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Electronic Structure of the Surface of the Ionic Liquid [EMIM][Tf₂N] Studied by Metastable Impact Electron Spectroscopy (MIES), UPS, and XPS

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The near-surface electronic structure of the room-temperature ionic liquid (RT-IL) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) has been investigated with the combination of the electron spectroscopies metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS (HeI and HeII)), and monochromatized X-ray photoelectron spectroscopy (XPS). We find that the top of the valence band states originates from states of the cation (see also ref 1). The ultimately surface-sensitive technique MIES proves that the surface layer consists of both cations and anions. The temperature dependence of the spectra has been measured between about 160 and 610 K. Information on the glass transition and the possibility for low-temperature distillation of [EMIM][Tf₂N] at reduced pressures is derived from the present results.

1. Introduction

Room-temperature ionic liquids (RT-ILs) have attracted much attention for their excellent properties, as a wide temperature range of liquid phase, very low vapor pressure at RT, chemical stability, their potential as “green” solvents,^{1,2} and their high heat capacities. These properties make them good candidates for use in many fields,^{2,3} such as thermal storage,⁴ electrochemical applications,⁵ homogeneous catalysis,^{2,6,7} and dye sensitized solar cells.⁸ Moreover, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) is a member of a class of ILs that can apparently be distilled at moderate temperatures at reduced pressure, although the distillation rates are low.^{9,10} To be able to refine the performance of RT-ILs, detailed knowledge of the geometric, electronic, and vibronic structure of RT-ILs in the temperature regime between 100 and 700 K appears indispensable.

In the present work, we apply the metastable impact electron spectroscopy (MIES), in combination with various photoelectron spectroscopies (XPS and UPS (HeI and II)), to the study of the electronic structure of a typical RT-IL, [EMIM][Tf₂N] (see inset in Figure 1), deposited on a polycrystalline Au substrate. MIES is ultimately surface sensitive (zero depth information) because the He⁺ atoms of thermal kinetic energy, employed as probe atoms, interact only with the outer edge of the charge density of the toplayer forming the IL–vacuum interface.^{11,12} Thus, MIES

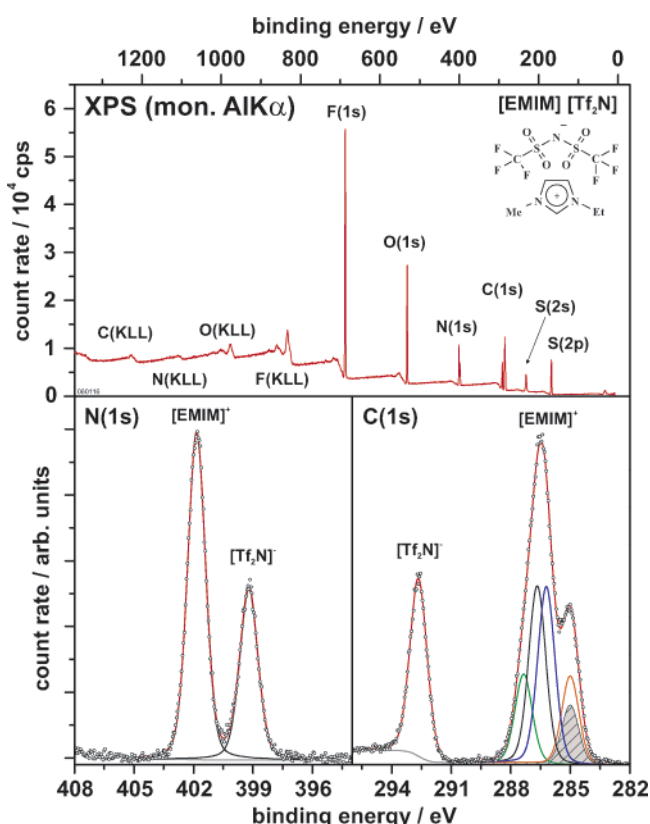


Figure 1. XPS spectra of [EMIM][Tf₂N]: survey spectra and high-resolution spectrum dealing with the C(1s) and N(1s) photoemission. Details concerning the simulated fit to the experimental data can be found in the text. The inset shows the molecular structure of [EMIM][Tf₂N].

