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X-ray-induced fragmentation of imidazolium-based ionic liquids studied by soft x-ray absorption spectroscopy

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Abstract

We investigated the x-ray absorption spectroscopy (XAS) fingerprint of EMImTFSI ionic liquid (IL) and its fragmentation products created by x-ray irradiation. To accomplish this, we used an open geometry where an IL droplet is directly exposed in the vacuum chamber, and an enclosed geometry where the IL is confined in a cell covered by an x-ray transparent membrane. In the open geometry, the XAS signature was stable and consistent with experimental and theoretical spectra reported in the literature. In contrast, when the IL is enclosed, its XAS evolved continuously under x-ray illumination due to accumulation of volatile fragmentation products inside the closed cell, while they evaporate in the open geometry. The changes in the XAS from the core levels of relevant elements (C, N, S, F) together with density functional theory (DFT) calculations, allowed us to identify the chemical nature of the fragment products and the chemical bonds most vulnerable to rupture under soft x-ray irradiation.

Key words: Ionic Liquids, Imidazolium, Beam Damage, X-ray absorption spectroscopy

Ionic liquids (ILs) are salt compounds that remain liquid at or near room temperature (e.g., $<100^{\circ}\text{C}$). They have promising industrial applications in lubrication,¹ catalysis,²⁻⁴ CO₂ capture,^{5,6} and energy storage.⁷⁻¹¹ In particular, ILs are considered as promising solvents because of their unique physical and chemical properties compared to traditional organic solvents, including low vapor pressure, good chemical and thermal stability, and potential recyclability.^{3,11,12} Moreover, countless combinations of cations and anions make it possible to design and optimize ILs with desired properties. To do so, however, requires a fundamental understanding of structure-property relationships in various ILs systems, especially under *in-situ* and *operando* conditions.

Many characterization techniques have been used to study different aspects of the physicochemical properties of ILs. For instance, vibrational spectroscopy provides insights on the nature of ionic interactions, anion-cation hydrogen bonds, and molecular conformation.¹³ X-ray and neutron scattering provides information about local molecular configuration.¹⁴⁻¹⁷ Electron spectroscopies, such as x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), provide chemical composition as well as chemical state information of the elements on the IL surface.¹⁸⁻²² Soft x-ray absorption/emission spectroscopy (XAS/XES) can access the K-shell orbitals of light elements such as C, N, O, and F, commonly present in various IL molecules. Recently, XAS/XES has received considerable attention as a powerful tool to characterize the electronic structure of ILs.^{20,23-26}

It is noteworthy that many of the above-mentioned techniques require highly energetic excitation sources such as x-rays, electrons, and neutrons, which are known to cause excitation-induced side reactions, particularly for organic compounds.²⁷ During *in-situ* and *operando* experiments, such side reactions and the resulting products may have a significant impact on the performance of the electrochemical system as well as the interpretation of reaction mechanisms. For this reason, it is essential to understand the potential chemical changes of IL molecules under irradiation, so that proper measures can be taken to avoid or minimize their effects.

The imidazolium-based ILs are among the most studied in the IL family and

have been recently examined using various characterization techniques including XAS/XES.^{24,26,28} In these experiments, thanks to their extremely low vapor pressure, ILs can be introduced directly into the high vacuum (HV) chamber in the form of droplets supported on a substrate. In this paper, we compare the XAS spectra of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) acquired in an open geometry where the x-ray induced fragmentation products can easily desorb and escape detection, with those obtained with the IL enclosed in a cell separated from the vacuum by x-ray transparent membranes (SiO_2 or Si_3N_4), commonly used in *in situ/operando* XAS measurements.^{29–31} In such closed geometry the fragment products remain in the cell and their XAS signatures can be obtained. As we shall see, important differences were observed in the spectra acquired using these two methods. From the results and in combination with XAS calculations, we were able to identify the chemical nature of the spectral variations of all the products and thus obtain a complete picture of the fragmentation reactions induced by soft x-ray irradiation.

