

**IONIC LIQUID INTERFACES:
AN X-RAY PHOTOEMISSION
SPECTROSCOPY PERSPECTIVE**

by

Yehia Khalifa

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

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ABSTRACT

The evolution of ambient pressure X-ray photoelectron spectroscopy (AP-XPS) in recent years has allowed for the investigation of ionic liquid interfaces in the presence of a gas phase. In this thesis the vacuum structure and effects of water vapor on the interface of ionic liquids of interest are examined. There are three systems considered in this dissertation, namely, water interactions with a hydrophobic ionic liquid, water interactions with a hydrophilic system, and lastly the unique structuring that exists within an ionic liquid mixture containing both hydrophobic and hydrophilic anions with the same imidazolium-based cation. The total electron scattering cross-section at various kinetic energies was calculated from the hydrophobic ionic liquid [EMIM][Tf₂N]. For the hydrophilic ionic liquid system, the mole fraction of water and its inherent enhancement on the interface relative to the bulk was quantitatively assessed. In regard to the ionic liquid mixture the partitioning behavior of the hydrophobic anion at the surface was quantitatively calculated via angle resolved XPS (AR-XPS) using a simple methodology to probe vacuum-compatible liquids at a surface-sensitive grazing angle. Furthermore, the effect of water vapor on the ionic liquid mixture surface structure was quantitatively explored.

Chapter 1

INTRODUCTION

1.1 Introduction to XPS:

It is widely understood that most heterogeneous chemical phenomena involve surface chemistry. Some examples of scientific fields affected by interfacial properties include but are not limited to heterogeneous catalysis, nucleation phenomena, electrochemical kinetics and the area of semiconductor science.¹ The tools needed to study molecular scale phenomena have emerged during the 1960's as a result of the confluence of three major factors: ultrahigh vacuum technology (UHV), development of fundamental surface science based on single crystal substrates and the advancement of the physical understanding of electron-solid interactions.² Many advancements to scientific and technological problems in interface science have been solved with the aid tools such as X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA).

1.1.1 X-ray Photoelectron Spectroscopy Working Principle

Photoelectron spectroscopy is fundamentally based on the photoelectric effect, in which a light source of sufficient energy shines on a sample surface of interest and as a result ejects photoelectrons. By utilizing a monochromatic photon source with a known energy and by analyzing the kinetic energy of the electrons one is effectively able to measure the binding energy of the electron and deduce information about the elemental make-up of the vacuum-liquid or vacuum-solid interface. Regarding XPS,

X-rays (normally between 100 eV to 2,000 for most applications) are utilized to eject and analyze inner core electrons. This is illustrated below in Figure 1.1.

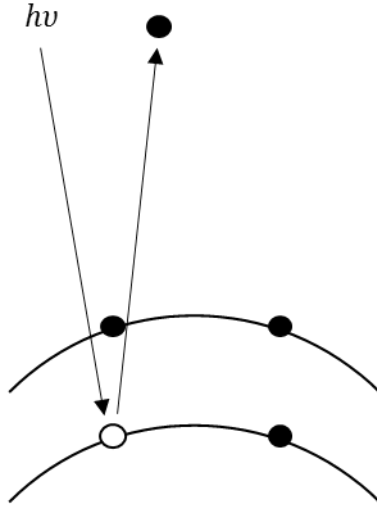


Figure 1.1: Fundamental principle of the photoelectric effect. Electron ejection from inner shell due to absorption of photon.

Inelastic scattering contributes to the background of a spectrum whereas the detected elastically scattered electrons make up the unique photoemission peak. For the photoemission of electrons, a simple equation (Eq. 1.1) can be utilized that describes the relationship between kinetic energy, binding energy, light source energy ($h\nu$) and the work function (ϕ_A) associated with the sample surface and the analyzer. A layout depicting the major components of XPS is shown in Figure 1.2.