appears to be ideally suited to probe the outermost edge of the RT-IL film and to provide information on the termination of the RT-IL surface. By combining MIES with UPS and XPS, covering a wide range of depth resolution, we obtain not only information

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on the termination of the RT-IL film but also on its surface-near region. We have recently applied the same combination of methods to study the surface-segregation of salt ions interacting with the surface of condensed molecules and show the special ability of amorphous solid water, but not of methanol, to surface-segregate heavier halide ions (iodide, I^-).¹³

The electronic structures of several RT-ILs, including 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]), were studied recently by UPS with synchrotron radiation ($h\nu = 60$ eV) under UHV conditions.¹ In contrast to what is found for the usual inorganic ionic solids, with NaCl as an example, the valence band maximum (VBM) in the near-surface region is ascribed to states of the organic cation. Details of the electronic structure of the surface layer itself could not be studied in detail because UPS provides spectroscopic information that is averaged over several layers of the IL film, and for this reason, the composition of the surface layer at the IL-vacuum interface could not be established unambiguously.

2. Experimental Section

Both UHV systems employed for the present studies are equipped with XPS and UPS (HeI and II), enabling a cross referencing of the collected data on the different systems. The sample support consists of a polycrystalline Au film of about 250 nm thickness deposited on Si(100), separated by a Ti adhesion layer. The samples were prepared by depositing one droplet of the ultrapure RT-IL onto the Au substrate and were, after outgassing carefully, introduced into the UHV chamber. The [EMIM][Tf₂N] samples prepared in this way have very low vapor pressure, and no change of the base pressure could be detected during measurements performed at RT. All chambers are equipped with LN₂ cooling. The sample temperature is measured with a thermocouple at the sample holder or in direct contact with the front of the Au target, respectively.

Experimental details of the apparatus equipped with a source for He metastable atoms, suited for performing MIES and HeI (TU Clausthal), can be found in refs 14–16. A gas discharge produces metastable He* atoms with about 20 eV potential energy, but only thermal kinetic energy and HeI photons ($h\nu = 21.2$ eV) for UPS (HeI). Metastable atoms of thermal kinetic energy (60–100 meV) approach the surface, and the electron exchange processes with the species of the surface (resonant electron exchange and Auger processes) take place well in front of the surface (0.2 nm typically). Thus, it is believed that MIES is nondestructive and highly surface sensitive (see refs 11 and 12 for more detailed introductions into MIES and its various applications in molecular and surface spectroscopy). Spectral analysis was made with a hemispherical analyzer, and all spectra possess an energy resolution of 0.25 eV. By applying suitable biasing, the vacuum level of the analyzer coincides with the Fermi level of the substrate. Thus, in MIES, electrons emitted from the Fermi level, E_F , are registered at 19.8 eV (the potential energy of He*(2³S)). Moreover, the onset of the spectra at low kinetic (high binding) energies occurs at the work function of the sample.

In the second apparatus, valence band spectroscopy is performed by combining HeI and II and XPS (TU Ilmenau). It is equipped with a monochromatized X-ray source (Al K α) and a source for HeI and HeII (40.8 eV) radiation. It features an energy resolution below 0.6 eV (on Ag 3d_{5/2} at a pass energy of 15 eV) for XPS; a resolution below 150 meV (as estimated from the Fermi edge of a polycrystalline Ag-sample) has been employed for the UPS (HeII) measurements. Electrons under normal emission are collected with a hemispherical

analyzer equipped with 7 channeltrons. Thus, the apparatus provides excellent conditions for the collection of high quality spectra.

In parallel to the electron spectroscopic studies, measurements with high-resolution electron energy loss spectroscopy (HREELS) were carried out (TU Ilmenau) that will be reported elsewhere.

3. Results

XPS (Al K α) survey spectra displayed in Figure 1 indicate that a closed [EMIM][Tf₂N] film was successfully prepared. From the absence of any substrate (Au) related spectral features, we estimate a film thickness of more than 10 nm. The expected elements F, N, O, S, and C are detected, and no evidence of impurities by other elements could be found. A calculation of the chemical composition based on the observed peak areas leads to a F:O:N:C:S ratio of about 6:3.9:3.3:10.8:2.2 (close to the expected ratio of 6:4:3:8:2).

