

Surface Electronic Structure of Imidazolium-Based Ionic Liquids Studied by Electron Spectroscopy*

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We have measured the bulk and surface electronic structure of several ionic liquids of alkyl-imidazolium cations with different alkyl chains (EMIm, BMIm, HMIm, OMIm) and bis(trifluoromethylsulfonyl)imide anions (TF_2N) by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS He I and He II) as well as metastable induced electron spectroscopy (MIES). The results are compared with the densities of states (DOS) calculated by density functional theory (DFT). By XPS we found the stoichiometry of the respective ILs reproduced, and different carbon atom positions reflected by the splitting of the $\text{C}(1s)$ - from the trifluor-methyl groups (CF_3) of the anion with highest binding energy to the alkyl chains of the cation with the lowest one. Furthermore with increasing alkyl chain length the peak related to the alkyl group appears at slightly lower binding energy. The more bulk-sensitive XPS spectra reveal only minor differences in the valence band structure for the studied ionic liquids, whereas the more surface-sensitive methods UPS and especially MIES display distinct changes in the peak-intensities for varying the alkyl chain length. This is a strong indication for either a non-stoichiometric composition of the upmost molecular layer of the IL-surface and/or a reorientation of the cations, probably turning the alkyl chains to the surface. [DOI: 10.1380/ejsnt.2010.241]

Keywords: Liquid surfaces; Surface electronic phenomena; X-ray photoelectron spectroscopy (XPS); Metastable induced electron spectroscopy (MIES); Density functional theory (DFT)

I. INTRODUCTION

The behavior of liquids at semiconductor or metal surfaces has been an important subject of study. Among them, room-temperature ionic liquids (RT-ILs) have recently attracted considerable attention not only as a new organic solvent but also as many functionalized materials [1, 2]. They typically remain in liquid phase for a wide temperature range, possess very low vapor pressures and are of high ion-conductivities at room temperature. Their superior physical and chemical properties have been utilized for electrochemical applications in double layer capacitors, dye-sensitized solar cells, or Li-ion batteries just to mention a few [3–5]. The bulk and surface electronic structures of RT-ILs have been investigated with various techniques, e.g., angle-resolved X-ray photoelectron spectroscopy [6–8], soft X-ray emission spectroscopy [9, 10], and scanning atom probe [11].

In the present work we study the valence-band structure of imidazolium-based ionic liquids in the bulk as well

as on the surface in dependence of a systematic variation of the alkyl chain length. For this purpose we have chosen four different cations: 1-ethyl-3-methylimidazolium ($[\text{EMIm}]^+$), 1-butyl-3-methylimidazolium ($[\text{BMIm}]^+$), 1-hexyl-3-methylimidazolium ($[\text{HMIm}]^+$) and 1-octyl-3-methylimidazolium ($[\text{OMIm}]^+$). The complementary anion has been bis(trifluoromethylsulfonyl)amide ($[\text{TF}_2\text{N}]^-$). The X-ray photoelectron spectroscopy (XPS) of core-shell electrons provided information not only about the general stoichiometry of the IL-bulk. Additionally, by a combination of XPS, ultraviolet photoelectron spectroscopy (UPS (He I and II)) and metastable induced electron spectroscopy (MIES), which have different surface-sensitivities, we have obtained distinguishable information about the bulk and the surface valence band structure. The interpretation of the experimental results has been supported by quantum-chemical calculations based on density functional theory (DFT) [12, 13].

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Experimental

We have carried out XPS, UPS (He I and II with photon energies of 21.2 eV and 40.8 eV, respectively) and MIES experiments in two different UHV systems (with a base

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pressure below 2.0×10^{-10} Torr; see Ref. [14]). Briefly, one experimental apparatus is equipped with a discharge source for UPS (He I and II) and a monochromatized X-ray source ($\text{AlK}\alpha$) for photoelectron spectroscopy. The electrons emitted from the sample have been detected by a hemispherical energy analyzer equipped with seven channels. The overall energy resolution has been below 0.6 eV (on Ag $3d_{5/2}$ for pass energy of 15 eV) for XPS measurements and below 150 meV (as estimated from the Fermi edge of a polycrystalline Ag sample) for UPS.

