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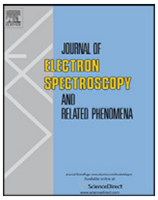

Electronic structures of imidazolium-based ionic liquids

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ABSTRACT

Electronic structures of ionic liquids formed by 1-buthyl-3-alkylimidazolium ion $[C_n mim]^+$ ($n = 4$ and 8) with various inorganic and organic anions have been investigated by ultraviolet photoemission, X-ray photoemission, inverse photoemission and soft X-ray emission spectroscopies (SXES). The comparison of the calculated density of states with the observed spectra revealed that the molecular orbital energies of these ionic liquids are significantly affected by the electrostatic Madelung potential among the ions. The SXES results clearly show that the both highest occupied and lowest unoccupied states of $[C_4mim]^+PF_6^-$ are derived from the cation as a result of strong Madelung potential. On the other hand, the SXES results show the valence electronic structures of ionic liquids with larger anion molecules, $[C_n mim]^+Tf_2N^-$ and $[C_n mim]^+OTf^-$ are contributed from the both cation and anion.

1. Introduction

Ionic liquids (ILs) are salts in liquid phase at room temperature. ILs consist of cations (usually organic) and inorganic or organic anions. ILs have been attracting much interest due to their unique and interesting physical properties which are attractive in chemical and industrial applications such as electrochemistry, organic synthesis, catalysis and green chemistry [1–4]. 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 [5–8]. The structure and electronic structure of ILs are also interesting subjects for basic research. Bulk and surface structures of ILs have been studied by many techniques such as sum-frequency generation [9–11], X-ray reflection [12], Raman spectroscopy [13], direct recoil spectrometry [14] and neutron scattering [15,16]. On the other hand, there have been few studies on the electronic structure of ILs. Detailed information of the electronic structure is useful for the synthesis of new ILs, especially for electrochemical applications.

Yoshimura et al. reported the studies on the electronic structure of ILs, $[C_4mim]^+PF_6^-$, $[C_4mim]^+BF_4^-$ and $[C_4mim]^+OTf^-$, where $[C_4mim]^+$ stands for methylbutylimidazolium cation, by ultraviolet photoemission spectroscopy (UPS) [17]. Their conclusion is that the highest occupied state of these ILs is contributed from the highest occupied molecular orbital (HOMO) of the $[C_4mim]^+$ cation by comparing the observed UPS spectra with the simulated spectra which were obtained by overlapping the calculated density of states (DOS) of the cation and anion based on the density functional theory (DFT) calculations. In Ref. [17] they employed a simple analysis method where the energy axes of calculated DOS for the cation and anion were individually shifted to best explain the observed UPS spectra. This shift in the energy axes is correlated with the electrostatic potential (Madelung potential) among the ions. On the other hand, Krischok et al. reported that the highest occupied state of IL, $[C_2mim]^+[Tf_2N]^-$ is contributed from $[Tf_2N]^-$ anion by comparing the observed UPS, X-ray photoemission spectroscopy (XPS) and metastable-induced electron spectroscopy with the simulated spectra by DFT calculations [18,19]. However, there remains some ambiguity in assignments of photoemission spectra of IL to calculated molecular orbitals (MOs) of the cation and anion because of severe overlap of the contributions from the cation and anion to the spectra. In order to remove such ambiguity we applied soft X-ray emission spectroscopy (SXES) to ILs. SXES spectrum is obtained by the detection of soft X-ray emitted after the relaxation of a core hole generated by incident soft X-ray. SXES is powerful tool to probe the valence electronic structure in wide range of materials since it provides element- and orbital-specific information of the valence electronic structure [20]. The schematic of the SXES optical processes in non-resonant mode (normal SXES) are shown in Fig. 1. When the excitation energy is enough above the ionization threshold of a particular atom (N in the case of Fig. 1), we obtain normal SXES spectrum that provides information about the par-

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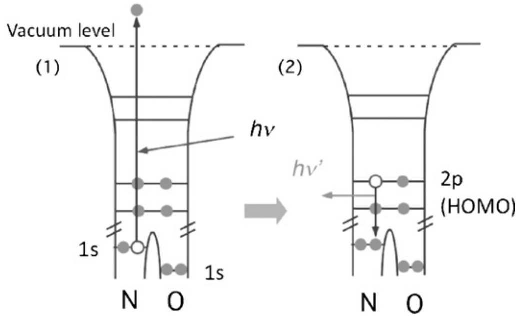

Fig. 1. Schematic of normal SXES optical process. (1) The 1s core electron (N 1s electron in this case) is excited by incident soft X-ray into the continuum above the vacuum level. (2) The valence 2p electron decays into the 1s core hole with soft X-ray emission.

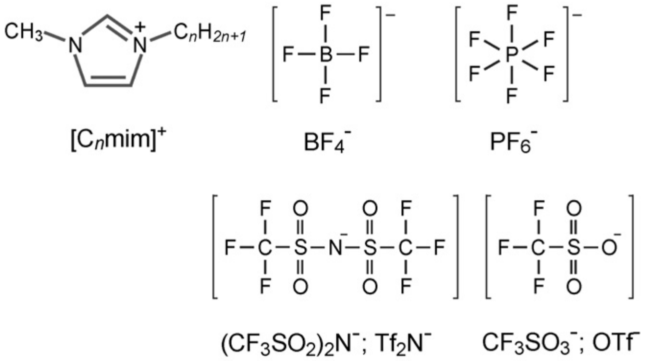

Fig. 2. The molecular structures of $[C_4mim]^+$ cation, BF_4^- anion, PF_6^- anion, Tf_2N^- anion, and OTf^- anion.

tial density of states (PDOS) of a particular atom according to the dipole selection rule. Normal SXES spectrum measured above 1s-absorption edge provides the PDOS for the contribution from the p states [21–23]. Such element- and orbital-specificity makes SXES attractive for the investigation of complex electronic structure of ILs.