The F(1s), N(1s), O(1s), S(2s), and C(1s) emissions (see Figure 1 for the C(1s) and N(1s) regions of the spectrum) display well-resolved and narrow spectral features. The expected chemical shifts are clearly observed: whereas the F(1s), O(1s), and S(2s) peaks show a single narrow peak with a maximum FWHM below 1.6 eV (F(1s), N(1s), and the C(1s) are split into several components).

Previous high-resolution XPS work on the low-binding energy region of the C(1s) emission has been reported for 1-ethyl-3-methyl imidazolium ethyl sulfate, also possessing the [EMIM] cation,¹⁷ and for [C₄MIM][Tf₂N].¹⁸ As in these works, a detailed analysis of N(1s) and C(1s) was made; GL(27)-peak shapes, symmetrical Gaussians (73%), and Lorentzians (27%), were used. N(1s) is split into two well-distinct components with FWHM of 1.08 and 1.04 eV, respectively, and a relative peak area of 1:1.9. The larger peak, observed at the higher binding energy, is assigned to N located at the [EMIM] cation ring (the lower binding energy peak related to N from the [Tf₂N] anions). The good correspondence of the obtained relative peak areas with the stoichiometry of the IL provides evidence for a homogeneous vertical distribution.

Due to the presence of C in various chemical environments, the structure of C(1s) is, as expected, more complicated (see Figure 1). Previous studies on fluorocarbon samples^{19,20} suggest that the peak at 293.7 eV is associated with the CF₃ groups of the [Tf₂N] anion due to the high electronegativity of fluorine. Further evidence for the association of this peak with the anion comes from the above mentioned study on 1-ethyl-3-methyl imidazolium ethyl sulfate¹⁷ where the peak at 293.7 eV was not observed.

For the fitting procedure of the low-binding energy part of the C(1s) structure each C atom of [EMIM] (see Figure 1) in a different chemical environment was represented by a separate peak (a total of 4 peaks). From the molecular structure of the [EMIM][Tf₂N] we expect for the cation two peaks with the same peak area as the anion (CF₃) related peak (caused by the two N–C–N atoms of the ring and caused by the two C atoms of the alkyl chains directly bonded to the nitrogen of the aromatic ring) and two peaks with half of the peak area (one caused by the N–C–N of the aromatic ring at higher binding energies than the first two components and one caused by the CH₃ end group of the ethyl group). Indeed, the relative peak areas display the

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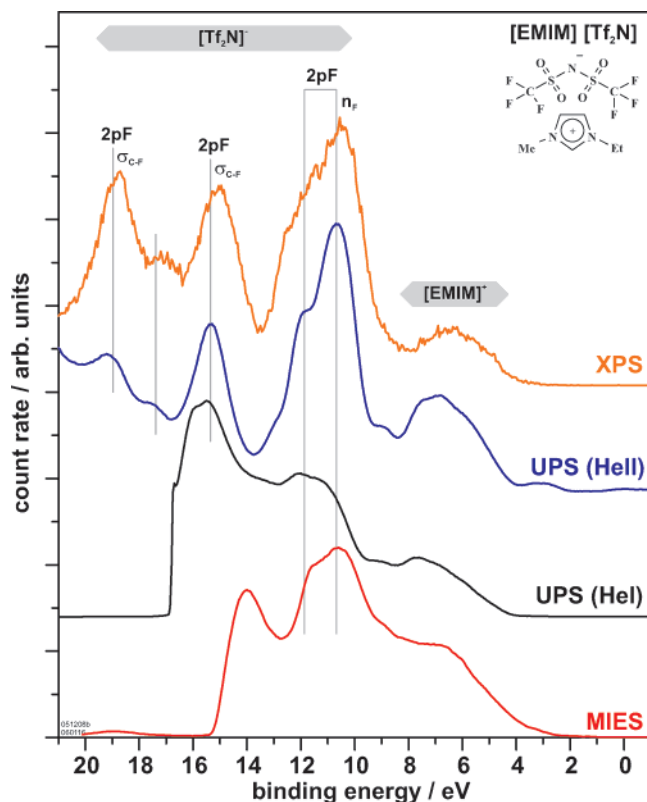


