

Photoelectron Spectrum of Isolated Ion-Pairs in Ionic Liquid Vapor

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The gas-phase valence binding energy spectrum of isolated ion-pairs of the commonly used [1-ethyl-3-methylimidazolium][bis(trifluoromethylsulfonyl)imide] room-temperature ionic liquid is obtained by photoionization of a molecular beam of ionic liquid vapor by extreme ultraviolet light. The isolated ion-pair nature of the ionic liquid vapor is corroborated by single photon ionization mass spectroscopy, complemented by computed vaporization energetics of ion-pairs and clusters of ion-pairs. The valence binding energy spectrum of the isolated ion-pairs is discussed in comparison with available liquid-phase data and theoretical density functional theory calculations.

Introduction

Room-temperature ionic liquids (ILs) are salts with a melting point near or below ambient temperatures.¹ They have a number of unique properties, including excellent solvation ability, extraordinarily low volatility, and high thermal stability.^{1–9} Because the physical and chemical properties of ILs can be varied by the choices of the cation and anion pair,¹ they can be used for many applications such as fuel cells,^{3–5} batteries,^{6,7} and solar cells.^{8,9} The vast number of possible anion–cation combinations¹⁰ makes it important to rationally predict IL properties based on their constituents. Considerable experimental and theoretical work has been performed to predict and measure ionic liquid properties.¹¹ Ab initio calculations, used to predict the structure and interactions of ILs, are typically performed on isolated “gas-phase” systems.^{12,13} It is therefore important to be able to study isolated ion-pairs. However, because of the very low volatility of ILs there is a lack of gas-phase experiments that probe the ion-pair system, isolated from the surrounding liquid. Recent works have reported the distillation of selected families of ILs without decomposition, albeit with no direct characterization of the volatile species in the vapor.¹⁴

In the present work, we use extreme ultraviolet (EUV) light, produced by high-order-harmonic generation¹⁵ to probe a molecular beam of [1-ethyl-3-methylimidazolium][bis(trifluoromethylsulfonyl)imide] ([emim][Tf₂N]) and related IL vapors by single photon ionization. Photoionization mass spectra of the positive ions and atomistic molecular dynamics simulations, carried out to compute the enthalpy of vaporization of isolated ion-pairs versus clusters of ion-pairs, indicate that the results correspond to the direct ionization of isolated ion-pairs. The valence electronic structures of the isolated [emim][Tf₂N] ion-pairs are found to be nearly similar to available liquid-phase

measurements^{16,17} and are well reproduced by recent density functional theory (DFT) calculations¹² of the cation–anion complex.

Experimental Setup

High-order-harmonic generation is a laser-based, table top setup that provides intrinsically pulsed, ultrafast laserlike EUV and soft X-ray light, which is well suited for photoelectron and photoion time-of-flight (TOF) studies. The experimental high-harmonic generation setup, previously described in detail,¹⁸ consists of a 1 kHz repetition rate, 801 nm, 2 mJ, and 80 fs Ti:sapphire-pulsed laser that is focused into a pulsed argon gas jet to generate high-order harmonics of the 801 nm fundamental radiation. For these experiments, the 15th harmonic (23.2 eV) is selected to ensure efficient single photon ionization of all possible vapor components. The harmonic is selected and refocused by grazing incidence optics; a spherical grating in zeroth-order and toroidal grating in first-order direct the beam to the interaction region, typically delivering 3×10^9 photons/sec.¹⁸

