Structure of maleic and succinic acid in aqueous solution by soft X-ray absorption spectroscopy

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In our laboratory, we have performed X-ray absorption spectroscopy (XAS) spectral calculations of a series of monocarboxylic and dicarboxylic acids aqueous solutions, and discussed the structures of the acids. In the XAS spectra of oxalic acid, the first peak at 532 eV was blue-shifts due to the break of the orbital π resonance caused by the twisting of the carboxylic group with increasing pH [1]. In this study, we performed theoretical XAS calculations for maleic and succinic acids, which include four carbon atoms in the molecule, and investigated their structures in aqueous solution.

Succinic and maleic acids have multiple stable conformations depending on the orientation of the substituent, so the most stable conformations were determined for neutral, anionic, and dianionic acids, respectively. From the molecular dynamics (MD) simulations at 300 K and 1 bar under the NPT ensemble, a cluster structure consisting of a dicarboxylic acid molecule and 30 water molecules around it was extracted, and XAS spectra were calculated for the cluster structure and compared with experimental spectra. Experimental XAS spectra at the O K-edge were measured at room temperature and atmospheric pressure at the soft X-ray beamline BL17SU at SPring-8. 0.3 M aqueous succinic acid at pH 0.01, 4.98, and 12.37 and 0.2 M aqueous maleic acid at pH 1.38, 4.16, and 11.70 were prepared.

Fig. 1 shows the experimental and theoretical XAS spectra of aqueous succinic and maleic acid. In the XAS spectra of aqueous succinic acid, the first peak around 533 eV shifts to higher energy with increasing pH, similar to acetic acid and malonic acid. In contrast, in aqueous maleic acid, the peak of neutral maleic acid is seen at a higher energy than the peak of anionic maleic acid. The XAS spectra of both succinic and maleic acid were theoretically reproduced. XAS spectra were calculated for a single molecule of neutral maleic acid by rotating the carboxy group, and it was confirmed that the peak shifts to higher energy as the carboxy group becomes more perpendicular to the molecular plane and the orbital resonance between the two carboxy groups is broken. This suggests that the orbital resonance between the carboxy groups is broken, so that the first peak of neutral maleic acid appears on the high energy side.

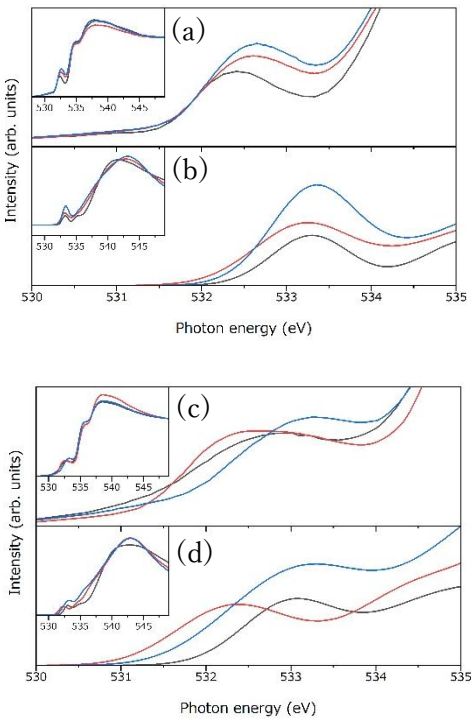

FIGURE 1. (a) experimental and (b) theoretical XAS spectra of aqueous succinic and (c) experimental and (d) theoretical XAS spectra of aqueous maleic acid.

REFERENCES

1. Yamamura, R et al, *Chem. Phys. Lett*, **738**, 136895 (2020).