Figure 2. MIES, UPS (HeI), UPS (HeII), and HR-XPS spectra from [EMIM][Tf₂N] deposited onto Au (polycrystalline film, 250 nm thick) at room temperature. Abbreviations and acronyms as explained in the text.

expected ratios very well, except of the low binding energy peak at 285 eV which is more pronounced than expected. The excess area of this peak is indicated in Figure 1 (shaded). It should be noted that for [EMIM][Tf₂N] the cation and anion contributions are, other than in ref 17, energetically well separated, and anion emission does not contribute to the low-binding energy part of the C(1s) structure. The origin of the shaded peak is presently unknown; possible sources for its origin are photon beam-induced damage, orientational effects (here the ethyl group would have to point towards the vacuum which is in accordance with the MIES results) or some C-contamination (probably hydrocarbons as concluded from the binding energy as well as from the absence of other chemical elements in addition to that originating from the IL itself). On the basis of the present analysis, the shaded peak accounts for about 2% of the total atomic concentration.

Figure 2 presents the valence band spectra collected at RT from [EMIM][Tf₂N] on Au with MIES, UPS (He I and II), and XPS; no beam-induced changes were noticed in the spectra. The structure, denoted by 2pF, σ_{C-F} , (see section 4 for the explanation of the notation), seen around 15 eV in UPS (HeII) and XPS, is neither seen clearly in MIES nor UPS (HeI) because the potential energy of the He* metastables and the HeI photons is not sufficiently large to eject electrons from the molecular orbital (σ_{C-F}), involved in the ionization process, into the vacuum. Both UPS (HeII) and XPS show an additional peak, denoted by 2pF; σ_{C-F} , around 19 eV. The emission seen between 0 and +4 eV in the UPS (HeII) spectra is caused by HeII β photons (48.4 eV) and will not be discussed any further. The photoelectron spectra for [BMIM][Tf₂N] ($h\nu = 60$ eV) of ref 1 agree well in essential features with our UPS (HeII) results. We can then conclude that the structure seen in the MIES, UPS, and XPS spectra at binding energies > 8 eV is dominated by contributions from the [Tf₂N] anion. Moreover, again following ref 1, the emission seen close

to the Fermi energy (binding energies < 8 eV) appears to be caused mostly by the ionization of the highest-lying MOs of the [EMIM] cation. A detailed discussion of the spectra will follow in section 4.

All recorded spectra show little dependence on the sample temperature between 230 K and 300 K (not shown). However, upon cooling the IL layer further, the spectra change drastically. Especially in the UPS measurements where a high photon flux was used, first a shift (at 229 K) and finally the disappearance (at 168 K) of the spectral features is observed. In parallel, all peaks observed by XPS shift by about 10 eV towards lower kinetic energy, and their width increases drastically, indicating that strong charging is the origin of the observed behavior. It occurs at a temperature which is close to the accepted glass transition temperature of 175 K.^{21,22} Similarly, in MIES and UPS (HeI), a strong decrease of the anion emission intensity is observed around 154 K and may also be related to the glass transition. Upon annealing, starting from 130 K, the anion-induced intensity reappears around 184 K, which is again close to the glass transition temperature.

We have also studied the T-dependence of the MIES and HeI spectra in the range between 300 and 610 K. The temperature for the onset of the IL decomposition is reported to be between 727 and 742 K.²² We find, however, a strong decrease of the intensity from both cation and anion between 430 and 490 K. On the other hand, this is not connected with a change in the shape of the IL-induced spectra. Thus, decomposition can be excluded as the reason for the observed intensity decrease. This finding appears to lend additional support to the recent observation^{9,10} of an early volatilization of [EMIM][Tf₂N] under reduced pressure. (Note added in proof: a vapor pressure, as measured with the integral effusion Knudsen method at an residual pressure of $< 10^{-5}$ Torr, of 1.24×10^{-4} Torr was reported at 455.2 K; the absence of IL decomposition during the evaporation process was established by infrared spectroscopy.²³)

4. Discussion

The following results will be further discussed:

(1) The UPS (HeII) results are rather similar to the corresponding photoelectron spectra for [BMIM][Tf₂N] reported in ref 1, in particular as far as the anion contribution to the spectra is concerned.