The IL vapor source is composed of an aluminum oven body heated by four home-built resistive heating cartridges. The reservoir for the IL is a glass vial inside the oven as shown in Figure 1. IL samples (Sigma, $\geq 97\%$ purity) were kept under vacuum ($\sim 5 \times 10^{-8}$ Torr; $\sim 6.7 \times 10^{-6}$ Pa) at 323 K temperature before the experiment for more than 12 h to remove volatile impurities such as water. When the oven is heated to 473 K, IL vapor is emitted as an effusive beam through an opening in the oven (Figure 1). At this temperature, the vapor pressure of [emim][Tf₂N] is estimated to be about 4.3×10^{-4} Torr (5.6×10^{-2} Pa).¹⁹ The beam is skimmed by a 1 mm skimmer before it crosses the high-harmonic beam that ionizes the vapor to produce photoions and photoelectrons that are analyzed in two different sets of experiments. In one set of experiments, photoelectron spectra are recorded using a 1.3 m

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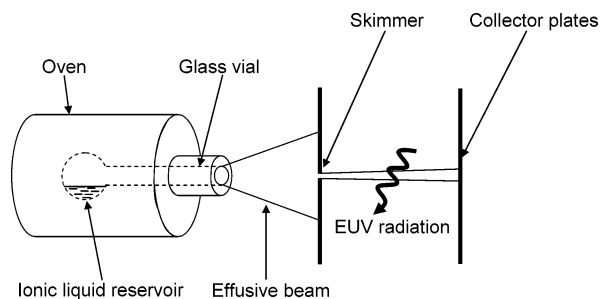


Figure 1. Schematic view of the ionic liquid vapor source and interaction region.

magnetic bottle TOF spectrometer with typical photoelectron energy resolution of $\sim 4\%$,¹⁸ while in another set of experiments mass spectra of positive ions produced by photoionization of the vapor are measured with a Wiley–McLaren type TOF mass spectrometer²⁰ that is used in place of the magnetic bottle. The TOF measurement is calibrated using the mass spectra of air and xenon isotopes ionized by the 15th harmonic with 1 amu/q mass over charge resolution (at mass ~ 130 amu/q). For both experiments, data are recorded as a function of temperature. Low oven temperature data (373–423 K) are used for subtraction of background signal due to scattered light and residual gas ionization. The molecular beam of IL vapor recondenses on a dedicated collector plate behind the interaction region. The ambient pressure in the interaction vacuum chamber during operation does not exceed 1×10^{-7} Torr (1.33×10^{-5} Pa), indicating that the volatilized IL vapor is efficiently recondensed on the skimmer and collector plates that are at ~ 323 K. The residual IL in the reservoir and the recondensed vapor on the stainless steel plates do not show any signs of decomposition such as coloration or solid residues. The recondensed [emim]-[Tf₂N] liquid is also analyzed by ¹H and ¹⁹F NMR, confirming that no significant decomposition occurs, in agreement with previous experiments.¹⁴ A small, undetectable amount of possible residual impurities or decomposition products are not expected to have an effect on the results presented here.

Results and Discussion

The photoelectron binding energy spectrum obtained for [emim][Tf₂N] vapor is shown by the solid line with error bars in Figure 2. The ionization energy of the [emim][Tf₂N] vapor is found to be 8.9 ± 0.2 eV. The spectrum shows photoelectron peaks corresponding to binding energies of 11.4, 15, 16.3, and 19.7 eV. These features appear and increase in intensity as the temperature of the IL oven is increased. Within the experimental resolution, the structure of the spectrum does not depend on the oven temperature, indicating negligible or no contribution from possible residual volatile impurities in the IL sample. The direct comparison of the [emim][Tf₂N] vapor binding energy spectra to similar binding energy measurements of the liquid surface^{16,17} gives information on the electronic structure of the gas-phase constituents compared to the liquid phase, although some experimental differences may be expected due to the different sample temperatures and EUV wavelengths. The dotted line in Figure 2 shows the [emim][Tf₂N] liquid surface^{16,21} binding energy spectrum, and the alkyl substituted [bmim][Tf₂N] liquid surface spectrum¹⁷ is shown with the dashed line (where [bmim]⁺ is 1-butyl-3-methylimidazolium). Except for an overall shift of -0.7 eV, which is tentatively assigned to [bmim][Tf₂N] surface polarization energy, we find the liquid [bmim][Tf₂N] valence photoelectron spectrum (dashed line) obtained with a 60 eV synchrotron light source¹⁷ to be identical to the [emim]-

