

Resonant Inelastic Scattering Spectra of Ionic Liquid

Kaname Kanai¹, Daiki Haratake¹, Yukio Ouchi², Hideharu Niwa³, Masaki Kobayashi^{3,4},
Yoshihisa Harada^{3,4} and Masaharu Oshima^{3,4}

¹Department of Physics, Tokyo University of Science

²Department of Chemistry, Graduate School of Science, Nagoya University

³Department of Applied Chemistry, School of Engineering, The University of Tokyo

⁴Synchrotron Radiation Research Organization, The University of Tokyo

Ionic liquids (ILs) are salts that consist of cations (usually organic) and anions (either inorganic or organic). The molecular structures of cation bmim^+ and anions TFSI^- , OTf^- are displayed in Fig. 1 we have studied in this work. ILs are liquid below 100 °C, or even at room temperature. ILs have been gathering much interest due to their unusual and interesting physical properties which are attractive in chemical and industrial applications such as electrochemistry, organic synthesis, catalysis and green chemistry. Especially, ILs form a new class of solvents with many advantages such as negligible vapor pressure, thermal stability, large electrochemical window, high solubility and miscibility with most inorganic and organic materials.

The structure and electronic structure of ILs are also interesting subjects of basic research. Although they are liquids, the ions are weakly coordinated. Bulk and surface structures of ILs have been studied by many techniques such as sum-frequency generation, x-ray reflection, Raman spectroscopy, direct recoil spectrometry and neutron scattering. On the other hand, study on the electronic structure of ILs has been limited, although information of the electronic structure should be useful for the design of new ILs, especially for electrochemical applications. The authors have reported that the soft x-ray emission spectroscopy is quite useful to probe the electronic structure of ILs due to its site-selectivity^[1,2]. We showed that the non-resonant SXES provides us detailed information about the occupied partial density of states for cation and anion that are forming IL.

In this works the resonant inelastic soft x-ray inelastic scattering (RIXS) have been performed to investigate the ultrafast dynamics of the molecule during the recombination process, especially the vibrational excitations in the ground state of the cation for ILs.

The RIXS spectrum for $[\text{bmim}]\text{PF}_6$ is shown in Fig. 2 (top spectrum) cited from the previously reported work^[1], which was measured at the N 1s-edge. The abscissa is the energy loss measured from the elastic peak. The excitation energy of $h\nu = 402.4$ eV corresponds to the strong N 1s $\rightarrow\pi^*$ absorption energy. Long low-energy tail of the elastic peak is observed which reaches to 3 eV of the energy loss. Similar large tailing of elastic peaks were also reported in RIXS spectra of the light elements solids and originally discussed on the x-ray recombination process in C 1s SXES spectra of diamond and graphite by Ma *et al.* Such low-energy tail is interpreted as caused by participator decay and this feature provides us information about the dynamics of the molecule during the recombination process. Recently, Hennies and coworkers reported the well-resolved vibrational progression in RIXS spectra for free molecules O_2 .^[2] Similarly, the result for $[\text{bmim}]\text{PF}_6$ in Fig. 2 gives us an opportunity to

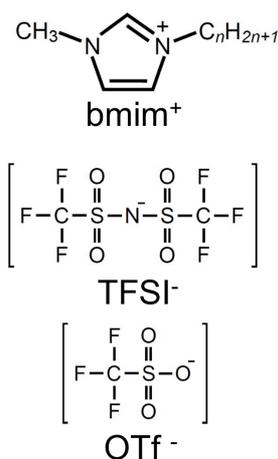


Fig. 1. Molecular structures of bmim^+ cation and TFSI^- and OTf^- anions.