Figure 1A shows structural models of the cation and anion components of the EMImTFSI molecule. For open geometry XAS measurements (Figure 1B), a droplet of IL on Au foil is directly introduced into the x-ray beam-line vacuum chamber. For the encapsulated IL approach, we used a home-made cell covered by an x-ray transparent window, as illustrated in Figure 1C (more details in SI). The XAS spectra were all collected in total fluorescence yield (TFY) mode at beamline (BL) 8.0.1 of the Advanced Light Source (ALS), the Berkeley synchrotron facility, except for the F K-edge measurements, some of which were acquired at ALS BL 6.3.1.2. Since the mean free path of soft x-ray photons is typically of the order of micrometers, the TFY-XAS can be considered a bulk-sensitive measurement.²⁸

The N K-edge XAS spectrum collected in the open geometry (bottom curve in Figure 2A and Figure S1A) agrees very well with reported XAS spectra in the literature.^{24,26} The sharp peak at 402 eV is characteristic of the transition from $\text{N}1s$ to the π^* orbital of the imidazolium ring.^{24,26} The other broader features shown in the peak deconvolution in Figure S1A originate from transitions to σ^* orbitals of both

cations and anions.^{24,26} Even after ~60 min exposure to the x-ray beam at BL8.0.1.3, the N K-edge spectrum remains unchanged with time within the probing depth of the TFY signal (~ μm). Using the closed cell however, the spectrum exhibits noticeable differences compared to the spectrum of the free IL in vacuum. Over the course of 120 min, the intensity of the sharp π^* resonance peak decreased while new features emerged, particularly two low-energy peaks at 398.9 and 400.0 eV, as shown in Figures 2A and S1.

The sharpness and energy of the two component peaks suggests that they are also related to transitions to N-containing π^* orbitals. It is reasonable therefore to assign them to some modified imidazole rings produced by x-rays. As experimentally demonstrated by Rodrigues et al.²⁴ when one alkyl chain on the imidazolium cation is removed and substituted by a H atom, the change in N K-edge spectra of the IL molecule depends on the anions. For bulky anions like TFSI⁻, very little change was observed in N K-edge spectra of H-substituted IL molecules; whereas for small and highly coordinating anions such as Cl⁻, a new peak emerges at an energy 1.4 eV below that of the main π^* peak. This new peak arises from the strong interaction between the highly acidic H atoms on the imidazole ring and the Cl⁻ anion, which substantially modifies the electronic density around the neighboring N atom and red-shifts the corresponding π^* peak. For the bulky TFSI⁻ anion, however, steric hindrance prevents its close encounter with the acidic H atoms on the imidazole ring. Therefore, simply replacing an alkyl chain with a H atom in EMImTFSI will not generate the observed low energy features. However, as will be shown later, x-ray irradiation can break C-F bonds in anions creating free F⁻ ions. These F⁻ ions, trapped in the liquid cell, can interact even more strongly with the acidic H atoms than Cl⁻ ions, producing a π^* peak with a large red shift.

Another possible category of products is radical cation species, whose alkyl chains are removed but without H substitution. To test this possibility, we followed the methods described in the literature^{28,26} to calculate XAS spectra for possible radical cation species. The calculations are based on density functional theory (DFT) in the Kohn–Sham scheme using a single-ion model, which proves to be sufficient to

predict the electronic structures and XAS peak positions of imidazolium-based IL molecules.^{24,26,28} We calculated the XAS spectra for N atoms in the cation (N1 + N2 in red), and in the anion (N3 in blue), separately (shown in Figure 2E). The sum spectrum (in grey) qualitatively matches the spectrum of intact EMImTFSI molecules. When one of the alkyl groups is removed from the cation, the π^* resonance of the intact N atom remains unchanged whereas the other N atom produces a broad compound peak around 400 eV (Figures 2B and C). When both alkyl groups are removed, the two N atoms become equivalent and produce a single peak at 399.4 eV, as shown in Figure 2D. The red shift of π^* resonance peak in all three species is the result of electron density loss in the π^* ring. We thus propose that these radical cation species are also products responsible for the observed low energy π^* peaks in N K-edge spectra. On this basis, we conclude that x-ray irradiation leads to cleavage of C-N bonds, with the consequent removal of the alkyl groups attached to the imidazole ring.

