqueous C2-C4 Dicarboxylic Acids by Soft X-ray Absorption Spectroscopy

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Soft X-ray absorption spectroscopy (XAS) is a spectroscopic technique that observes the excitation of inner-shell electrons to outer shells when X-rays are incident on a material. Because the absorption energy varies significantly depending on the element, element-selective excitation is possible. Since the 21st century, advances in measurement technology have enabled spectral measurements of soft X-ray absorption spectroscopy in liquid samples. XAS studies have been conducted on liquid samples such as water, alcohols, and aqueous solutions of organic acids. The behavior of substances in liquids is more complex than in the gas phase or solid state owing to intermolecular interactions. Furthermore, by varying the pH of the solution, changes due to the valence states can be observed. Our research group previously reported that the peak shift observed at approximately 532 eV in the pH-dependent XAS spectrum of oxalic acid, originating from the carbonyl oxygen, indicates resonance effects between the two carboxyl groups [1]. In this study, following the oxalic acid work, we targeted malonic, succinic, and maleic acids as our molecules of interest. Dicarboxylic acids play a crucial role in the metabolic pathways of living organisms. They also exist in the atmosphere and soil, with low-molecular-weight dicarboxylic acids such as oxalic, malonic, and succinic acids being abundant in atmospheric aerosols. Theoretical calculations of the pH-dependent XAS spectra of aqueous solutions of malonic, succinic, and maleic acids were performed, and the spectra were analyzed.

After conducting conformational searches using the CONFLEX program, structural optimization and vibrational frequency calculations were performed using Gaussian. The most stable conformation was determined by comparing the energies of the different conformations. To account for stabilization via hydrogen bonding with water molecules, conformational search calculations were performed for one dicarboxylic acid molecule and multiple water molecules in the system.

MD simulations were conducted using GROMACS. The force constants for bond stretching and bending, and bond angle changes required for the simulation were calculated by plotting the energy change when the bond length was varied by 0.01 Å or the bond angle by 2° and, then fitting the data to a quadratic function. The

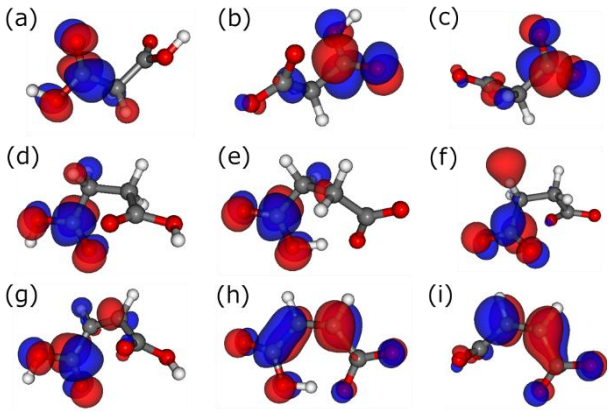

FIGURE 1. π* orbital of (a) neutral (b) anionic (c) dianionic malonic acid and (d) neutral (e) anionic (f) dianionic succinic acid and (g) neutral (h) anionic (i) dianionic maleic acid.

charge parameters were obtained using the RESP method with Gaussian. Simulations were performed at 300 K with a time step of 0.1 fs for 20 ps in the NVT ensemble, followed by 10 ns in the NPT ensemble. From the MD simulation results, a cluster structure composed of one dicarboxylic acid molecule and surrounding water molecules was obtained. XAS calculations were performed using deMon2k. The obtained line spectrum was convolved with a Gaussian function and averaged to obtain the theoretical spectrum.

Figure 1 shows the most stable conformations and π* orbitals of the excited states of neutral, anionic, and dianionic malonic, succinic, and maleic acids. For neutral maleic acid, the conformation with intramolecular hydrogen bonding was the most stable in a single molecule. However, when water molecules were arranged around it, the conformation without intramolecular hydrogen bonding became stable because of stabilization via hydrogen bonding with the water molecules. Figure 2 shows the XAS spectra obtained for the most stable conformations. Theoretical calculations reproduced the relative energy of the first peak in the XAS spectrum. With increasing pH, a high-energy shift of approximately 0.3 eV was observed in the malonic acid aqueous solution and approximately 0.2 eV in the succinic acid aqueous solution, respectively. This is thought to result from the deprotonation of the carboxyl group, similar to the behavior observed in acetic acid aqueous solutions [2]. In contrast, in the maleic acid aqueous solution, the peak for anionic maleic acid appeared at a lower energy than the peaks for neutral and dianionic maleic acids. This differs from the spectrum of oxalic acid aqueous solution, where those for dianionic oxalic acid shows a large high-energy shift. This peak behavior is thought to result from the stereoisomerism adopted by maleic acid in aqueous solutions, which varies with its valence. Anionic maleic acid adopts a planar conformation owing to intramolecular hydrogen bonding, leading to delocalization of the π* orbital via resonance (Figure 1). Consequently, compared to neutral and dianionic maleic acids where no π* orbital resonance is observed owing to the twisting of the carboxyl group, the peak of anionic maleic acid appears at a lower energy. Malonic and succinic acids did not adopt planar conformation. Consequently, the π* orbital localizes on one side of the carboxyl group, and thus, it does not exhibit the same peak behavior as maleic acid. The steric arrangement between the two carboxyl groups is thought to contribute to the peak behavior observed in the pH-dependent XAS spectra.

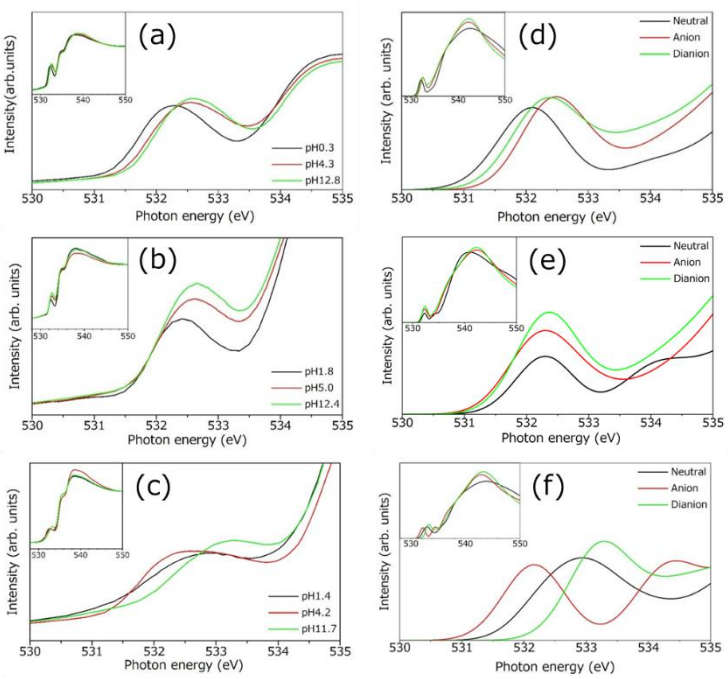

FIGURE 2. Experimental XAS spectra of aqueous (a)malonic (b)succinic (c)maleic acid and theoretical XAS spectra of aqueous (d)malonic (e)succinic (f)maleic acid.

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