[Tf₂N] vapor binding energy spectrum presented here. The binding energy spectrum is also similar to the [emim][Tf₂N] liquid surface spectrum obtained with a HeII light source¹⁶ (dotted line), albeit with small differences in the relative peak intensities. The relative scale of the [emim][Tf₂N] spectrum by Hoff et al.,¹⁶ shown in Figure 2, is shifted by $+4.8$ eV corresponding to the substrate Fermi level.²⁷ The remaining $+0.3$ eV shift of the binding energy is within the experimental error of the substrate Fermi level measurement.²⁷ The similarity in the valence electronic structure of the IL vapor and liquid phases indicates that the electronic structure of the gas-phase species is not changed significantly by possible decomposition or by removal of the liquid environment. Recent DFT density of states calculations¹² of the [emim][Tf₂N] cation–anion complex are compared in Figure 3 with the measured vapor binding energy spectrum. The theoretical spectrum is shifted by $+3.05$ eV with respect to the calculated results to match the highest occupied molecular orbital (HOMO) peak in the spectrum. Both the relative peak positions and intensities of the measured and calculated spectra are in good agreement.

Further insight into the identity of the volatile species in the IL vapor is provided by the single photon ionization mass spectra presented in Figure 4. Trace (a) in Figure 4 shows the positive photoion mass spectrum obtained for the [emim][Tf₂N] vapor. The predominant photoion mass peak that appears in the spectrum with the increase of IL oven temperature is 111 amu/q corresponding to the intact [emim]⁺ cation. A small and broad peak beginning at mass 82 amu/q with a tail toward higher masses is observed with the same temperature dependence as the [emim]⁺ peak. The tail toward higher masses (i.e., longer TOF) is indicative of post ionization fragmentation of a larger ion. Thus, this peak can be tentatively assigned as the methylimidazolium ion, [mim]⁺, produced by fragmentation of [emim]⁺. This peak may also contain a small contribution from the ionization of methylimidazole, which would be a neutral species produced by thermal decomposition of the IL. Figure 4 also shows the mass spectra of anion-substituted and cation-substituted ILs, respectively, [emim][Pf₂N] and [dmpim][Tf₂N] (where [Pf₂N]⁻ is bis(pentafluoroethylsulfonyl)imide and [dmpim]⁺ is 1,2-dimethyl-3-propylimidazolium). In both cases, the predominant and only peak observed within the experimental signal-to-noise corresponds to the mass of the intact cation, masses 111 and 139 amu/q, respectively. The observed photoion mass spectra suggest that the overall neutral vapor species undergoes dissociative ionization resulting in intact cations and undetectable neutral fragments from the anions.

Earle et al.¹⁴ suggest that the volatile species could be in the form of multiple-ion clusters, and they also consider the possibility of proton- or alkyl-ion-transfer from the cation to the anion as a potential mechanism for volatilization. The photoionization of neutral species corresponding to both the deprotonated (or dealkylated) cation, as well as the protonated (or alkylated) anion, should lead to photoions of distinguishable masses that are not detected in our experiment. Therefore, the observed mass spectra negate the possibility of a proton- or alkyl-ion-transfer contribution. It is therefore correct to consider the presence of volatile ion-pairs or clusters of ion-pairs in the gas phase.

