Valence band photoelectron spectra of [EMIM][BF₄] ionic liquid vapor: Evidences of electronic relaxation

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Experimental ultraviolet photoelectron spectra of [EMIM][BF₄] molecules were recorded and analyzed. The low binding energy tail of the HOMO peak in the UPS spectrum is about 7.5 eV, in agreement with previous estimations of the liquid phase HOMO-LUMO gap. These gas-phase spectra reveal detailed information about the electronic structure of the molecules of this common ionic liquid and enable comparison with ab initio calculation methods like density functional theory (DFT) and Möller–Plesset perturbation theory (MP2). The ab initio calculations are able to explain most of the features in the spectra.

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1. Introduction

Ionic liquids have many interesting properties, like low melting temperatures, excellent solvation ability, low volatility and relatively high thermal stability. They have possible applications in diverse fields, such as chemical synthesis, catalysis, biocatalysis, separation technology, electrochemistry, analytical chemistry, nanotechnology etc. [1]. With the selection of many available anions and cations it is possible to synthesize a vast number of different ionic liquids with varying properties.

As Nishi et al. [2] pointed out, understanding the electronic structure of the ionic liquids is important and an essential question is how the electronic structures of the cations and the anions are combined to form the overall ionic liquid electron structure. As noted by Yoshimura et al., the understanding of the electronic structure of room-temperature ionic liquids, especially the top of the valence band, is very important in the study of ionic liquids [3]. It is therefore of interest to compare gas phase experimental data to theoretical calculations, since the calculation of liquid phase properties of ionic liquids is often complicated and therefore many calculations are based on gas-phase systems. Furthermore, experimental gas-phase photoelectron spectra can help to validate ab initio studies, their theoretical models and approximations.

Although ionic liquids have very low vapor pressures, vaporization is still occurring in vacuum, thus making gas phase experiments possible. Some of the ionic liquids can even be distilled in vacuum with minor thermal degradation [4,5].

Previously we studied the evaporation and photodissociation of this simple ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) using time-of-flight mass spectroscopy [6]. [EMIM][BF₄] consists of the EMIM cation and the BF₄ anion. The simplest notation for the cations and anions ([CATION][ANION]) has been used in this study, while many different designations have been used for this compound: [emim][BF₄], EMIM-BF₄, [C₂mim][BF₄], [C₂C₁IM][BF₄], [EMI][BF₄], EMI-BF₄ etc.

It has been already established that the ionic liquid vapor is composed of neutral species [7–9]. It is expected that ion-pairs evaporate from the ionic liquid and little or no clusters are present. It is also known that under electronic excitation or ionization, the ionic liquids are relatively unstable to fragmentation [6,10].

Using this knowledge that the intact ionic liquid ion-pairs are indeed evaporating from the ionic liquid upon heating, the experimental gas phase UPS (ultraviolet photoelectron spectroscopy) spectrum has been recorded and will be compared to ab initio calculations.

To the best of our knowledge this is the first presentation of a vapor phase UPS spectra of [EMIM][BF₄]. The UPS spectrum of [EMIM][Tf₂N] has been measured by Strasser et al. [11]. However, very few vapor phase UPS spectra of ionic liquids have been reported to date.

2. Experimental and computational details

The experiment was performed at an undulator source beamlne 1411 of the MAX-II synchrotron radiation facility (Lund, Sweden) [12]. The beamlne was equipped with a modified SX-700 monochromator with 1220 lines/mm plane grating and an elliptical focusing mirror. The incidence photon energy during the photoemission measurements was 60.6 eV and the photon beam diameter was about 1 mm. The
kinetic energies of the photoelectrons were determined with a hemispherical electron analyzer Scienta SES-200. Pass energy of 100 eV was chosen for the measurements. These operation conditions lead to a total energy resolution below 0.15 eV fwhm (full width at half maximum).

The [EMIM][BF₄] ionic liquid with a stated purity of >99% was purchased from Sigma-Aldrich and was used without further treatment. It was thermally evaporated to the sample region of the analysis vacuum chamber from a quartz crucible of an effusion cell (MBE Komponenten NTEZ-40). The temperature of the ionic liquid in the effusion cell was at 190 °C and no thermal decomposition is expected at that temperature.