In this study, UPS, XPS, inverse photoemission spectroscopy (IPES), and SXES were applied to typical ILs having the imidazolium-based $[C_nmim]^+$ ($n = 4$ and 8) cation and Br^-, PF_6^-, Tf_2N, and OTf^- anions (the molecular structures are shown in Fig. 2). The normal SXES above the N 1s-, the F 1s- and O 1s-edges clearly provided replicas of the DOS for the cation and anions. The comparison between the normal SXES results and calculated DOS shows the cation's HOMO contributes to the highest occupied state of $[C_4mim]^+PF_6^-$, while both the cation's and anion's DOS are overlapped at the valence states of $[C_4mim]^+Tf_2N^-$ and $[C_4mim]^+OTf^-$.

2. Experimental

ILs were synthesized according to literature with a slight modification. Details of the synthesis were presented elsewhere [10,11]. The purities of the ILs were checked by using ^{1}H-NMR and UV–visible absorbance spectroscopies and it was confirmed that the ILs were pure enough to be applied to spectroscopic analysis. Water content of the ILs determined by Karl Fischer titration was less than 60 ppm.

SXES of ILs were performed in BL17SU of SPring-8 [24]. The SXES measurements were carried out with a high efficiency soft X-ray emission spectrometer [25]. The energy resolution of SXES measurement system is better than 0.3 eV around the N 1s-absorption edge. The typical pressure of measurement chamber is about 3×10^{-5} Pa. UPS and XPS measurements were performed by ESCA probe-MK III (Omicron) with He I resonance line ($h\nu = 21.22$ eV) and monochromatic X-ray (Mg Kα, $h\nu = 1253.6$ eV), respectively. Photoelectron energy of XPS spectra was carefully calibrated using the energy positions of Au $4f_{5/2,7/2}$ photoemission lines. The typical pressure of the measurement chamber is about 2×10^{-9} Pa. The IPES measurements were performed in isochromat mode using a homemade apparatus. The bandpass-type photon detector at $h\nu = 9.2$ eV consists of a channeltron coated with KCl and placed behind a SrF_2 window. A low-energy electron gun was used to produce a monoenergetic electron beam. The pressure of the measurement chamber is less than 1×10^{-7} Pa.

The specimens for the measurements were prepared by putting a droplet of IL onto scratched Au substrates. After the preparation the specimens were immediately introduced into the vacuum chamber. The cleanliness of synthesized ILs was checked by monitoring absence of O 1s signal in XPS spectra. The MO calculation for the isolated ions is performed by the program GAUSSIAN 98 with B3LYP parameters and 6–311G basis set. The calculated DOS was obtained by broadening the calculated MOs with 0.6 eV FWHM to reproduce the observed spectra.

3. Results and discussion

3.1. Electronic structure of $[C_8mim]^+Br^-$ and $[C_8mim]^+BF_4^-$

Fig. 3 shows the comparison of UPS, IPES spectra between $[C_8mim]^+BF_4^-$ and $[C_8mim]^+Br^-$. In the UPS spectrum of $[C_8mim]^+Br^-$, a distinct peak is observed at 3.5 eV unlike with that of $[C_8mim]^+BF_4^-$. The estimated energy gaps by the onset of the spectra of $[C_8mim]^+BF_4^-$ and $[C_8mim]^+Br^-$ are 9.1 and 5.3 eV, respectively. The energy gap of $[C_8mim]^+Br^-$ is much smaller than that of $[C_8mim]^+BF_4^-$ due to lower biding energy of the highest occupied state. The valence region of $[C_8mim]^+Br^-$ measured by XPS is shown in Fig. 4. The UPS spectrum is also presented for comparison. The photoionization cross-sections σ of C 2p and N 2p orbitals at photon energy of 1253.6 eV are very small (σ(C 2p) ~ 1.0×10^{-5} and σ(N 2p) ~ 7.2×10^{-5} Mb) [26]. Therefore, we are scarcely able to observe the photoemission from valence states derived from $[C_8mim]^+$ cation. On the other hand, the photoionization cross-section of Br 4p orbital is 4.5×10^{-3} Mb, which is more than a hundred times as large as that of C 2p. The XPS spectrum also shows a distinct peak at 3.5 eV. By taking the fact photoionization

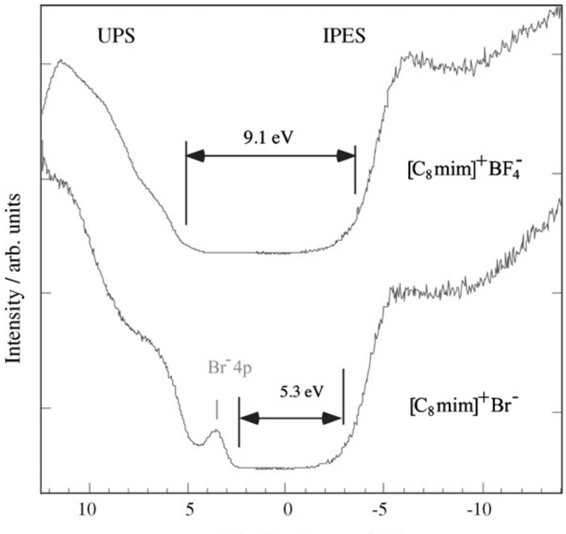

Fig. 3. The UPS and IPES spectra of $[C_8mim]^+BF_4^-$ and $[C_8mim]^+Br^-$. The vertical bars point at the onset of the spectra.