Ion-pairs, isolated or within larger clusters, are likely to undergo a small chemical change between the liquid and the gas phase, which could be reflected by an overall shift of the binding energy spectrum as well as broadening of the spectral structures in the liquid due to the different environment of the ion-pairs. The presence of large clusters in the vapor beam could

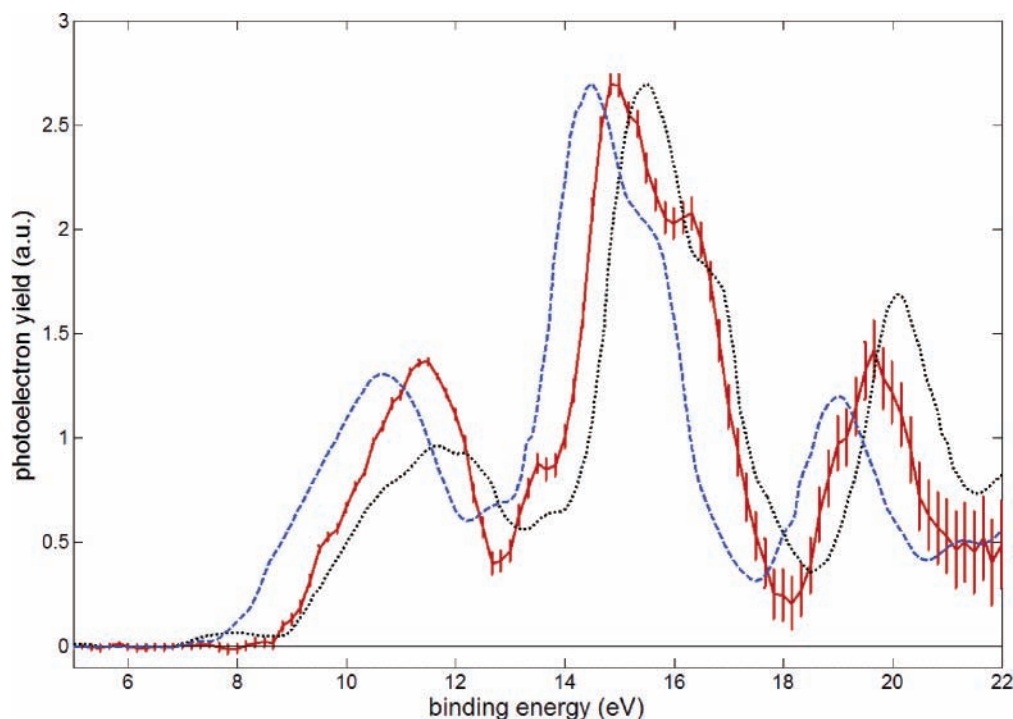


Figure 2. Photoelectron spectra of [emim][Tf₂N] vapor (solid bold red line with error bars), [emim][Tf₂N] liquid surface obtained with a HeII light source^{16,21} (dotted black line), and [bmim][Tf₂N] spectrum obtained with 60 eV synchrotron light source¹⁷ (dashed blue line).