The N atoms in the TFSI⁻ anions, have relatively broad σ^* features overlapping with the σ^* features of the cation N atoms, making it difficult to extract information regarding the changes in TFSI⁻ anions under irradiation. However, XAS measurements of the S L-edge, C K-edge, and F K-edge provide evidence for chemical changes occurring in the anions under x-ray illumination, as shown in Figure 3. In Fig. 3A we show that the S L-edge spectrum collected in the open geometry exhibits only a single peak corresponding to the sulfonyl groups in the TFSI⁻ anions. After 120 min x-ray (~400 eV) exposure in the closed cell, two new peaks appear at 171 and 181.6 eV, possibly related to sulfate or sulfonic radicals.^{32,33} The C K-edge spectrum of presumably intact EMImTFSI molecules in the open geometry, as shown in Figure 3B, exhibits at least three prominent features around 287, 289, and 295 eV, which can be assigned to the π^* resonance of the imidazole ring, the σ^* resonance of the alkyl groups in the cations, and the σ^* resonance of $-\text{CF}_3$ groups in the anions, respectively.²⁶ After 120 min x-ray irradiation in the cell, the intensity of all three features decreased and a small low energy shoulder appeared around 285 eV. The decreasing intensity of the σ^* resonance of the alkyl groups is

consistent with the earlier conclusion of alkyl group removal from the imidazole ring. Such a conclusion is further corroborated by the emerging pre-edge feature around 285 eV, similarly related to the modified π^* orbitals in the altered imidazolium cations. The decrease of the peak around 295 eV clearly indicates that the TFSI anions lose CF_3 groups under x-ray irradiation.

In the F K-edge spectra, subtle changes in line shape occurred after 120 min of x-ray exposure in the cell (Figure 3C). Nevertheless, time-lapsed XAS measurements showed again continuous chemical changes to the F atoms in the anions under x-ray illumination. The time-lapsed XAS measurements were carried out using the same liquid cell at BL 6.3.1.2, where the photon flux (10^{11} photon/s) is about 2-3 orders of magnitude lower than BL 8.0.1. As can be seen in Figure S2, F K-edge spectra acquired at BL 6.3.1.2 have a noticeably higher noise level due to the lower signal, but still evolve across five consecutive spectra over the course of 60 min. As a comparison, the spectrum collected in the open geometry at BL6.3.1.2 exhibited almost identical line shape as the one acquired at BL8.0.1. The variation in F K-edge spectra indicates the occurrence of C-F breaking. However, each of the F K-edge spectrum show a broad feature that is difficult to deconvolute; therefore, no further attempts were made to determine the exact nature of these F species.

Combining all the information obtained from the XAS spectra discussed above, we can now describe the decomposition process of EMImTFSI under soft x-ray irradiation as summarized in Figure 4: a) both methyl and ethyl groups can detach from the imidazole ring of the cations; b) the N-S, S-C, and C-F bonds in the anions are also prone to cleavage; c) these bond-breaking processes produce many reactive fragments that can further react with each other and produce more stable compounds such as free imidazole molecules, imidazolium fluoride, alkanes (e.g., CH_4 and C_2H_6), fluorinated alkanes (e.g., CHF_3 and CH_3CF_3), and sulfate/sulfonic species.

With this picture in mind we can now explain the difference between the open geometry and the closed geometry in XAS spectra acquisition. When the droplet of ILs is directly exposed in the HV environment, the majority of the small molecules resulting from x-ray induced decomposition can readily escape into the vacuum,

leaving intact IL molecules in the droplet. The partial pressure of the decomposition products is too small in the vacuum environment, so that their contribution to the XAS signal is negligible. When enclosed in the liquid cell, however, the decomposition products cannot escape, except through a small opening in the O-ring located a few mm away from the illuminated portion of IL behind the x-ray transparent membrane. The high viscosity of ILs makes it even more difficult for these products to diffuse and dilute inside the IL droplet. As a result, some of these decomposition products are inevitably trapped inside the cell and contribute to the XAS signal.

