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In Situ XPS Monitoring of Bulk Ionic Liquid Reactions: Shedding Light on Organic Reaction Mechanisms

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Ionic liquids (ILs), which are materials that are composed solely of ions and have a melting point below 100 °C, have been a source of fascination for scientists and engineers alike for many decades. The unusual combination of large liquid range, substrate–reactant solubility, and general stability has led to a explosion in their use as solvents for a host of processes ranging from the ubiquitous Heck coupling through electroplating and refining to lubrication, and particularly in challenging aerospace-related environments.[1,2] Indeed, application in deep space is only possible because of the remarkably low vapor pressures exhibited by ILs in general. The ability of these materials to remain liquid across such an extreme range of experimental conditions is unique to ILs, opening a vast range of experimental techniques that, until relatively recently, had been confined to the investigation of solid samples only.[3]

In 2005/6, although working totally independently from one another, two groups almost simultaneously published reports on the investigation of IL-based systems using X-ray photoelectron spectroscopy (XPS).[4] Together, these publications triggered an interest in the field, and since then, many groups have analyzed ILs or IL-modified surfaces by XPS in the course of their investigations.[5] The investigation, and indeed application of ILs under such ultrahigh-vacuum (UHV) conditions, is now almost commonplace as researchers are now aware of the advantages and opportunities that the ultraclean UHV environment can provide. Significant contributions are noted in the development of in situ microscopies, particularly the use of scanning electron microscpy (SEM) and related methods for the investigation of metal deposition and the control of nanoparticle growth during chemical vapor deposition onto neat IL coated substrates.[3b,6] The scientific platform offered by the combination of ILs in an ultraclean UHV environment is mind-boggling: New ideas and applications occur every day, and as each experiment is carried out, we learn more about the attributes and roles that ILs can offer in each case.

The initial report in this area was focused on the oft-observed reduction of palladium(II) during the course of a simple palladium-catalyzed coupling reaction.[4b] The undesired formation of Pd^0 was successfully monitored; this formation was traditionally followed qualitatively by a change in the color of the reaction solution from a glowing gold color to a murky dark suspension of colloidal Pd^0. The experiment was surprisingly simple and the spectroscopy was remarkably clear. The palladium-containing liquid sample was spread onto a standard sample holder and then pumped into the UHV chamber in a matter of hours. The spectra were sharp, defined, and gave exactly what was anticipated. Of course, these results were incredibly serendipitous, and the experience of XPS spectroscopists was crucial in their recording and analysis. However, the results of this extremely simple experiment served to prove a concept, and the concept has blossomed over the past years.

XPS, UPS (UV photoelectron spectroscopy), and indeed a whole range of other UHV-dependent techniques have since been applied in the characterization of IL based systems. The growing field of IL-based surface science is now bearing down on real chemical questions, including the structure of ILs in both the bulk and crucially at interfaces[7] and the role that ILs can have in the tuning of catalytic processes both at solid heterogeneous catalyst surfaces[8] and indeed at coordinated/solvated metal centers in homogeneous catalysis. The adsorption of small molecules onto the surface of an IL layer is a hot topic, particularly in the context of separation science and gas sequestration; XPS and related techniques can give insight into molecular interactions and indeed changes in structure as an adsorbant species is laid down. The ability to investigate cumulative weak interactions will be crucial in the development of new materials that facilitate catch and release of small molecules of interest, namely, CO_2, NO_x, SO_x, and H_2, without any significant costs in terms of energy or performance.[9] The opportunities for these experiments and materials are boundless, yet there is no doubt that although the experiments themselves are both technically and scientifically challenging, they are crucial in the development of an understanding of the fundamental processes that govern process efficiency and reactivity.

A recent communication,[10] and a follow-up full paper,[11] have quite literally pushed XPS into a new domain, the direct monitoring of bulk reactions in the liquid phase. Until now, XPS has been predominantly applied to the investigation of both the composition and structure in the near-surface region.

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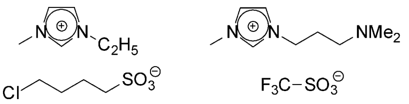
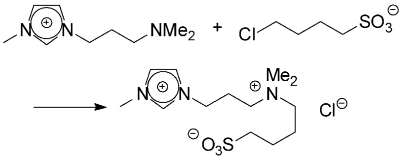
The ability to follow bulk reactions is truly a departure from the experimental norm. Tagging a reactant or material with a property-modifying group is a strategy that has found success in many fields of materials and surface science. However, this very simple yet elegant approach has never been used to reduce the vapor pressure of liquid-phase reaction components. By simply adding suitable ionic tags to individual reaction components (Scheme 1), the authors instantly facilitated the investigation of traditional liquid reactions by XPS and other related UHV-dependent techniques. When mixed, the anion of **IL1** and the cation of **IL2** react by an S_N2 reaction to produce a new ionic liquid **IL3** (Scheme 2). All reaction components are nonvolatile and are thus suitable for analysis by XPS. The product is observed as a mixture of both **IL3** and $[C_2C_1Im][OTf]$. Clearly, this approach offers new fundamental insight into organic reactions in the liquid phase, including information on surface composition, orientation, and the role these can play in determining both mechanism and kinetics under solvent-free ultraclean conditions.



