

XPS analysis of an Ionic liquid

Keywords

Ionic liquid,
ARXPS

Application Note MO422(1)

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Overview

An AXIS spectrometer was used to probe the surface chemistry of a widely used ionic liquid. The elemental surface composition was analysed and information was gained regarding the various chemical environments of the surface elements. Traditional surface analysis techniques such as ARXPS were exploited to determine the orientation of the mobile molecules in the uppermost layer of the liquid. The stability of the liquids under X-ray irradiation was also investigated.

Introduction

In the past ten years ionic liquids have become an area of increasing popularity in academic research which has resulted in the stellar rise in the number of publications in this field. This rise can in part be attributed to the wide ranging applications these novel materials can be adapted to. Only recently has this new field attracted the attention of a growing number of surface scientists interested in exploring the interactions at the both the liquid/gas and liquid/solid interfaces. Of particular interest is the structure and composition of the liquid/gas interface as this is where the adsorption and absorption of gasses occurs. These processes are known to play key roles in processes such as heterogeneous catalysis and gas distillation and separation. Aside from such obvious applications, the surface analysis of ionic liquid helps in the fundamental understanding of these unique materials.

Here we decided to analyse a common ionic liquid to highlight the ways in which a high performance x-ray photoelectron spectrometer can be used to investigate the chemistry and structure of the liquid/gas interface.

Experimental

In this study we utilise the technique of XPS to analyse the surfaces of an ionic liquids. The AXIS Supra was used to analyse the liquid using Al k-alpha X-ray radiation. Liquid [EMIM][NTf₂] was prepared using literature methods to ensure a high purity. For analysis a single drop of each sample was pipetted onto a copper sample stub which was pumped for >3 hours before introduction to the analysis chamber. This allowed all remaining solvents to be pumped away.

Results

Figure 1 shows the survey spectrum acquired for the ionic liquid [EMIM][NTf₂]. This spectrum allows us to accurately identify the elemental composition of the surface region using the auto peak ID function. Here we can see that all of the elements attributed to the ionic liquid (C, O, F, S and N) are present in the surface region. It is also possible to observe any contaminant which may still be present in the liquid.

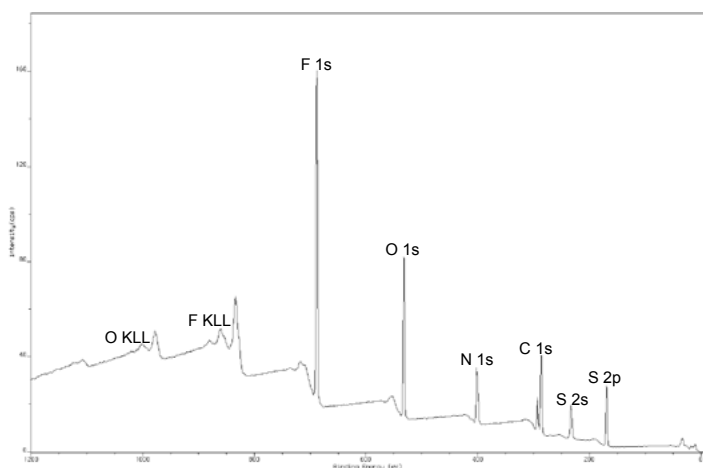


Figure 1: Survey spectrum of [EMIM][NTf₂].

A quantification report is automatically generated by the software accurately identifying the relative atomic concentration of the near surface region (see Table 1)

Element	O	C	F	N	S
Atomic conc. (%)	16.11	32.23	29.71	12.32	8.63

Table 1: Quantification report from survey scan for [EMIM][NTf₂].