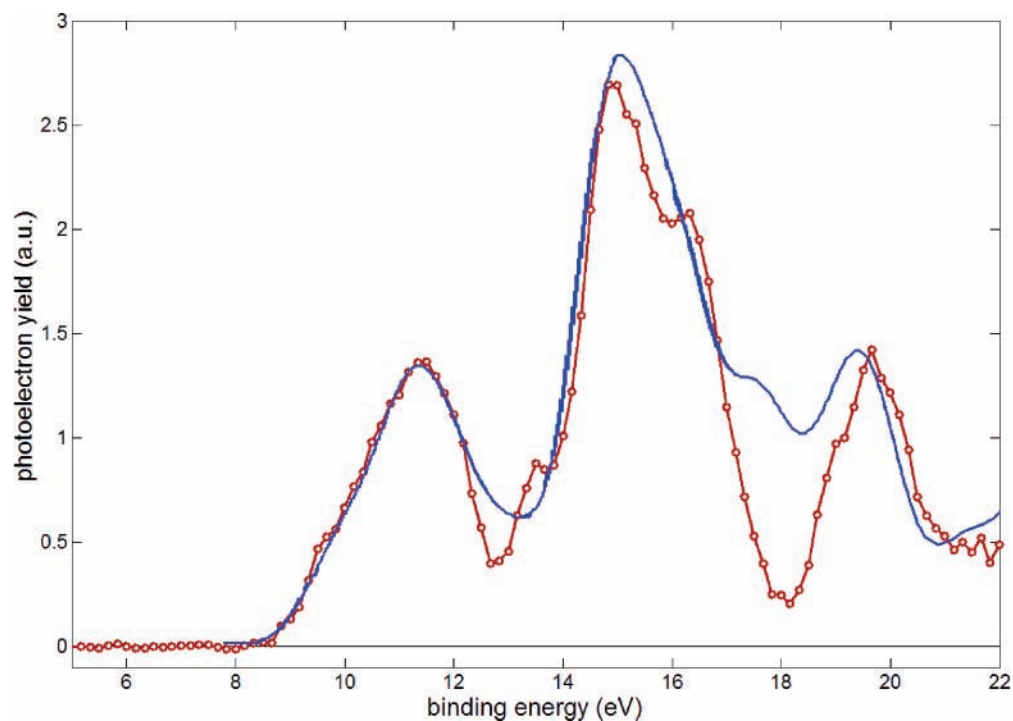


Figure 3. Photoelectron spectra of [emim][Tf₂N] vapor (red circles) compared to density of states calculations convoluted with a 0.8 eV Gaussian performed by Krischok et al.¹² (solid blue line). The calculated spectrum is shifted by +3.05 eV with respect to the published figure to match the HOMO peak in the experimental spectrum.

in principle explain the observed similarity between the gas- and liquid-phase spectra. Large clusters could undergo a photodissociative ionization to produce the observed [emim]⁺ cation that is observed in the mass spectra along with undetectable neutral cluster fragments. However, it is anticipated that ionization of ion-pair clusters would also produce stable cluster ions^{22,23} such as {[emim]_{n+1}[Tf₂N]_n}⁺, but these are not observed in our gas-phase photoion mass spectra of the IL studied so far (not shown).

To further consider the possibility of ion-pair clusters in the IL vapor, classical atomistic molecular dynamics simulations are carried out to determine the relative energetics of vaporization for ion-pairs as well as clusters of ion-pairs. The force field is taken from previous studies^{24,25} in which it has been shown to accurately reproduce the thermodynamic properties of bulk ionic liquid. Details of the simulation method can be found elsewhere.²⁶ The vaporization process for [emim][Tf₂N] is examined by first conducting a 2 ns molecular dynamics