Due to the relatively low vapor density of the ionic liquid, some background gases also appear in the spectra, most notably N₂, which contributes peaks at 15.6 eV, 16.7 eV, 16.9 eV, 17.1 eV and 18.7 eV [13, 14]. Only the 16.9 eV N₂ peak is significantly affecting the intensity of a peak (J) from the ionic liquid. Fortunately, the peaks from the background gases are weak and do not influence the interpretation of the spectra (see Fig. 1).

Ab initio DFT (density functional theory) and MP2 (Møller–Plesset perturbation theory) calculations were performed using Spartan 14 software [15]. The Gaussian basis sets 6-311G** (d, p-polarized basis set) has been used in the calculations. The density of states (DOS) type spectra shown in Fig. 1 were obtained by convoluting the calculated discrete states with a Gaussian function (0.4 eV fwhm) under the assumption that the electron emission intensities from each orbital are the same and that the photoemission process is non-adiabatic, i.e. the emission process of the photoelectron is much faster than the rearrangement of the electron system after the absorption of the photon (the sudden approximation). It will be shown later, that this approximation is not always valid for the [EMIM][BF₄] molecules.

For compensating the difficulty in the energy scale of the ab initio calculations, the energy scales were contracted and shifted for better fit to the observed spectrum. A scaling factor of 1.1 has been used for the DFT and MP2 calculated energies of the [EMIM][BF₄] molecule. The corresponding shifts used are 2 and −3.7 eV. Despite the relatively high values of the correction terms, the absolute energy shifts are below 4 eV.

This somewhat large value of the scaling factor had to be used to get the carbon 2s derived orbitals (instead of the N 1s core orbitals like Reinmöller et al. [16] and Ulbrich et al. [17]) to the experimental energy, since the calculation tends to underestimate the binding energies of the carbon 2s orbitals (N, M peaks).

The principles outlined here are used in many other works [2,3,9,18–21] and the method is the simplest approximation for the UPS valence spectra. The absolute values of the binding energies depend on the basis set and functionals used for the calculation, but as noted by Reinmöller et al. the general shape of the DOS seems to be robust against changes in the basis set [16]. A quantitative fit of the shape of the UPS spectra cannot be expected because the intensities of the different spectroscopic methods do not depend on the DOS only [18], but also on the experimental geometry, electron analyzer transmission function, incident photon energy, photoemission cross sections among other parameters. It has been shown, that the intensities can be described better, if the photoemission cross sections are taken into account [16,17].

Therefore, the focus of this study is mainly on the shape and structures of the experimental UPS spectrum in order to better understand the electronic structure of the ionic liquid molecules and make the comparison with the liquid phase electronic structure possible.

Also, it is believed that different conformers do not noticeably influence the shape of the UPS spectra [16].

The so-called non-relaxed calculation refers to the calculation of the “ion-pair cation” (positively charged [EMIM][BF₄] molecule) in the geometry of the neutral ion-pair (the Franck-Condon principle). This calculation is non-relaxed in terms of vibronic (nuclear motion) degrees of freedom but relaxed in terms of electronic configuration. In other cases the geometry of the calculated structures was optimized.

3. Results and discussion

The experimental UPS spectrum of [EMIM][BF₄] is shown in Fig. 1. The spectrum is composed of two groups of stronger peaks – one group at around 11–14 eV binding energies (and lower) and the other group around 15–18 eV (and higher) while in-between (at energies 14–15 eV), there appears to be a gap. These regions will be referred to as the outer and inner valence bands respectively. In contrast to the experimental liquid phase photoelectron spectra of [BMIM][BF₄] [3,17] or [EMIM][BF₄] (not shown, but very similar to [BMIM][BF₄] in [3]), where three wide peaks are visible, the gas phase spectra are free from inelastic scattering and show much more details. The comparison between gas phase and liquid phase UPS spectra will be pursued in a forthcoming paper.

The inner valence band peaks (H–N) are represented very well in the case of MP2 calculation of the bare EMIM (Fig. 2), therefore they have mostly cationic origin. The outer valence band is represented best by the DFT calculation of the full [EMIM][BF₄] ion-pair (molecule). The fluorine atoms of the anion are contributing most to the outer valence band.

