

XAS Measurements and Simulations for Aqueous Solutions of Organic Compounds

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Keywords: X-ray absorption spectroscopy; Aqueous solution; Ionic liquid; Metal acetate

Soft X-ray absorption spectroscopy (XAS) is an effective method to study local structures around excited atoms in liquid samples. In this study, N K-edge and C K-edge XAS measurements were conducted for liquid samples at BL3U at UVSOR and BL7A at PF using an apparatus developed by Nagasaka et al. [1]. A liquid sample cell equipped with a Si₃N₄ (SiC) membrane was used, and the thickness of the liquid layer was controlled by the He gas pressure surrounding the cell. The N-K edge XAS spectra for aqueous solutions of 1-ethyl-3-methylimidazolium chloride (EmimCl) at concentrations of 0.20 M and 0.10 M are shown in Figure 1. A clear peak at 401.0 eV was observed. This peak was found to be characteristic of the nitrogen atoms in imidazolium, independent of the concentration or substituents. Additionally, N-K edge XAS spectra for other related nitrogen-containing molecules were measured, revealing that the peak position is dependent on the charge of the nitrogen atom.

For the analysis of obtained spectra, advanced theoretical calculations of the XAS spectra have been carried out using the finite differences method near-edge structure (FDMNES) program starting from the optimized structures of isolated molecules (B3LYP/6 -31G) using Gaussian 16. The simulation spectra of isolated EmimCl are shown in Figure 2. The results can fit the characteristic peaks of experimental data and the π^* , σ^* peaks of absorbing atoms and energy shifts are discussed.

1) Nagasaka, Masanari, et al., *J. Electrosc. Relat. Phenom.* **2010**, 177, 130.

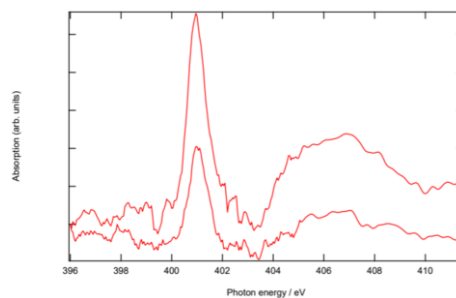


Fig. 1. N-K XAS spectra measured for EmimCl aqueous solutions (Upper 0.20 M, Lower 0.10 M)

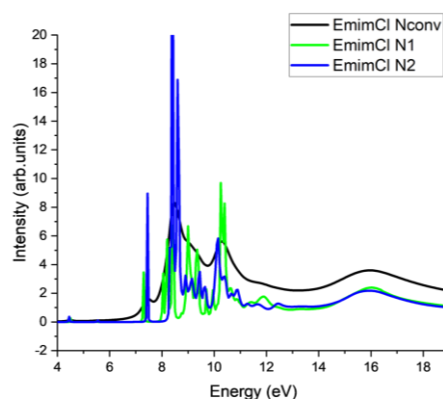


Fig. 2. N-K XAS simulation spectra for isolated EmimCl. Blue/Green curve: spectrum of each N atom. Black curve: convolution spectrum.