The other important question is what causes the fragmentation to the IL molecules. Namely, is it due to x-ray photons or to secondary electrons generated by x-ray absorption? Although damage might be caused directly by the x-ray photons, it is well known that secondary electrons can also trigger reactions, especially in organic systems. The majority of the core holes (>99%) excited by soft x-ray photons decay through Auger and other secondary electron channels, generating large numbers of secondary electrons. These secondary electrons are therefore important contributors for the observed beam damage of the IL molecules. In addition, the x-ray transparent membrane can also produce secondary electrons, which may enhance the beam effect particularly at the solid/liquid interface.

To demonstrate the effect of high energy electrons on ILs, we carried out an experiment where small droplets of EMImTFSI IL were exposed to the electron beam (kinetic energy 5keV) of a scanning electron microscope (SEM). As can be seen in the consecutive SEM images (Figure S3), the pattern of the IL droplets kept changing and shrinking, vanishing after just 70 seconds of scanning. Shkrob et al. reported systematic electron paramagnetic resonance (EPR) studies on fragmentation of imidazolium-based ILs induced by an electron beam (3MeV) and found fragmentation pathways similar to what we have seen in our x-ray experiments.^{34,35} Such similarities indicate that the same chemical bonds are vulnerable under soft x-rays and electron beams and that the proposed fragmentation pathways may be universal under different types of high-energy excitations.

In conclusion, we used x-ray absorption spectroscopy to investigate how EMImTFSI IL decomposes under soft x-ray irradiation. The nature of the fragment products provides information of the most susceptible bonds to the broken following excitation. These include those in C-C bonds attaching the alkyl groups to the imidazole ring in the cations, and the chemical bonds in the anions. When the IL is exposed to the HV environment, the decomposition products can easily escape so that they are not detected. Inside closed cells these fragment molecules accumulate and can be detected in XAS spectra. Our findings can help understand the chemical stability of the various inter-molecular bonds in IL subjected to ionizing radiation. It also illustrates the cautionary precautions to be taken when utilizing x-ray and electron spectroscopies to characterize catalytic and electrochemical systems *in situ* and *operando*. Many of these *in situ/operando* studies are conducted using different types of closed cells,^{29–31,36,37} as a result, the secondary electrons from both the electrolyte and the solid membranes may have severe impact on the stability of the interfacial solvent molecules. One has to be extremely careful in these experiments to eliminate or minimize beam damage effect, particularly for organic solvent molecules. Possible precautions include reducing photon flux, reducing dead time in data collection, avoiding unnecessary exposure, and most importantly, performing necessary control experiments to examine the beam effect.³⁸

Associated Content

Supporting Information

Materials and sample preparation, XAS measurements and spectra analysis, calculation method of XAS spectra, SEM measurements, and supporting figures.

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Notes

The authors declare no competing financial interest.

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Figure 1. Schematic illustrations of (A) the molecular structure of EMImTFSI IL, (B) the open geometry and (C) the closed geometry in XAS measurements.

Figure 2. Experimental and simulated N K-edge XAS spectra. (A) Comparison of time-lapsed spectra acquired from an encapsulated IL sample with that acquired with the open IL droplet in vacuum (bottom). The collection time for each spectrum is about 12 min. (B-E) Simulated N K-edge spectra of intact IL molecules and various cation fragments. The molecular structure of the species in each simulation is displayed in the inset of each panel. The colors of the simulated spectra correspond to the N atoms marked with the same color. The grey spectrum is the sum of spectra from all the N atoms in each case.

Figure 3. Comparison of (A) S L-edge, (B) C K-edge, and (C) F K-edge XAS spectra acquired in open geometry (blue) and in a closed cell after 120 min x-ray irradiation (red).

Figure 4. Schematic illustration of x-ray-induced changes to anions (left) and cations (right) of EMImTFSI IL.

Supporting Information

Experimental

Materials and sample preparation

EMImTFSI (99.6% purity) IL was purchased from Ionic Liquids Technologies GmbH. Prior to XAS measurements, the IL was dried under vacuum at 120 °C and stored in an Ar glovebox. For the open-geometry XAS measurements, a droplet of IL (~50 μL) was cast onto a Au foil ($\sim 10 \times 10 \text{ mm}^2$) attached to a regular sample holder inside a glovebox and then sealed in a laminated Al foil pouch. Immediately before the measurements, the bag was cut open at the beamline and the sample was quickly transferred into the load-lock and pumped down. The exposure time in air was kept to just a few seconds to minimize reabsorption of moisture from the atmosphere.

