



Photoelectron spectroscopy on ionic liquid surfaces — Theory and experiment



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ABSTRACT

We have studied various ionic liquids by photoemission spectroscopy. For a more in depth interpretation of the experimental results, in particular of valence spectra, a theoretical reconstruction of these spectra by means of density functional theory is desired. In order to obtain correct binding energies and peak intensities a simple calculation of the density of states is not sufficient. A self-developed method, which bases on known elementary cross sections for the photoeffect and adjustments of the kinetic energy of emitted electrons, is applied. Particular attention is paid to the necessary relative shift for a cation and anion due to their different Madelung potentials. In order to study this effect, we have varied the cations and the anions of the ionic liquids under investigation, systematically.

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1. Introduction

Ionic liquids (ILs) are an attractive class of materials with manifold interesting properties (see e.g. [1] for an overview). Additionally, their physico-chemical properties (e.g. liquid state, chemical inertness, viscosity, heat capacity, density, polarity, etc.), which depend on the diverse possibilities of combining cations and anions, can be tuned over a wide range. This makes them an interesting class of material attending enormous scientific interest. Due to these properties they are also interesting for many applications (see e.g. [2–9]). However, a detailed understanding of the interface between ILs and the environment is important for many applications (for example in catalysis [2,3], electrochemical deposition [4], tribology [8], etc.).

Ionic liquids are suitable for examination under UHV conditions required for many surface sensitive techniques because of their commonly low vapor pressure [10–12]. In the past e.g. sum-frequency generation (SFG) [13–18], X-ray and neutron reflectometry [18–20] and grazing incidence diffraction [21], as well as metastable induced electron spectroscopy (MIES) [22–26], high-resolution electron energy-loss spectroscopy (HREELS) [23], low-energy ion scattering (LEIS) [27], high-resolution Rutherford backscattering (HRBS) [28], direct recoil spectroscopy (DRS) [29,30] and surface tension measurements [17,31] are utilized techniques furnishing insight into the surface properties of ILs. The photoelectron spectroscopy is another surface sensitive method which has been successfully applied to investigate the chemical composition as well as the ionic arrangement at the surface of ionic liquids [24,32–34]. However, for studies of the valence region the interpretation calls for strong theoretical support [35–38]. In this study we use a previously developed method for the reconstruction of photoemission spectra [26] following the

intensity model by Gelius [39] to an extended range of ionic liquids and discuss the necessary energetic shift of cation and anion related contributions with respect to a “Madelung-type” contribution.

2. Selected ionic liquids, sample preparation and basic characterization

In this study we have analyzed three series of ionic liquid samples, where (i) the cation 1-butyl-3-methyl-imidazolium ($[BMIm]^+$) is given and the anions vary in size from chloride (Cl^-), over tetrafluoroborate ($[BF_4]^-$), dicyanamide ($[DCA]^-$), and trifluoromethanesulfonate ($[TfO]^-$), to bis(trifluoromethane-sulfonyl)imide ($[Tf_2N]^-$); (ii) the alkyl chain in the 1-alkyl-3-methyl-imidazolium cation varies in length from ethyl ($[EMIm]^+$) over butyl ($[BMIm]^+$) and hexyl ($[HMIm]^+$) to octyl ($[OMIm]^+$) for the given anion $[Tf_2N]^-$; and (iii) with the cations 1-ethyl-1-methyl-pyrrolidinium ($[EMP]^+$), 1-propyl-1-methyl-pyrrolidinium ($[PMP]^+$), and 1-butyl-1-methyl-pyrrolidinium ($[BMP]^+$) all combined with the anion $[Tf_2N]^-$.

The ionic liquids $[BMIm]BF_4$, $[XMI]Tf_2N$ ($X = E, B, H, O$), $[EMP]Tf_2N$, $[PMP]Tf_2N$, and $[BMP]Tf_2N$ were purchased from IoLiTec in ultra-pure quality; $[BMIm]Cl$ was provided by the group of P. Wasserscheid (Friedrich-Alexander Universität Erlangen-Nürnberg), and $[BMIm]TfO$ was one of the reference samples distributed in the priority program (SPP 1191 Ionic Liquids). $[BMIm]DCA$ was provided by F. Endres group (TU Clausthal).

All samples were prepared by depositing one droplet of the liquid, with a volume of about 0.01 ml, onto a polycrystalline Au film of about 250 nm thickness deposited on Si(100), separated by a Ti adhesion layer, as sample support. Supposed that the droplet wets the whole sample surface of $\sim 1 \text{ cm}^2$, the resulting film thickness is in the range of $\sim 100 \mu\text{m}$. After outgassing in a load lock system the sample

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was transferred into a UHV chamber with a base pressure of less than $2 \cdot 10^{-10}$ mbar [40].

For all samples XPS spectra were recorded by using monochromated Al K_{α} radiation ($h\nu = 1486.7$ eV), with a spot diameter of ~ 1 mm at the sample surface. For the photoelectrons emitted at an angle of $\theta_e = 53^\circ$ with respect to the surface normal, the kinetic energies were determined with a hemispherical electron analyzer. Pass energies of 50 eV in case of the survey spectra, 15 eV for core-level spectra, and 35 eV for valence spectra were chosen. The operation conditions lead to a total energy resolution below 0.6 eV (on Ag 3d_{5/2} at a pass-energy of 15 eV for single scans). For data analysis of the recorded spectra, a Shirley-type background was applied and the photoemission peaks were fitted using Gaussian–Lorentzian functions.

For UPS He II ($h\nu = 40.8$ eV) radiation was used and the pass energy of the analyzer was set to 5 eV resulting in a total energy resolution of less than 150 meV.