$$E_{BE} = h\nu - E_{KE} - \phi_A \quad (\text{Eq. 1.1})$$

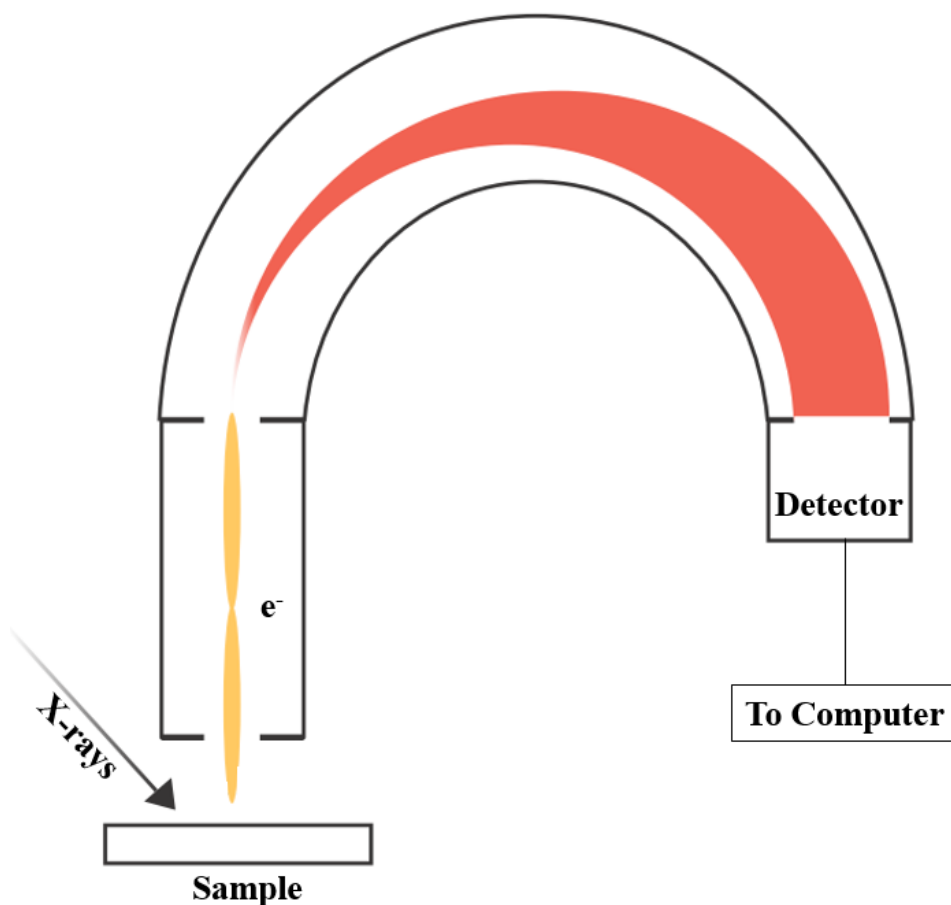


Figure 1.2: Traditional UHV XPS layout.

1.1.2 Vacuum Requirements

Vacuum operating conditions in electron spectroscopy are needed for a variety of reasons. The first reason concerns contamination which would contribute to attenuation and distortion of the collected spectra.³ The interaction or impingement rate (ϕ) shown in Eq. 1.2⁴ between a sample surface and a gas phase molecule and the formation of a monolayer on a solid surface (t_c , shown in Eq. 1.3) can be described by the following:

$$\phi = \frac{N_A P}{\sqrt{2\pi m R T}} \quad \text{Eq. 1.2}$$

$$t_c = \frac{\rho_s}{\phi} \quad \text{Eq 1.3}$$

where N_A is Avogadro's number, P is ambient pressure, m is the molecular mass of the impinging particle, k_B is the gas constant and T is temperature and ρ_s is surface density. A solid surface typically has $\sim 10^{15}$ sites / cm^{-2} available for interaction. For a clean model solid surface exposed to a model gas such as nitrogen with a pressure of one atmosphere and a hypothetical sticking coefficient of 1, the time needed for a complete monolayer to form is in nanoseconds. It quickly becomes apparent that UHV conditions (lower than 10^{-9} Torr) are needed to maintain a clean surface for a reasonable analysis time.

The vacuum requirement is also needed to avoid damage to components such as the analyzer. The damage can be incurred via arcing due to the high voltage differences imposed in the electrostatic lens system and the analyzer. Additionally, the X-ray source also needs to be protected from oxidation as it is being bombarded by electrons. A third important reason concerns the minimization of scattering of electrons by intercepting gas molecules in the pathway from the sample surface to the analyzer. Having a vacuum elongates the inelastic mean free path of the electrons (IMFP) which is relevant to the attenuation length and escape depth of photoelectrons from the sample. IMFP is defined as the mean distance an electron can travel before an event occurs where energy is lost. As an example of how pressure affects IMFP, e^- travelling at a kinetic energy of ~ 100 eV in a pressure environment of 1 Torr have an IMFP value of ~ 1 mm.