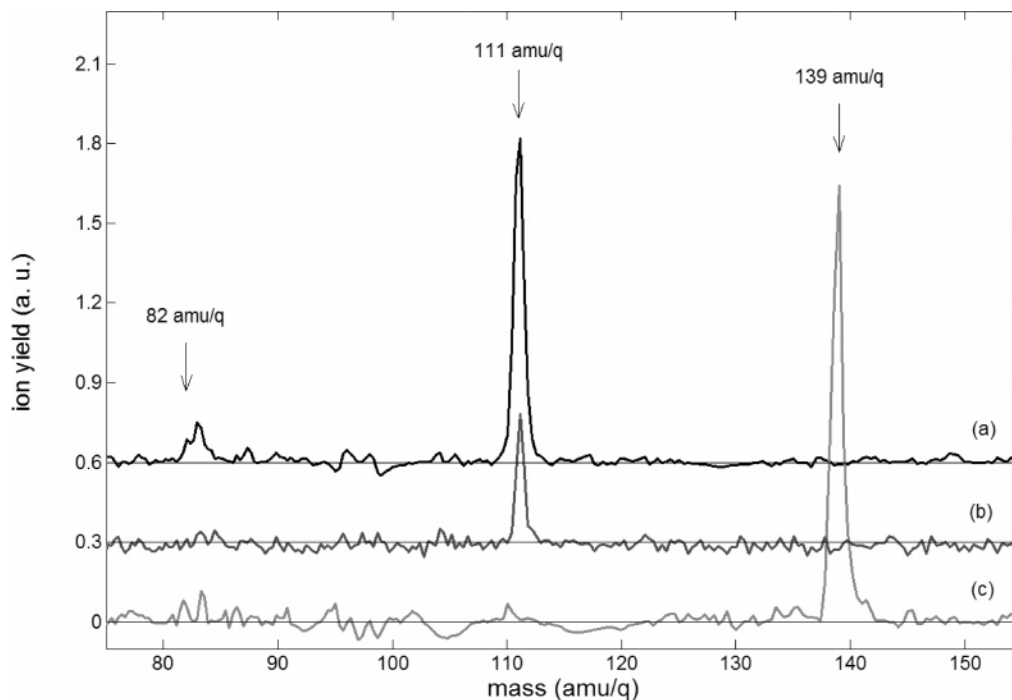


Figure 4. Positive photoion mass spectra of (a) [emim][Tf₂N] vapor, (b) [emim][Pf₂N] vapor, and (c) [dmpim][Tf₂N] vapor. The arrows indicate the [mim]⁺(82), [emim]⁺(111), and [dmpim]⁺(139) mass peaks.

TABLE 1: Enthalpies of Vaporization for Different Size Neutral Clusters, Computed on a Per Mole of Cluster Basis at 293 K^a

species	Δh_{vap} (kJ/mol)
[emim][Tf ₂ N]	146
[emim] ₂ [Tf ₂ N] ₂	187
[emim] ₃ [Tf ₂ N] ₃	227

^a The experimental enthalpy of vaporization¹⁹ for this ionic liquid at 298 K is reported to be 135.3 ± 1.3 kJ/mol.

simulation of 200 ion-pairs of [emim][Tf₂N] in the liquid phase at 1 bar and 293 K and an ideal gas at the same temperature to compute the liquid-phase internal energies. Gas-phase internal energies of the different ion-pair clusters are computed by carrying out molecular dynamics simulations of 40 independent ion-pairs for 5 ns at 293 K. The enthalpies of vaporization Δh_{vap} for isolated ion-pairs as well as ion-pair clusters calculated from these simulations are summarized in Table 1. It is clear that the single ion-pair [emim][Tf₂N] has the lowest enthalpy of vaporization ($\Delta h_{\text{vap}} = 146$ kJ/mol). For the ion-pair dimer, [emim]₂[Tf₂N]₂, Δh_{vap} is 187 kJ/mol, and for the trimer, [emim]₃[Tf₂N]₃, Δh_{vap} is 227 kJ/mol. Not surprisingly, enthalpies of vaporization for non-neutral ion clusters are significantly higher than neutral clusters, and therefore they are not expected to be present to any significant extent for this particular ionic liquid. The calculated Δh_{vap} for the [emim][Tf₂N] ion-pair is in reasonable agreement with the temperature dependence of the photoion and photoelectron yield in the present study as well as the experimentally obtained enthalpy of vaporization for this IL at 298 K, which is 135 kJ/mol,¹⁹ also indicating that isolated ion-pairs are the predominant species in the vapor.

Experimental evidence for [emim][Tf₂N] vapor together with theoretical simulations, presented in this study, suggest that the IL vapor is mainly composed of cations and anions as isolated ion-pairs, also in agreement with another recent electron impact mass spectrometry study.²⁷ In our experiment, vaporized isolated ion-pairs are likely to undergo a dissociative photoionization

to produce the intact cation and neutral fragments of the anion. More studies are required to further experimentally confirm the presence of and examine the structure of isolated ion-pairs in the IL vapor. These results demonstrate the possibility for direct investigation of isolated ion-pairs and provide the first gas-phase photoelectron spectrum of isolated IL ion-pairs. Furthermore, the good agreement of the measured valence binding energy spectrum of the isolated ion-pairs and the calculated density of states shows that the level of the calculation is sufficient to reproduce both the relative peak position and intensity. Moreover, the similarity of our results with data in the liquid phase endorses “gas-phase” modeling of the electronic structure and interactions of ionic liquids.

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