For the liquid cell approach, the IL was enclosed in a liquid cell as illustrated in Figure 1C. The main body of the liquid cell (grey part in Figure 1C) is made of polyether ether ketone (PEEK). The liquid reservoir was covered with a x-ray transparent membrane, which was sandwiched between the stainless steel lid and a Viton O-ring. For IL measurements, the liquid cell was assembled inside a glovebox and transported in a laminated Al foil pouch to prevent reabsorption of water from the atmosphere. For measurements at BL 8.0.1, a SiO_2 membrane (300 nm in thickness, $0.5 \times 0.5 \text{ mm}^2$ in area, supported on a $5 \times 5 \text{ mm}^2$ Si frame) was used so that N K-edge XAS could be measured. For measurements at BL6.3.1.2, a conventional Si_3N_4 membrane (100 nm in thickness, $1 \times 1 \text{ mm}^2$ in area, supported on a $10 \times 10 \text{ mm}^2$ Si frame) was used instead. In addition, from our previous failed attempts, we noticed that x-ray irradiation can generate a lot of gaseous species in such IL measurements and substantially increase the pressure inside a sealed liquid cell, which makes the x-ray transparent window more vulnerable to break inside the vacuum chamber. Therefore, the O-ring was intentionally cut to provide pressure relief under x-ray irradiation.

XAS measurements and spectra analysis

The soft X-ray adsorption spectroscopy measurements were conducted at Beamline 8.0.1 and 6.3.1.2 in the Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL). TFY signal was collected using a negatively biased channeltron detector at both beamlines. All the XAS spectra were first normalized by the photon flux profile represented by a TEY current collected on a Au mesh in the upstream x-ray pipeline. After a linear background was subtracted from each spectrum based on

the slope of the pre-edge region, the spectra were normalized again by setting the pre-edge intensity to 0 and post-edge intensity to 1. For peak deconvolution, an arctan background was subtracted from the already processed spectra and Gaussian peaks were introduced to fit the overall shape of the spectra.

Calculation method of XAS spectra

The theoretical method used here for N K-edge XAS is the so-called transition potential method (TP-DFT)^{1–3} based on density functional theory (DFT) in the Kohn–Sham scheme. All results presented here were obtained using the CP2K program package⁴ based on a single ion model. In our calculations, we adopted the optimized geometry of the single ion reported by Horikawa et al.⁵ The details of calculation methods were described in Ref (5) and (6) and references within. It has been reported that the single ion or single ion pair models are sufficient to reproduce the XAS peaks of similar ILs,⁶ although an explicit solvent model is more appropriate.^{5,6} It was also found, both experimentally and theoretically, that the resonance features related to the excitation states in the cations are rather insensitive to the length of alkyl chain (C_n , $n \geq 1$) and types of anions,⁷ because the interaction between imidazolium cations and anions is dominated by intermolecular forces rather than Coulombic forces. An empirical shift of -1.6 eV was introduced to align the experimental and theoretical spectra. All the molecular structure illustrations were generated by an open-source molecular visualization tool Avogadro.⁸

SEM measurements

The EMImTFSI IL was drop-cast on an HOPG substrate. The excess liquid was blown away using compressed nitrogen, leaving only micrometer-sized IL droplets on the substrate. The sample was then imaged using a Zeiss Supra 55VP Field-Emission Scanning Electron Microscope (FE-SEM) with a 5kV accelerating voltage. The pressure inside the SEM chamber was 3×10^{-6} Torr during the measurements, and the morphology of the IL droplets was continuously recorded in SEM video mode at the rate of 10 sec/frame for 80 second.

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Supporting Figures

Figure S1. Peak deconvolution of N K-edge spectra collected (A) in the closed geometry after 120min exposure and (B) in the open geometry.

Figure S2. Comparison of F K-edge XAS spectra acquired at BL6.3.1.2 in the open geometry (bottom curve in dark blue) and in the closed liquid cell over 60 min of continuous irradiation.

Figure S3. Consecutive SEM images (under 5 keV electron beam) of EMIImTFSI IL droplets drop-cast on an HOPG substrate over the course of 80 seconds.