The reader is referred to Table 1 for the peak assignment. It is important to point out that the ab initio calculation shows, that many valence states of the [EMIM][BF₄] ion-pair are delocalized over the full molecule and therefore it is difficult to assign the “strongest contributing atoms”. If the removal of charge during photoemission is taken into account, then the DFT calculation (Fig. 1) is also able to represent the inner valence band and the MP2 calculation (Fig. 2) is capable of describing the outer valence band. However, in both cases, as either the inner or outer valence band description is improved, the outer or inner (respectively) valence band description gets worse. This is due to the fact that the simple calculation performed here neglects orbital relaxation and correlation effects. In many cases these two effects cancel each other (partially), Koopmans’ theorem [22,23] holds and the UPS spectrum reflects the ground state molecular orbital energies. The orbital relaxation...
energies are usually not >1–2 eV, but can be larger in strongly correlated materials (e.g. in case of transition metal compounds) [24].

To gain some further insight to the electronic relaxation process the charge distribution was calculated. The comparison between the charge distributions of the neutral ion-pair and the positively charged non-relaxed ion was made. In case of MP2 wavefunctions the analysis shows that the negative charge is preferably removed from the cation (predominately from the atoms of the aromatic ring – C1–C3, N1, N2) while the anion should remain mostly unaffected. In case of the DFT calculation however, the comparison shows that the anion and the cation should both be affected during the photoemission process (lose some negative charge).

When comparing the DFT calculated DOS to the experimental UPS spectrum (see Fig. 1), the following conclusion can be drawn – if the electron is removed from the inner valence band, there is almost complete relaxation of the electronic structure. This conclusion is not surprising since the correlation effects should be strong in the inner valence band. This is also supported by the fact that the MP2 calculation of the bare EMIM gives a very good agreement with the inner valence band (see Fig. 2).

In case of outer valence band photoemission, little relaxation seems to be happening, since the outer valence band of the non-relaxed B3LYP calculation does not agree well with the experimental spectrum, while the DOS of the uncharged molecule (ion-pair) does (see Fig. 1).

However, in case of the MP2 calculation of the inner valence band, different peaks shift by different amounts: peaks H, I, J, K, N seem to shift (relax) too much, while the L and M peaks shift to the correct location (see Fig. 2). Therefore, the MP2 calculation either predicts too much relaxation or there is incomplete relaxation in the inner valence band. This could be due to the fact that the MP2 calculation predicts that most of the negative charge should be “lost” from the cation and therefore strong electronic relaxation in the inner valence band may occur.

In contrast to the DFT calculation, the MP2 calculation correctly predicts that there is no significant relaxation in the E and D peaks of the outer valence band. Also, the F peak correctly shifts to lower binding energies, but the A and B photoelectron peaks disappear in the calculated non-relaxed cation DOS. Since the F, E and D peaks are mostly associated with the anion and the A–C peaks are cation related, it can be concluded that there is no significant relaxation in the anion and the outer valence band states of the cation (peaks A–C).

The photoelectron peaks A–C are not represented in any B3LYP calculation (Fig. 1) and neither in the non-relaxed MP2 calculation (Fig. 2). Only two of the A–C peaks are present in the bare EMIM or the neutral ion-pair [EMIM][BF4] MP2 calculation.

Yoshimura et al. observed a shoulder to the strong fluorine 2p derived outer valence band states in [BMIM][PF6] and [BMIM][BF4] and assigned it to C 2p and N 2p [3]. The authors came to the conclusion that the top region of the valence levels is not derived from the anion, but rather from the cation, in contrast to usual salts like alkali halides. Indeed, both MP2 calculations show that the HOMO level is mostly associated with the cation (i.e. no contribution from fluorine). The B3LYP calculation also assigns the HOMO to C1, C2, C3 and it shows up as a shoulder to the D peak (see Fig. 1). Kanai et al. showed that in [BMIM][PF6] the top of the valence band is derived from the cations HOMO level [25,20]. Ulbrich et al. also calculated the top of the valence band to be cationic origin in a similar ionic liquid [BMIM][BF4] [17]. Nishi et al. showed that for both [BMIM][PF6] and [BMIM][BF4] the HOMO level is derived from the cations [2]. However, in case of [EMIM][Tf2N], Krischok et al. concluded that the first 2–3 eV from the HOMO level were associated with the anion [21] and found it to be strange that the HOMO level of [EMIM][Tf2N] could be associated with the organic cation [21].