1.1.3 Depth of Information & Surface Sensitivity

The surface sensitivity of XPS lies in the fact that electrons with hundreds of eV's in kinetic energy do not travel very far in condensed media without losing some energy. Although X-ray interaction and ionization with a material is typically in the order of microns, electrons that are ejected from the surface and make it to the analyzer without energy loss is limited to the top few nanometers of depth. This is primarily due to scattering events (elastic and inelastic) occurring between when the electron is ejected from an inner core orbital and the short-lived journey to the sample surface. The relationship between the mean free path of electrons in condensed phase media and kinetic energy is described best by Figure 1.3.⁵

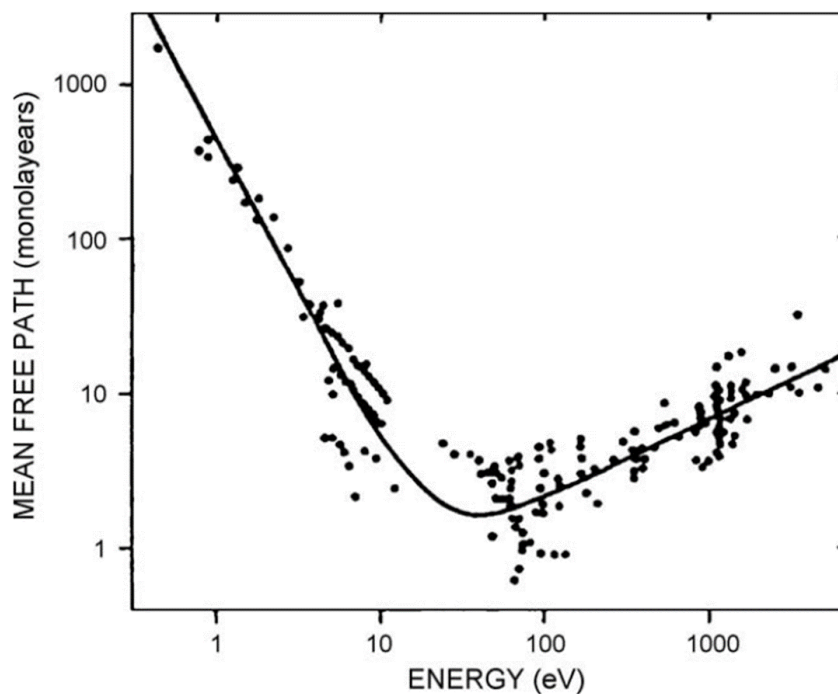


Figure 1.3: Universal curve of electron free path in solids. Reprinted with permission from Gao, et al.⁵

Depth of information varies primarily on three factors, namely:

- i. Energy of electron (which determines IMFP).
- ii. Density and nature of the material.
- iii. Emission angle of electrons

1.1.4 Angle Resolved XPS

The sampling depth of XPS (defined as 95% of the signal collected) is estimated typically using $3\lambda\cos\theta$ where θ is the angle of electron emission from the sample normal.⁶ With increasing θ the information depth increases. Figure 1.4 below depicts the difference of the depth of information gathered as a function of IMFP at 0° and 80° .

