

Spectral Changes of Phosphates from Solid to Liquid Phases in Oxygen K-edge X-ray Absorption Spectroscopy

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1 Introduction

High-energy phosphoric compounds have important roles for energy production and transport in most living cells. For understanding the mechanism of biological phenomena, it is necessary to correlate the reactivity of phosphate groups. X-ray absorption spectroscopy (XAS) can observe the electronic structures of phosphates, but the P K-edge XAS spectra in the hard X-ray region show small spectral differences among different phosphates and minimal spectral changes from solid to liquid phases [1]. The electronic structures of P=O orbitals in phosphate groups can be observed using the O K-edge XAS in the soft X-ray region [2, 3]. In this study, the double-bond character of phosphates in the solid and liquid phases was investigated based on the P=O π^* peaks observed in O K-edge XAS [4].

2 Experiment

The XAS experiments of phosphates in liquid phases were performed at the soft X-ray beamline BL-7A, utilizing a transmission-type liquid cell comprising two 100 nm-thick Si₃N₄ membranes [5]. The phosphate ions were prepared based on the pH titration, where aqueous Na₃PO₄ solution with pH of 12.22 was prepared by neutralizing 200 mM phosphoric acid with 1 M NaOH. For comparison, the XAS spectra of solid phosphates in the total electron yield were obtained at the soft X-ray beamline BL3U of UVSOR.

3 Results and Discussion

Figure 1 shows the O K-edge XAS spectra of aqueous Na₃PO₄ solution and solid Na₃PO₄. The XAS spectrum of solid Na₃PO₄ exhibits the prominent P=O π^* peak at 532.3 eV and the shoulder peak at 533.4 eV. It means that the double-bond character of PO₄³⁻ ions is large in the solid phase. By contrast, no P=O π^* peaks were observed in the XAS spectrum of aqueous Na₃PO₄ solution. Likewise, the P=O π^* peaks were not observed for other phosphates in aqueous solutions. Because the concentration of aqueous Na₃PO₄ solution (133 mM) exceeds the detection threshold (100 mM), the double-bond character of PO₄³⁻ ions is substantially decreased in aqueous solution. Note that

strong absorbance around 535 eV corresponds to the pre-edge peak of liquid water.

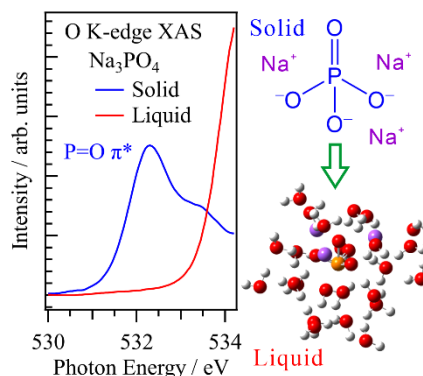


Fig. 1: O K-edge XAS spectra of aqueous Na₃PO₄ solutions and solid Na₃PO₄.

For analyzing the changes in the double-bond character of phosphate groups from solid to liquid phases, the inner-shell spectrum of aqueous Na₃PO₄ solution was calculated using the 1100 molecular structures extracted from the snapshots of the molecular dynamics simulation, which includes the deviation of liquid structures [6]. The intensities of the P=O π^* peaks in aqueous Na₃PO₄ solution were drastically decreased compared to those in solid Na₃PO₄ and isolated PO₄³⁻ ions, which were consistent with the XAS spectra shown in Fig. 1. These results indicate that the double-bond character of phosphate ions is decreased by the interaction of Na⁺ ions and the formation of hydration structures.

References

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