The low binding energy tail of the peak A is about 7.5 eV. The HOMOLUMO gap predicted by the DFT calculation is 6.8 eV. Kanai et al. [25] claimed a HOMO-LUMO gap of 7.2 eV in [BMIM][BF4]. They also claimed that the gap is determined by the cation alone. Nishi et al. estimated the HOMO-LUMO gap to be 7.2 eV [2] for both [BMIM][PF6] and [BMIM][BF4]. Kanai et al. also showed by both XPS and SXES that the energy gap in [BMIM][PF6] is around 7.2 eV [20]. Kuusik et al. showed that the photodissociation threshold of [EMIM][BF4] is 7.4 eV [6].

The peak G is very weak in the experimental UPS spectrum, but the intensity around the G peak is higher than the background or “dark count” around that energy. The ab initio calculations predict a state or even a two states around that energy. Only the MP2 calculation shows a small gap around that energy. Looking at the decomposition (C4–C6, H6–H11) of the calculated MO’s that correspond to the weak experimental G1 and G2 peaks, it is evident, that the peak(s) seems to originate from the ethyl and methyl groups of the cation. The low cross sections of the hydrogen atoms and the s-symmetry orbitals may explain their low intensity in the experimental spectrum.

As it was pointed out by Reimmöller et al., the cross section of photoemission is much larger in case of F 2p orbitals compared to C 2p orbitals [16]. Therefore the fluorine derived states have higher intensities in the experimental spectra. In case of the BF4 anion, this implies that the anion contributes much more to the UPS spectra. This is true for most ionic liquids [16,17,19].

### 4. Conclusions

UPS valence band spectrum of [EMIM][BF4] ionic liquid molecules have been measured and analyzed. The experimental spectrum shows

<table>
<thead>
<tr>
<th>Peak</th>
<th>Bind. energy (eV)</th>
<th>Strongest contributing atoms and character</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>7.8</td>
<td>C1–C3, N1, N2 (n-bonds in the imidazolium ring)</td>
</tr>
<tr>
<td>A2</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>9.4</td>
<td>N1, N2, (C1, C2, C4–C6)</td>
</tr>
<tr>
<td>C</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>11.8</td>
<td>Mostly F 2p (except the low b.e. shoulder which is C 2p)</td>
</tr>
<tr>
<td>E</td>
<td>12.8</td>
<td>Mostly F 2p</td>
</tr>
<tr>
<td>F</td>
<td>13.6</td>
<td>Mostly F 2p</td>
</tr>
<tr>
<td>G1</td>
<td>14.4</td>
<td>C4–C6, H6–H11 (methyl and ethyl groups)</td>
</tr>
<tr>
<td>G2</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>15.8</td>
<td>F, B, C3, C6, N1 (both anion and cation atoms)</td>
</tr>
<tr>
<td>I</td>
<td>16.2</td>
<td>C3, H3, (C1, C2, N1, N2, no ethyl or methyl groups)</td>
</tr>
<tr>
<td>J</td>
<td>16.9</td>
<td>Mostly C 2s (σ-bonds)</td>
</tr>
<tr>
<td>K</td>
<td>17.8</td>
<td>C1–C3, C6, N1, N2 (n-bonds)</td>
</tr>
<tr>
<td>L</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>21.4</td>
<td>C 2s (σ-bonds)</td>
</tr>
</tbody>
</table>
that the valence band seems to be composed of two regions: inner and outer bands. There is an overall qualitative agreement between the experimental UPS spectrum and the calculated DOS. However, it is difficult to describe the shape of the inner and outer valence bands with one type of calculation. It was shown that electronic relaxation during photoemission is happening in the inner valence band, while little or no relaxation occurs in the anion.

Although the simple MP2 calculation overestimates the relaxation in the inner valence band, there are discrepancies in the L, K and F peak energies and fails to describe the C (or B) peak, it still seems to offer the best overall description of the electronic structure of the [EMIM][BF4] ionic liquid molecules.

Most importantly, the MP2 calculation seems to describe the HOMO level correctly.

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References