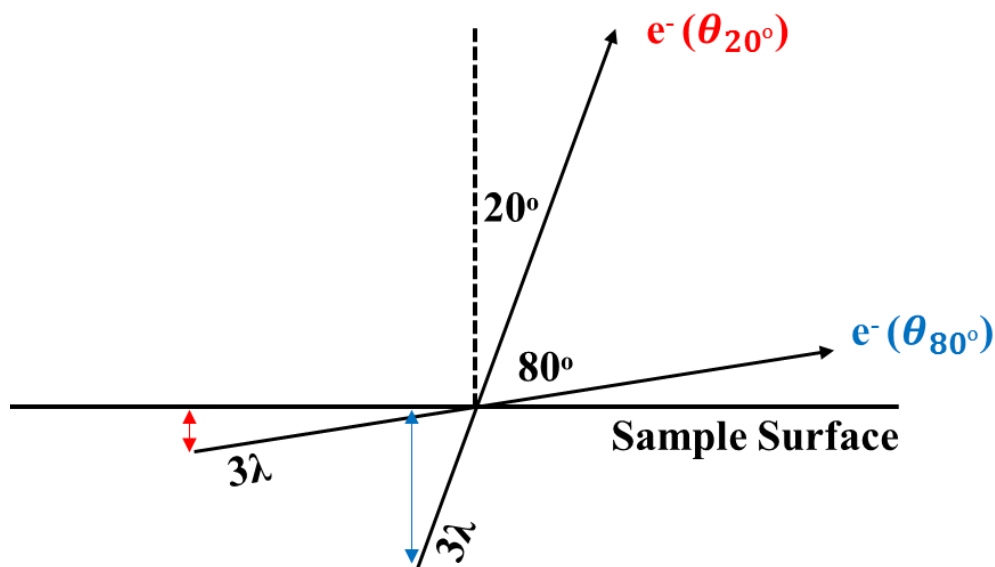


Figure 1.4: Varying the collection angle of photoelectrons varies the depth of information.

The capability of resolving the angle of the ejected electrons is a very useful tool in the non-destructive depth profiling of substrates. It is a commonly used method to quantify over layers of materials, gather information about surface orientation of larger molecules and examine enrichments of certain species as examined in chapter 4.

1.1.5 Quantitative Aspect of XPS

The popularity and utility of XPS as a surface analysis tool is due significantly to its inherent quantitative nature. Quantification methods used to quantify material on interfaces that utilize peak area and sensitivity factors are typically the most accurate for relative concentrations, this is given by the following equation for a homogenous sample⁷:

$$I = nf\theta\gamma\lambda AT \quad \text{Eq. (1.4)}$$

where n is number of atoms per unit area, f is the X-ray flux, γ is the photoelectron formation efficiency, θ is an angular efficiency factor, λ is the attenuation length described by the IMFP, A is the area of interaction and T is the detector efficiency. When comparing quantitatively the concentration of material that contains the same element, all terms in Eq. 1.5 (apart from n) are dropped, allowing for a relative concentration assessment of material at the interface.

1.1.6 Chemical Information from Binding Energy

Slight shifting or deviation from a known binding energy of an element is descriptive of the chemical state that element is in. Core electron binding energy measurements of elements can be directly related to the oxidation state of an atom or the effective

charge a particular electron experiences.⁷ For example, fluorinated carbons show a higher binding energy due to the valence electrons of the carbon atoms being distorted heavily towards the electronegative fluorine atoms. This has a direct effect on the inner core electrons of carbon as there is essentially a charge transfer to the fluorine atoms, making the inner core electrons experience a more positive charge there by increasing the binding energy.³ This can be contrasted with alkyl carbon connected to hydrogens where the valence electrons are properly shielded by the nucleus leaving the inner core electrons experiencing a less effective positive charge and thereby not stabilized as much therefore showing up at a lower binding energy.

1.2 Evolution of Ambient Pressure X-ray Photoelectron Spectroscopy

Vacuum requirement hinders studies that require studying the behavior of the interfaces of relevant materials under ambient conditions. This has forced the scientific community to find ways to circumvent the issue of short IMFP of electron which poses a detection challenge. This in-situ perspective of XPS is usually identified as ambient pressure XPS (AP-XPS), near ambient pressure XPS (NAP-XPS) or environmental XPS. There are two philosophies to this approach. The first utilizes an ultrathin membrane that is essentially X-ray and electron-permeable. The sample of interest would be beneath the ultrathin membrane and isolated. Beneath the membrane, the target pressure is introduced of the gas of interest. By having the X-rays and electrons permeate through while the gas is restricted by the ultrathin membrane it enables studying interfaces under considerable pressures thereby simulating the heterogeneous atmospheric conditions most interfaces undergo. This ultrathin membrane typically is graphene or graphene oxides to aid in the study of solids,⁸ liquids⁹ and gases¹⁰.

Another philosophy of making AP-XPS possible is by introducing a set of differentially pumped stages between the sample chamber and the spectrometer to minimize the time electrons interact with the gas phase. This is done by approaching an aperture to the sample surface. The X-ray chamber is separated from the sample chamber through an X-ray transparent material such as silicon nitride. There are two approaches to differentially pumping a sample chamber. Either back filling the entire chamber (typically larger volume) or by having a “cell” within a chamber approach. Both approaches utilize a set of apertures to reduce the flow of gas from one stage to the next and pumping continuously using pumps such as turbo-molecular pumps. In the sample stage a cone shaped aperture is brought close to the sample surface. This is illustrated best by Figure 1.5 below.