IL1 **IL2**

Scheme 1. Task specific, functionalized ionic liquids **IL1** and **IL2**.



IL3

Scheme 2. S_N2 reaction of the anion of **IL1** and the cation of **IL2** to produce the new ionic liquid, **IL3**. XPS is used to distinguish the change in the chemical environment of Cl as the reaction proceeds.

The XPS spectra (Figure 1) clearly show the impact of the S_N2 reaction on the electronic environments of the free amine and the organohalide, respectively. The Cl 2p and N 1s XP spectra clearly show almost complete conversion (91 ± 5 %) of covalent chlorine (Cl_{cov}; $Cl\,2p_{3/2}$ at 200.2 eV) to chloride (Cl_{ion}; 197.0 eV) in the near-surface region. Ex situ analysis of the product by ESI-MS unambiguously confirmed the identity of the cation of **IL3** ($m/z = 304.2$). By rotating the sample inside the vacuum chamber, the authors also captured data at a so-called grazing emission angle ($\theta = 80°$). In this geometry the experiment becomes much more sensitive to the uppermost atomic layers at the liquid–vacuum interface. When $\theta = 80°$, the information depth (ID) is about 1–1.5 nm; by comparison, when $\theta = 0°$, the ID is much greater (ID ≈ 10 nm), and the data is reflective of the bulk sample. When comparing the data recorded at both 0 and 80°, the authors showed that the sample undergoes a structural change as the S_N2 reaction proceeds. Prior to the reaction, the uppermost layer of the sample is rich in covalently bound chlorine; this observation is consistent with other structural studies, which also suggest that the alkyl substituents of ionic liquids project outwards from the sample surface forming a hydrocarbon-rich layer. During the reaction, covalently bonded chlorine becomes chloride and the relative concentration of chlorine atoms decreases; this is especially clear in the spectra recorded at 80°. This observation suggests that the free chloride ions move away from the surface and become concentrated in an ion-rich underlayer, which is covered again by a hydrocarbon blanket. The ability to watch this rearrangement of the reaction components gives tremendous insight into quite fundamental reaction processes. As XPS is an atom-specific, oxidation-state-sensitive, and potentially surface-selective analytical technique, a significant amount of mechanistically relevant information on the surface structure and reactivity of reaction components may be extracted. The opportunities for this type of experiment really are boundless.

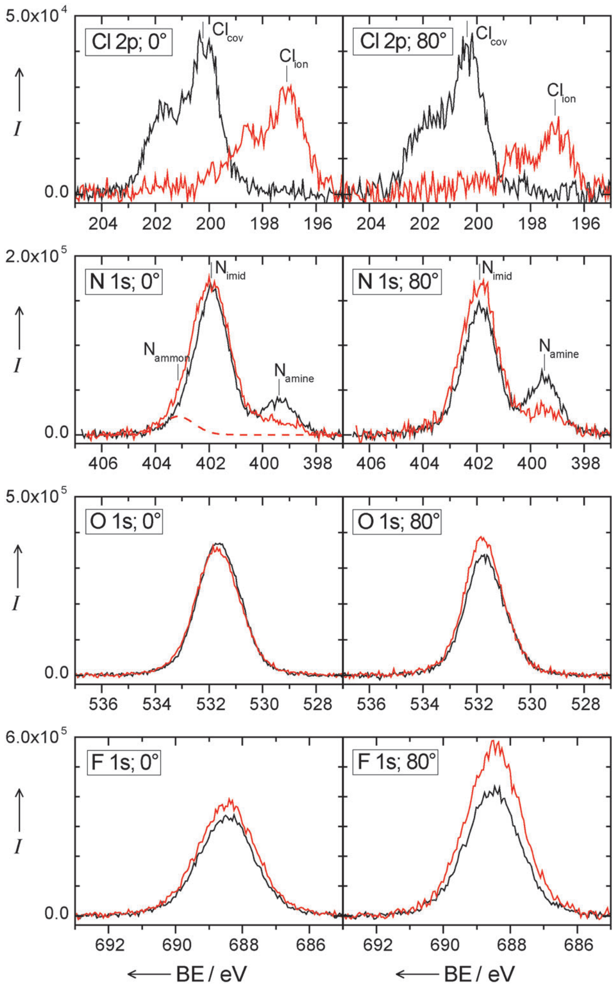


Figure 1. Element-specific high-resolution XP spectra of Cl 2p and N 1s regions of the **IL1**/**IL2** mixture in 0° and 80° emission modes. Data is shown for the sample both before (black line) and after heating (red line) to 100 °C for 2 h. (Adapted from Ref. [10]).

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