The other apparatus serves for analysis of the surfaces valance band structure by UPS (He I) and MIES. Both measurements are simultaneously performed by use of the same gas discharge at the helium metastable atom source. The beam of helium metastable atoms is produced by high-voltage discharging at a nozzle-skimmer space. The main component of the beam is He^*-2^3S with an excitation energy of 19.8 eV with an intensity ratio of 7:1 compared to the He^*-2^1S with an excitation energy of 20.6 eV [15]. During de-excitation processes of the incident metastable atoms in front of the surface electrons are emitted [16–18]. In the present case, the Auger de-excitation (AD) is dominant. Therefore, the MIES spectrum reflects very sensitive to the local density of states in the vicinity of the position, where the He^* atoms are reflected, i.e. around 0.2 nm above the sample surface. For spectral analysis of the emitted electrons serves a hemispherical analyzer equipped with a secondary electron multiplier. All together the equipment used in this apparatus guarantees an energy resolution of about 250 meV.

The sample substrate was prepared as a polycrystalline Au film of ~ 250 nm thickness deposited on a Si(100) surface with a Ti adhesion layer in between. The four different types of ultrapure imidazolium-based ionic liquids ([RMIm] Tf_2N) have been deposited as a droplet onto the Au substrate. Then the samples have been carefully outgassed in the load-lock system. For the very low vapor pressure of the used ILs the base pressure has hardly changed during each measurement at RT. Each new surface has first been characterized by monochromatized XPS ($\text{AlK}\alpha$) survey spectra for stoichiometry of the IL. These measurements have proven that the IL films have been well prepared and covered the complete substrate surface.

B. DFT calculations

In order to identify the measured structures in the valence band of the ILs, we have performed DFT calculations on IL ion-pairs using Becke's B3-LYP functional [19–22] and a 6-31G (d, p) basis set (as implemented in Gaussian03 [23]). The basis set extension by d -functions accounts for the hypervalent bonds mainly of the sulfur in Tf_2N [24, 25]. The calculations included structural optimization, for the isolated [RMIm] $^+$ cations and the $[\text{Tf}_2\text{N}]^-$ anion as well as an complex formed of the respective ion-pairs. The latter calculations base on the optimized single ions as initial guess.

For the relaxed structures, we determined the Kohn-Sham eigen-energies and the corresponding molecular orbitals. For applying a Gaussian broadening of 0.45 eV we obtained a density of states of states (DOS) comparable to

TABLE I: The energy position of each peak and the ratio of the calculated peak area at [RMIm] Tf_2N surface: high-resolution spectra related with N(1s).

Ionic liquid	Energy position (eV)		Ratio	
	Tf_2N^- (N^1)	[RMIm] $^+$ (N^2)	N^1	N^2
[EMIm] Tf_2N	399.68	402.32	1.00	2.00
[BMIm] Tf_2N	399.68	402.35	1.00	1.95
[HMIm] Tf_2N	399.68	402.34	1.00	1.95
[OMIm] Tf_2N	399.68	402.35	1.00	1.97

the experimental spectra. However, we have to consider that the cross-sections of the photoelectron emission may not be uniform for all eigenstates.

Though our calculations are simplified by the use of a single ion pair—which is not fully adequate to describe the [RMIm] Tf_2N system in liquid—but rather in gas phase, it was shown that the measured UPS spectra of [EMIm] Tf_2N (in both, gas phase and liquid state) fit quite well to the DOS, if one is mainly interested in the peak positions [26]. The reason may be that despite of the Coulomb interaction and possible hydrogen-bonds between two ions, other solvation effects are of minor influence on the valance-band structure.