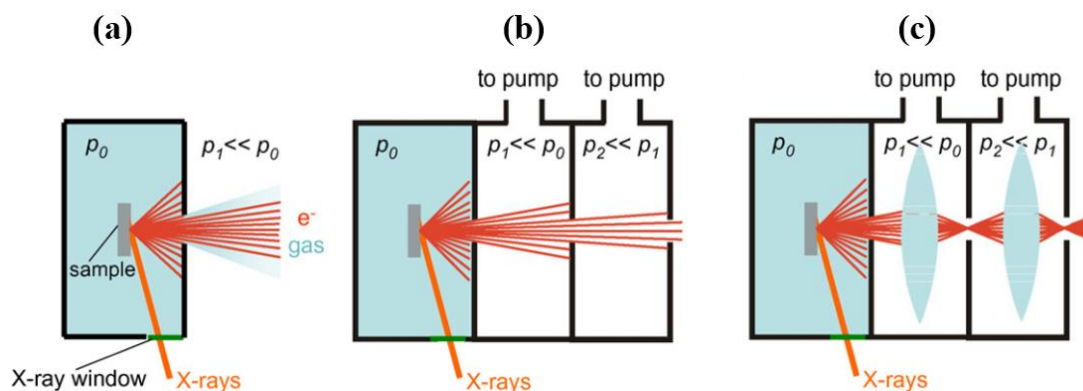


Figure 1.5: Concept of APXPS. (a) A differentially pumped aperture placed close to sample experiencing desired gas and pressure (p_0). (b) Several differential pumping stages introduced to maintain a vacuum lower than 10^{-6} Torr. (c) Electrostatic lens system introduced. Reprinted with permission from Bluhm, et al.¹¹

The aperture has a small diameter not exceeding 1 mm. In this way one can introduce a pressure gradient with Torr level pressures in the sample region and a high vacuum regime in the spectrometer to allow for safe operation. An electrostatic lens system is incorporated to channel the electrons to the spectrometer with minimal scattering. The electrostatic pre-lens system can be set to different configurations that enables the spectrometer to operate under three different modes, namely: transmission, angular and acceleration mode. These different configurations are discussed below.

1.2.1 HiPP-2 Spectrometer Details

Effects of slit size and pass energy on total signal and the full width at half maximum (FWHM) are discussed in relation to the HiPP-2 spectrometer (utilized in the AP-XPS studies discussed here) designed by Scienta Omicron. This spectrometer couples a 200 mm high resolution analyzer with an intricate electrostatic pre-lens system.¹² A layout of the system is shown in Figure 1.6 (color coded). The instrument utilizes a monochromatic X-ray source (Scienta MX650) 200 W Al K_{α} anode (1486.7 eV). The X-ray source utilizes seven toroidal α -quartz crystals packed (Rowland circle optimization) maintained at 55 °C to focus the X-ray spot onto an area of approximately 1.4×3.8 mm. The entrance slit of the spectrometer is interchangeable from the range of 0.2 mm to 4 mm.

There are two types of slits (straight or curved) which influence the shape of the spectra. The photoelectrons are detected via an MCP/CCD electron detector. The electrostatic pre-lens system has different configurations that enables the spectrometer to operate under three different modes, namely: transmission, angular and acceleration mode. For imaging purposes, the transmission mode is typically used where no bias is applied to the cone to resolve the spatial information of the detected photoelectrons.

Angular mode of operation enables for the resolving of the angle of electron emission of the photoelectrons up to 22° . The acceleration mode applies a large positive bias on the first aperture in stage zero effectively maximizing e^- signal intensity and dramatically reducing spectral collection time. This holds the advantage of minimizing X-ray exposure, avoiding unwanted effects such as beam damage.