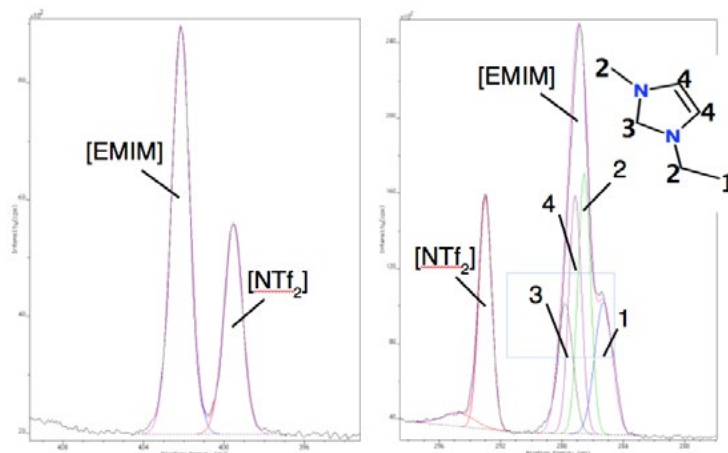


Figure 2: N 1s (left) and C 1s (right) spectrum of [EMIM][NTf₂].

Narrow region spectra were then acquired for the relevant elements to investigate the surface chemistry and the different electronic environments present. Figure 2 shows the narrow region spectra for both the N 1s and C 1s orbitals. Two peaks were observed in the N 1s spectra which can be attributed to the two different environments of nitrogen in the molecule. The higher binding energy peak is assigned as the [EMIM] cation whilst the lower peak is assigned to the [NTf₂] anion. The relative stoichiometry of these peaks also agrees with this conclusion. The C 1s spectrum exhibits several interesting features. The peak at 293.0 eV can be assigned to the fluorine bonded carbon atoms of the [NTf₂] anion. The lower binding energy feature can be peak fitted according to the different chemical environments of the [EMIM] cation.

By varying the angle of the sample and therefore the photoelectron emission angle, one can gain non-destructive depth information of the surface region. C 1s spectra were acquired at different emission angles to gain information regarding surface concentrations (see figure 3). A change in shape is clearly observed with an increase in intensity of the feature at 285.3 eV. This peak was previously attributed to the aliphatic chain carbon. This indicates an enrichment of the surface region with the aliphatic chain. This agrees with previous studies where the aliphatic carbon is thought to dominate the chemistry of the liquid surface, with the chain orientated away from the liquid towards the vacuum.

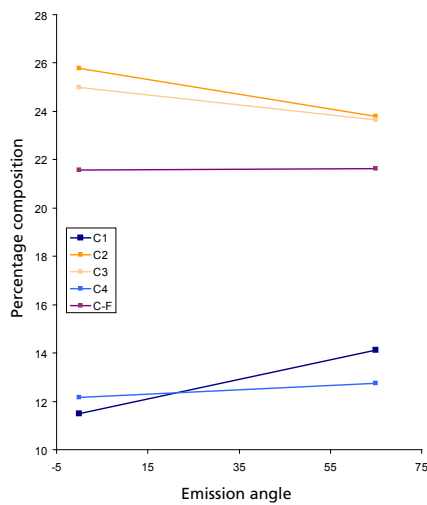
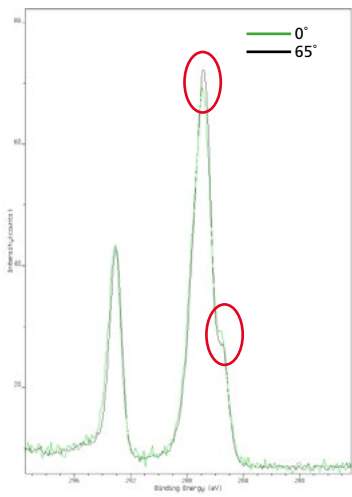


Figure 3: ARXPS of [EMIM][NTf₂].

Figure 3 further highlights the change in intensity of the different chemical environments of the carbon peak with respect to emission angle indicating the orientation away from the liquid towards the vacuum.

Conclusions

X-ray photoelectron spectroscopy was used to analyse the elemental composition and carbon chemistry of a commonly used ionic liquid [EMIM][NTf₂]. The chemical composition of the surface and the different chemical states of the carbon and nitrogen atoms were explored. Angle-resolved experiments indicate that the aliphatic carbon chain is orientated away from liquid towards the vacuum.

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