III. RESULTS AND DISCUSSIONS

A. XPS spectra from the four different types of imidazolium-based ILs

In the survey XPS spectra peaks for the expected compounds F, N, O, S, and C but no for impurities have been detected. The peak areas correspond quite well to the expected values for the stoichiometry of respective compounds. The F(1s), N(1s), O(1s), S(2s), and C(1s) emissions generally display well-resolved and narrow spectral features with the expected chemical shifts and relative peak areas. A more detailed discussion of the XPS spectra typical for the [EMIm] Tf_2N film may be found elsewhere [14]. The N(1s) and C(1s) emission (see Figs. 1(a) and (b)) shows split peak structures, related to the components of the [RMIm] $^+$ cation and $[\text{Tf}_2\text{N}]^-$ anion. The energetic position and intensity of the latter, we used for normalization. For a detailed analysis of N(1s) and C(1s) emission GL(27)-peak shapes (symmetrical Gaussians (73%) and Lorentzians (27%)) were used. The resulting energetic position of each peak and the ratio of the calculated peak areas are summarized in Tables I and II.

Both N(1s) peaks are identical for all ILs in this study. The peak at the lower binding energy of 399.68 eV (labeled as N^1) originated from the nitrogen in the $[\text{Tf}_2\text{N}]^-$ anion. The other peak (labeled as N^2) at around 402.33 eV we can attribute to the two nitrogen atoms of the imidazole-ring. Notably, the peak areas correspond exactly to the expected ratio of 2:1 between the N-contents of [RMIm] $^+$ cation and $[\text{Tf}_2\text{N}]^-$ anion (see Table I).