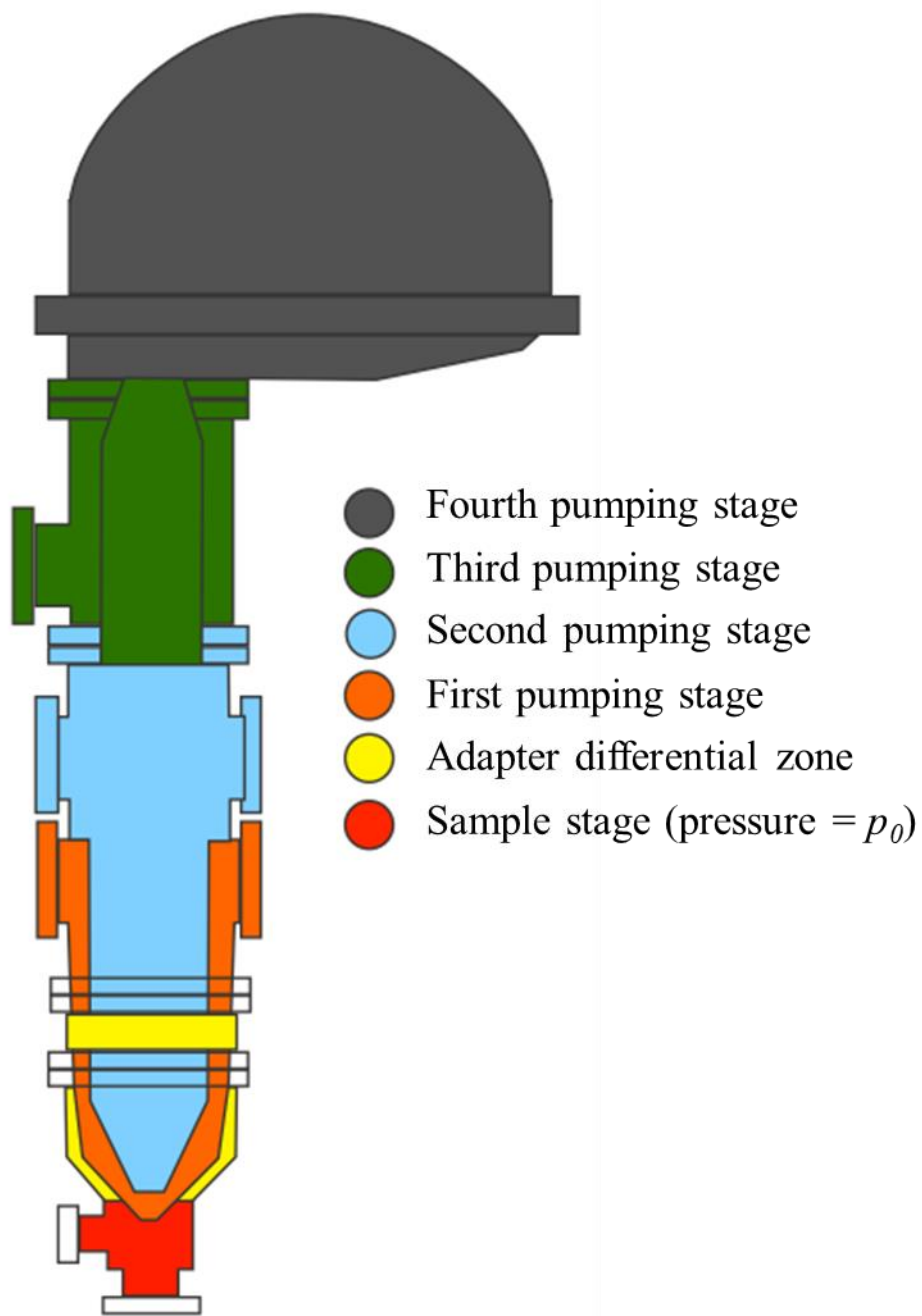


Figure 1.6: Layout of AP-XPS depicting the different pumping stages.

1.2.2 Resolution of HiPP-2

Signal detection through use of a hemispherical analyzer can have variable resolution of the photoemission peaks (ΔE) which is measured via FWHM of a well-defined peak. This variability is subject to several parameters (described by Eq. 1.2) including entrance slit (s), pass energy of electrons (E_p) and the radius of the hemisphere (r). s is simply the focal point of photoelectrons directed by the electron optics before analysis of the kinetic energy of emitted e^- . Regarding E_p , it is simply the energy of the emitted photoelectrons of particular energy accelerated (or retarded) to match the energy being detected. A simple relationship between those variables and ΔE is described by the following equation:

$$\Delta E \propto \frac{s E_p}{2r} \quad (\text{Eq. 1.5})$$

It is important to note that what contributes to ΔE is a combination of the electron energy analyzer, the X-ray source and monochromator and thermal broadening. From Eq. 1.2 we see a direct correlation between ΔE and slit width and pass energy and how they affect each other. In the following section we examine the contribution of the HiPP-2 analyzer parameters to the overall ΔE by monitoring the FWHM of a Ag 3d peak.