Prior to analyzing the valence structure of the investigated ionic liquids, all samples have been characterized in terms of chemical composition (possible impurities) and stability under experimental conditions in particular considering beam damage, as discussed in [40].

2.1. Sample purity

By analyzing the elements present at the ionic liquid sample surface, XPS enables us to identify surface contaminations, such as silicon [41], esters, carboxylic acids [28] or hydrocarbons. For each studied ionic liquid all expected elements contained in the respective chemical structures were detected in the XPS survey spectra. Exemplarily a survey spectrum of [BMIm]TfO is shown in Fig. 1.

The samples of [BMIm]Cl, [BMIm]BF₄ and [EMIm]Tf₂N contained small traces of impurities or substrate related signals, whereas for [BMIm]DCA a strong contamination layer was observed. By fitting the peak area of the core level states (N1s, C1s, F1s, O1s, S2s, B1s, Cl2s) the stoichiometry of the IL samples can be quantified. For this quantification, we assumed a homogeneous elemental distribution, an analyser transmission function inverse to the kinetic electron energy, and used photoemission cross sections and asymmetry parameters from Ref. [42]. The experimental stoichiometries of all investigated ionic liquids were calculated from the high resolution spectra and compared with the nominal values from the chemical formulae (Table 1).

All experimentally determined values are close to the nominal stoichiometries except for the [BMIm]DCA and [BMIm]BF₄ samples. For the [DCA][−]-based ionic liquid samples a significant contamination of unexpected oxygen occurs and the concentration of nitrogen is unexpectedly low, whereas for the [BF₄][−] containing sample, we observed strong

deviations from the expected 1:4 stoichiometry between the anion elements. In this context it is important to note, that this particular ionic liquid was also the subject of relatively strong changes under X-ray illumination (see next section). Minor deviations may be caused by an improper consideration of the transmission function of the energy analyser, which was assumed to be inverse to the kinetic electron energy. Moreover, the tendency to an enhanced carbon signal might be partially related to surface orientation effects of the cations in particular for longer alkyl chains [13,24,43–47]. Nevertheless, some minor carbon-impurities cannot be completely ruled out. However, the amount of the detected impurities for [BMIm]Cl and [BMIm]BF₄ is less than 0.1 atoms per ion pair. The gold induced signals (Au4f) in the [BMIm]Cl, [BMIm]BF₄ and [BMIm]DCA spectra are caused by emission of the substrate, which is related to an insufficient wetting of the substrate with the ionic liquids. The detected oxygen in the [BMIm]BF₄ and [BMIm]DCA spectra may be caused by additional water due to the hygroscopic nature of these ionic liquids. Taking the C1s signal of the [BMIm]DCA sample into account, also carbonyl groups could be responsible for the additional amount of oxygen. Hashimoto et al. have shown in a HRBS and XPS study that for [BMIm]DCA the surface can be covered by a thin contamination layer, which consists of carbonyl groups and aliphatic carbon [28]. Our XPS results are in line with these measurements. The detected chlorine (Cl2s) in the [BMIm]DCA sample may be caused by residues from the ionic liquid production process. Silicon (Si2p and 2s), which is detected in [EMIm]Tf₂N, is a known impurity of some ionic liquid samples [41].

2.2. Beam damage

A further aspect, which has been analyzed in prior more detailed studies of the valence states, is the influence of radiation on the ionic liquid. X-ray radiation may cause degradation effects during photoelectron spectroscopy at ionic liquid surfaces [40,41,47]. In one of these studies [40] the influence of the monochromated AlK_α radiation on the chemical composition of [EMIm]Tf₂N as well as the radiation-induced desorption of ionic liquid fragments has been demonstrated and discussed in detail. Concerning the selected ILs in this study, we could prove that monochromated X-ray exposure over time scales necessary for XPS analysis lead to negligible degradation effects in case of [XmIm]Tf₂N, [XMP]Tf₂N and [BMIm]TfO. In contrast to these relatively stable ionic liquids, [BMIm]Cl and [BMIm]BF₄ showed already strong degradation effects after 2–3 h irradiation with the monochromated AlK_α. These beam damages manifest themselves in a new structure in the N1s region (see Fig. 2) on the lower binding energy side of the imidazolium-related signal. After 3 h irradiation it has been increased to 10% of the

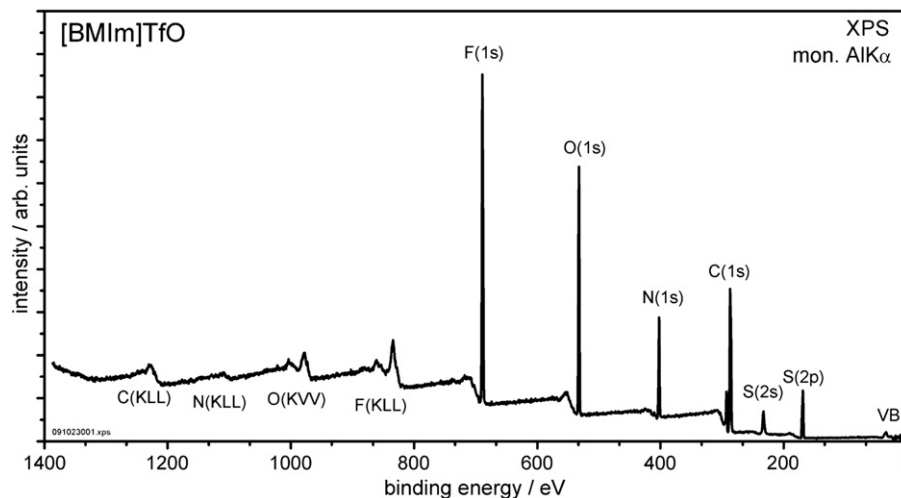


Fig. 1. XPS survey spectrum of [BMIm]TfO.

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