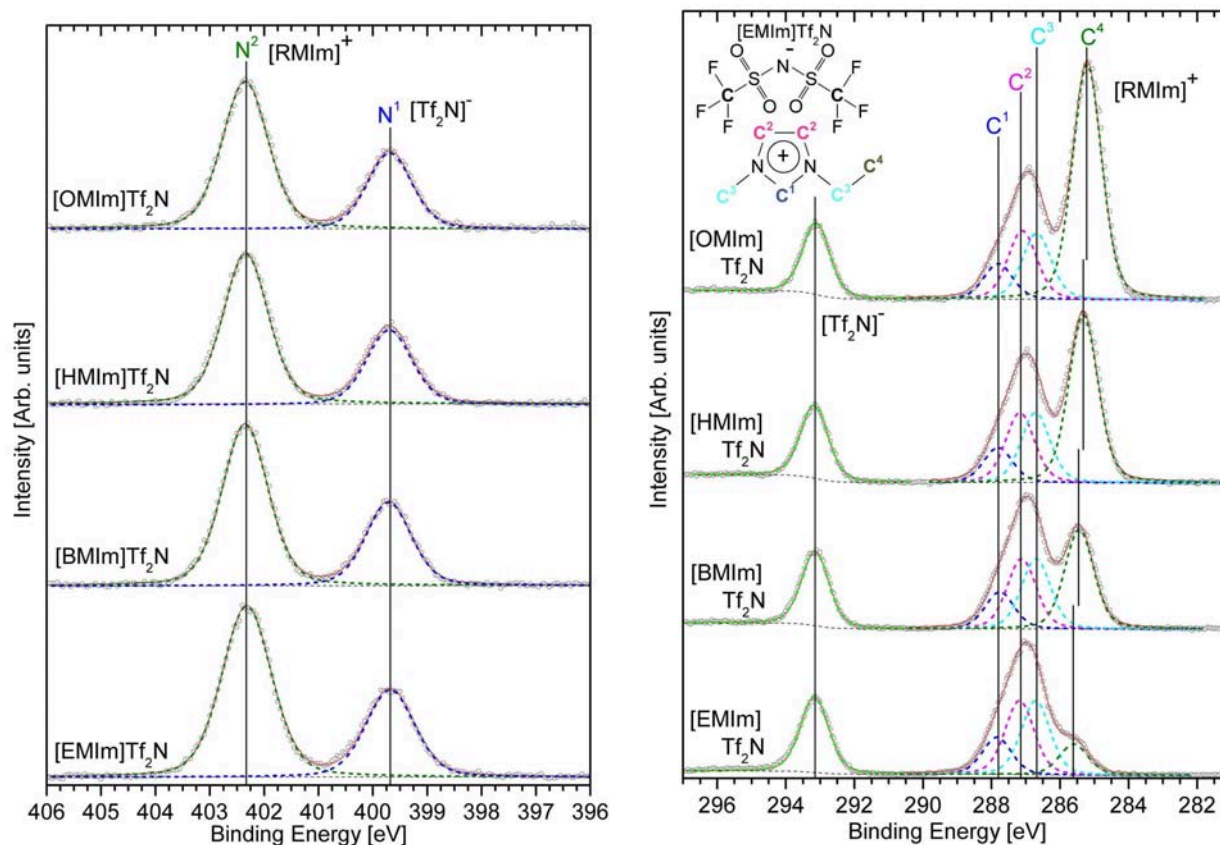


FIG. 1: The variations in the XPS spectrum taken from the four different types of imidazolium-based ILs ([RMIm]⁺Tf₂N) surface: (a) high-resolution spectra related with N(1s) and (b) C(1s). The black circles, the red line, the black dash line and the other color dot lines show raw XP spectrum, curve fitting data, back ground and each component induced atom in (a) and (b), respectively.

TABLE II: The energy position of each peak and the ratio of the calculated peak area at [RMIm]⁺Tf₂N surface: high-resolution spectra related with C(1s).

Ionic liquid	Tf ₂ N ⁻	[RMIm] ⁺ (C ¹)	Energy position (eV)				Ratio				
			[RMIm] ⁺ (C ²)	[RMIm] ⁺ (C ³)	[RMIm] ⁺ (C ⁴)	Tf ₂ N ⁻	C ¹	C ²	C ³	C ⁴	
[EMIm]Tf ₂ N	293.15	287.84	287.18	286.71	285.60	2.00	1.00	2.00	2.01	0.84	
[BMIm]Tf ₂ N	293.15	287.81	287.17	286.75	285.49	2.00	1.05	2.01	2.01	2.84	
[HMIm]Tf ₂ N	293.15	287.81	287.17	286.71	285.32	2.00	1.00	2.00	2.00	4.82	
[OMIm]Tf ₂ N	293.15	287.80	287.10	286.70	285.20	2.00	1.05	2.03	1.96	6.98	

For the C(1s) emission we have found a more complex peak-structure (see Fig. 1(b)). One peak at 293.52 eV (not labeled) originates from the carbons in the trifluoromethyl groups of the [Tf₂N]⁻ anion [13]. It is well separated from the others. The peak structure between 283 eV and 289 eV binding energy, however, varies significantly with the alkyl chain of the [RMIm]⁺ cation. The decomposition of this structure revealed four subpeaks (labeled as C¹-C⁴). The energy position of each peak and the ratio of their peak area in respect to the C(1s) peak area (= 2.00) of the [Tf₂N]⁻ anion are given in Table II. Based on the structure of the [RMIm]⁺ cation we can attribute the four subpeaks as follows (see also insert in Fig. 1(b)): The C¹ peak at the highest binding energy originates from the carbon between the two nitrogens in the imidazole-ring;

the C² peak slightly lower in binding energy represents the two other carbons in the imidazole-ring; the C³ peak in an intermediated energy region corresponds to the aliphatic carbons directly bound to the nitrogens in the imidazole-ring (C-N); the C⁴ peak, which is most separated from the others, represents the remaining aliphatic carbons in the alkyl chain. Most notably, the intensity of the C⁴ peak increases with the alkyl chain length and its energetic position shifted slightly towards to lower binding energies. The C⁴ peak area obtained from the decomposition is a little bit smaller than the expected theoretical. The observed shift in the peak energy agrees well with the angle-resolved XPS measurements by Lovelock *et al.* and Kolbeck *et al.* [7, 8]. Obviously the different chemical shifts of the C¹, C² and C³ peaks are induced by the elec-