(2) By comparing the UPS (HeII) results with the photoelectron spectra and the ab initio MO calculations reported in ref 1, it is concluded that the structure seen in the MIES and UPS spectra at binding energies > 8 eV is dominated by contributions from the [Tf₂N] anion and that seen at binding energies < 8 eV by the ionization of the highest-lying MOs of the [EMIM] cation.

(3) Emission from both the MOs of the anion and cation is seen in MIES simultaneously; this proves that both components of the IL under study are accessible to the He* probe atoms employed in MIES, and, for that reason, do not shield each other efficiently. The simultaneous presence of both ionic constituents within the surface is further supported by the observed relative N(1s) cation and anion emission intensities in XPS as well as by the HREELS measurements on [EMIM][Tf₂N] mentioned above but not shown here.

A more detailed identification of the structure seen in the anion emission can be arrived at by the comparison with the gas-phase photoelectron spectra of CH₃I²⁴ and the UPS (HeII)

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spectra from CF₃I adsorbed on Ag(111).²⁵ As indicated in Figure 2, the emission around 11 eV, denoted as n_F , is associated with the ionization of the 2pF lone pair electrons. The peak around 15 eV, denoted σ_{C-F} , is due to the ionization of the 1e₁ (C–F) bonding MO. According to refs 24 and 25, the 2pF-derived peak, seen in with UPS (HeII) and XPS around 19 eV, has 1a₁ character and is associated with the bonding (C–F) molecular orbital. The small peak noticed around 17 eV may be caused by the interaction between the CF₃ and SO₂ groups of the anion.

From the fact that the 2pF-derived emission is comparatively strong in MIES, we conclude that the CF₃ groups of the anions are pointing towards the vacuum. Some information on the origin of the emission attributed to the cation (between about 4 and 9 eV binding energy) can be obtained from a comparison with the UPS (HeI) “fingerprint” spectra of certain aromatic compounds, toluene and pyrrole in particular.^{26,27} This comparison suggests the following interpretation: if the observed emission would result from the cation ring mainly, it should consist of the contributions from the highest-lying π MOs mainly and should produce a narrow structure (about 2 eV wide) close to the Fermi energy. This is, however, not seen in our results. Instead, the emission is broad (4 eV wide), and the comparison with the spectra of short alkane molecules suggests that it may rather be attributable to π (CH₃) and π (CH₂) MOs of the alkane ligand molecules. Thus, our results suggest that the cation ring may be essentially hidden by the methyl and ethyl groups of [EMIM] which appear to be directed away from the IL surface into the vacuum.

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Moreover, some emission from the anion may also contribute to the region between 4 and 9 eV as the gas-phase photoelectron spectra of β -carbonyl sulfones (as [TF₂N] possessing a SO₂ group), reported in ref 28, suggest. These results let us expect that the ionization of MOs from the SO₂ group may contribute to the structure between 4 and 9 eV. In particular, we suggest that the SO₂ groups may be responsible for the weak peak around 8.7 eV, seen both in the MIES and the UPS spectra.

To arrive at a quantitative analysis of the top-layer composition using MIES, “fingerprint” spectra of both components [EMIM] and [TF₂N] need to be measured for the calibration of the relative sensitivity of MIES for the two molecular constituents.

5. Summary

The electronic structure of the room-temperature ionic liquid [EMIM][TF₂N] has been investigated with the combination of the electron spectroscopic techniques metastable impact electron spectroscopy (MIES), UPS (HeI and HeII), and monochromatized XPS. The highly surface-sensitive technique MIES proves that the surface layer consists of both cations and anions. However, the imidazolium ring is essentially shielded by its alkyl groups that apparently point towards the vacuum. In agreement with a previous study,¹ we find that the top of the valence band is dominated by states of the cation. Details of the structure seen in the valence band spectra can be understood from their comparison with fingerprint spectra of molecules having the same functional groups as [EMIM][TF₂N]. The temperature dependence of the spectra could be studied between the glass transition temperature and that for the onset of the distillation of [EMIM][TF₂N] under reduced pressure (490 K).

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