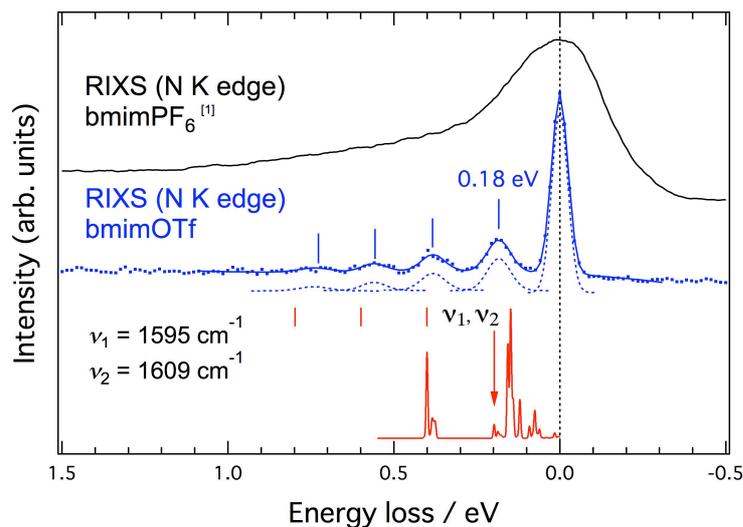


Fig. 2. Comparison between the experimental RIXS spectra for bmimPF₆ (top), bmimOTf (middle) and simulated normal vibration spectrum (bottom). The result for bmimPF₆ is cited from the literature^[1].

BL07LSU made it possible to resolve such fine structures. The observed vibrational progression is spanning about 1 eV of the energy loss range. The shape of vibrational peaks is symmetric and can be deconvoluted by almost pure Gaussians. Similar result for [bmim]TFSI is presented in Fig. 3. The RIXS was obtained with $h\nu = 401.6$ eV. The RIXS spectrum also shows a well-resolved vibrational structures. To compare the RIXS results with the theoretical results, the simulated normal vibration spectra are given at the bottom of the figures. One of the advantages for the RIXS at investigation of the molecular vibration is site-selectivity. An arrow in the Figs. 2 and 3 points the normal vibrations ν_1 and ν_2 where the nitrogen in the imidazolium moiety participates in. From the normal vibration analysis both ν_1 and ν_2 modes is caused by the out-of-plane vibration of the imidazolium ring accompanied by bending of C=N bonds and they are almost degenerate. The vibrational energy for ν_1 and ν_2 is about 0.2 eV, which is slightly larger than the observed interval ~ 0.18 eV in the RIXS spectra. More detailed analysis is needed by a help of the theory in near future to reveal the nature of molecular dynamics of bmim⁺ cation in the intermediate states of the resonant process.

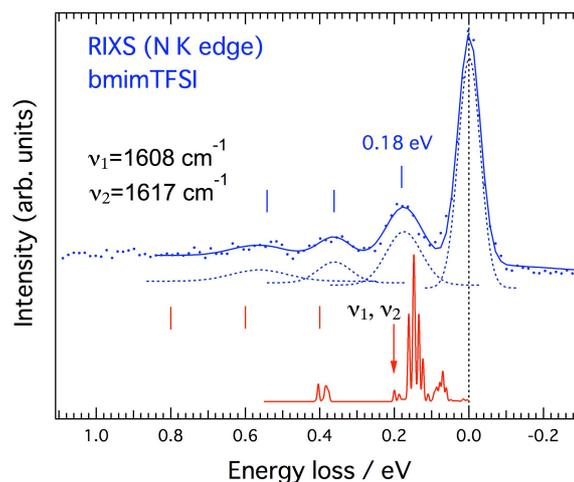


Fig. 3. Comparison between the experimental RIXS spectra for bmimTFSI (top) and simulated normal vibration spectrum (bottom).

discuss the dynamics of the large molecule as for more simple molecule (gas phase O₂). However, we are suffering from the unresolved tail of the elastic peak.

The RIXS spectrum of [bmim]OTf observed at $h\nu = 401.6$ eV where the strong N $1s \rightarrow \pi^*$ resonance occurs is presented in Fig. 2 (middle spectrum) measured in this work at SPring-8 BL07LSU. We have well resolved a series of vibrational fine structures with energy interval of ~ 0.18 eV. The cation is the same with [bmim]PF₆ and dramatically improved energy resolution in

References

- [1] K. Kanai *et al.*, *J. Chem. Phys.*, **129**, 224507 (2008); K. Kanai *et al.*, *J. Electron Spectrosc. Relat. Phenom.*, **174**, 110 (2009). [2] F. Hennies *et al.*, *Phys. Rev. Lett.*, **104**, 193002 (2010).