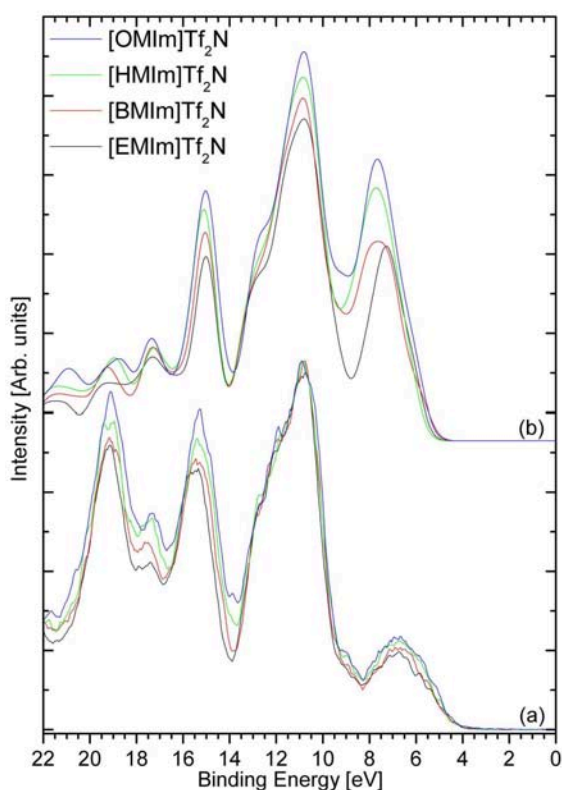


FIG. 2: The valence band structure at [RMIm] Tf_2N surfaces: (a) XPS measurement, (b) density of states for DFT calculation.

tron affinity of the imidazole nitrogens [27]—the closer the carbons are to both of them the higher the binding energy of their $1s$ electrons. For the same reason the energy position of the C^4 peak shifts to lower binding energy for longer alkyl chains.

B. Valence band spectra

The XPS spectra for the valence band structure of the four imidazolium-based ILs are shown in Fig. 2(a). We have normalized them to the fluorine peak of the $[Tf_2N]^-$ at 34 eV (not shown), which due to our DFT calculated DOS should be independent of the IL kind. Most peaks of the XPS spectrum are also found in the calculated DOS, though with different peak heights due to the unknown XPS cross-sections. A puzzling fact, however, is that the peaks of the normalized XPS spectra in the range from the valence band edge up to 13 eV binding energy are less dependent on the alkyl chain than the DOS (see Fig. 2(b)). Though, this may also result from the unknown cross-sections, here further investigations will be needed.

In addition to the XPS spectra we determined also electron spectra for the more surface-sensitive methods UPS (He I and II) and MIES for all four imidazolium-based ILs of interest in this study. In Fig. 3, these spectra have been arbitrarily normalized to the peak at 12 eV, in order to compare them with the XPS spectra (Fig. 3(a)). Though all spectra show qualitatively similar features, i.e. peaks around 7 eV, 11 eV and 12 eV for the more surface sensi-

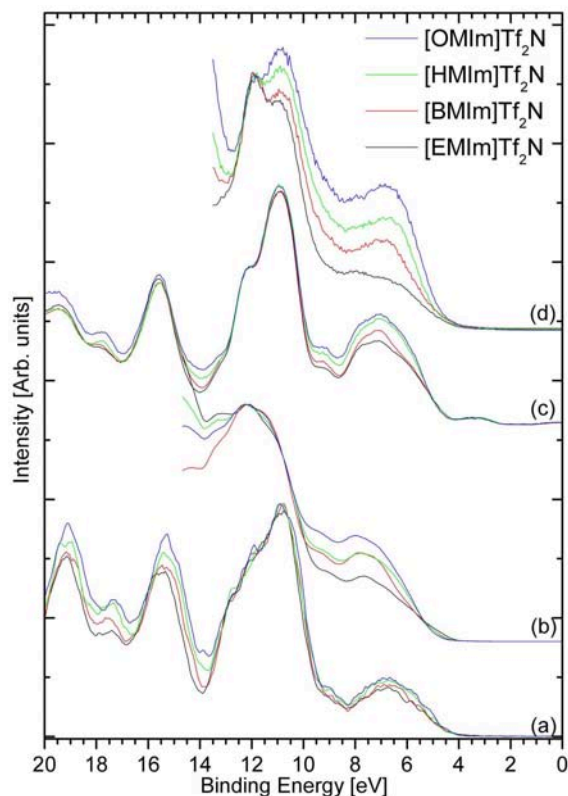


FIG. 3: The variations in the electron emission spectrum taken from the four different types of imidazolium-based ILs ([RMIm] Tf_2N) surface: (a) the valence band by XPS, (b) UPS (He I), (c) UPS (He II) and (d) MIES.

tive methods the dependence of the spectra on the alkyl chain length of the respective IL differs significantly from that found in the XPS spectra. In particular in the most surface-sensitive method MIES (Fig. 3(d)), the heights of the peaks about 7 eV compared to the normalized peak at 12 eV increases for longer alkyl chains much more than in XPS, where this effect is minor. For the intermediate surface-sensitivity, the UPS spectra (Fig. 3(b): He I, 3(c): He II), exhibit this effect less pronounced than the MIES spectra, but much more significant than the XPS spectra. The main difference between MIES and UPS spectra normalized to the peak at 12 eV, however, is the observation that in UPS spectra the peak at 11 eV shows only very small changes for different chain lengths, whereas in the MIES spectra this peak follows more the alkyl chain dependency of the peak at 7 eV, though to a lower extent.

These findings indicate clearly that the structure of the IL surface is different from the bulk, either for a different, non-stoichiometric composition or a decent orientation of the ions in the up-most molecular layer. Lovelock *et al.* [7] have interpreted their ARXPS measurements on imidazolium-based ILs with various alkyl chains in such way, that the alkyl chains stick up from the IL surface. Consequently, they should dominate the spectra from surface-sensitive methods more than the XPS spectrum representing the bulk valence band structure, where the ions may be assumed to be isotropic and stoichiometric distributed. For the unclear contributions of the alkyl chains to the valence band structure, however, we are cur-

rently not well able to confirm this interpretation also by our measurements. The found differences between MIES, UPS, and XPS spectra may be also result from a different composition of the surface compared to the stoichiometric bulk.

IV. CONCLUSIONS

In our XPS measurements of the nitrogen and carbon core levels we could clearly distinguish the anion and cations of the four different types of imidazolium-based ILs ([RMIm]⁺[Tf₂N]⁻ with R=Ethyl, Butyl, Hexyl, and Octyl). Moreover the peak-structure of the C(1s) emission from the [RMIm]⁺ cations could be correlated to different position of the carbon atoms in the imidazole-ring or alkyl chains. By the intensity as well as chemical shifts the length of the attached alkyl chain could be distinguished, too.

The comparison of XPS, UPS (He I and II), MIES spectra revealed distinguishable dependencies of the valence band structure on the alkyl chain in the bulk and at the surface of the ILs. The reason for this effect can be both, non-stoichiometric composition of the IL and/or specific orientation of the ions, e.g. sticking up of the alkyl chains, at the surface. This alternative could not be decided in the present work but will be subject to future research.

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