1.2.3 Effect of Pass Energy and Slit Width on FWHM

To examine the resolution of the HiPP-2 analyzer, the FWHM of Ag 3d peak from a polycrystalline silver foil was measured as a function of pass energy (at 100 and 200 eV) and slit size ranging from 4.0 mm to 0.5 mm (c and s for curved and straight respectively) at the three different modes of operation (Figure 1.7), acceleration (orange) transmission (teal) and angular (blue).

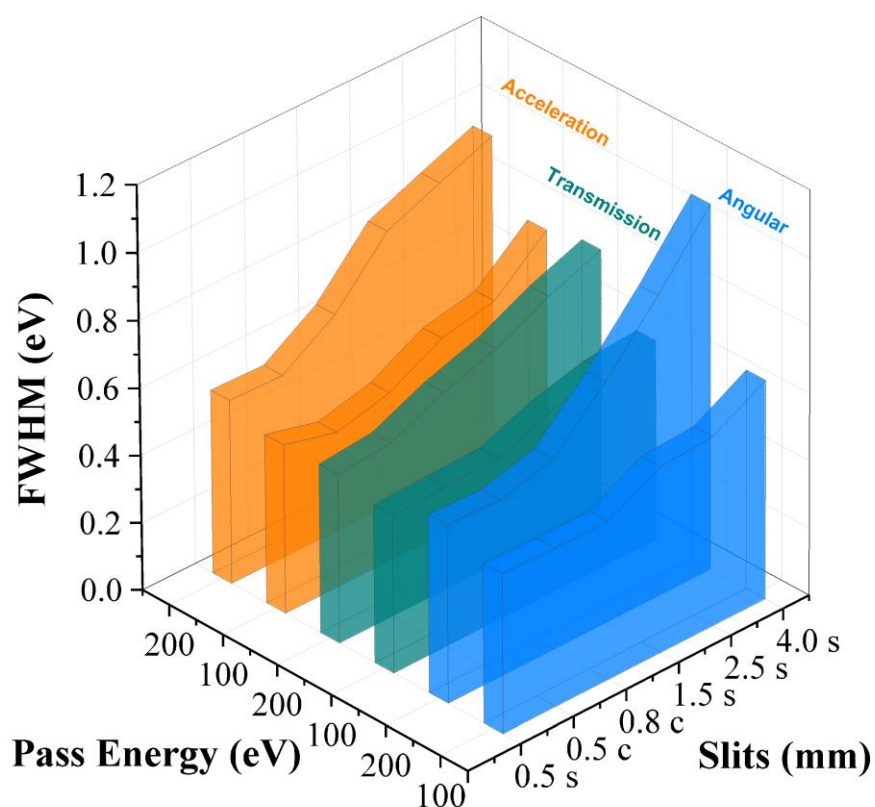


Figure 1.7: Effects of slit width (s and c for straight and curved slits respectively) and pass energy on the FWHM of Ag 3d from a Ag foil substrate in the three different modes of operation namely acceleration, transmission and angular.

The theoretical resolution of a Ag 3d has a value of 413 meV.¹³ In all modes of operation at the largest slit size of 4.0 mm straight slit and a pass energy of 200 eV we see a FWHM that exceeds 0.9 eV for the Ag 3d peak which is roughly double the expected value. The resolution improves dramatically with smaller entrance slit widths along with a decrease to 100 eV pass energy reaching a minimum of 501 meV, 469 meV and 473 eV for acceleration, transmission and angular respectively.

1.2.4 Effect of Pass Energy and Slit Width on Peak Area

While acceleration mode has a higher FWHM of the Ag 3d peak compared to transmission and angular it compensates for the loss of resolution by increasing the total signal significantly. Figure 1.8 shows the effect of the pass energy and slit width on the area of the Ag 3d peak.

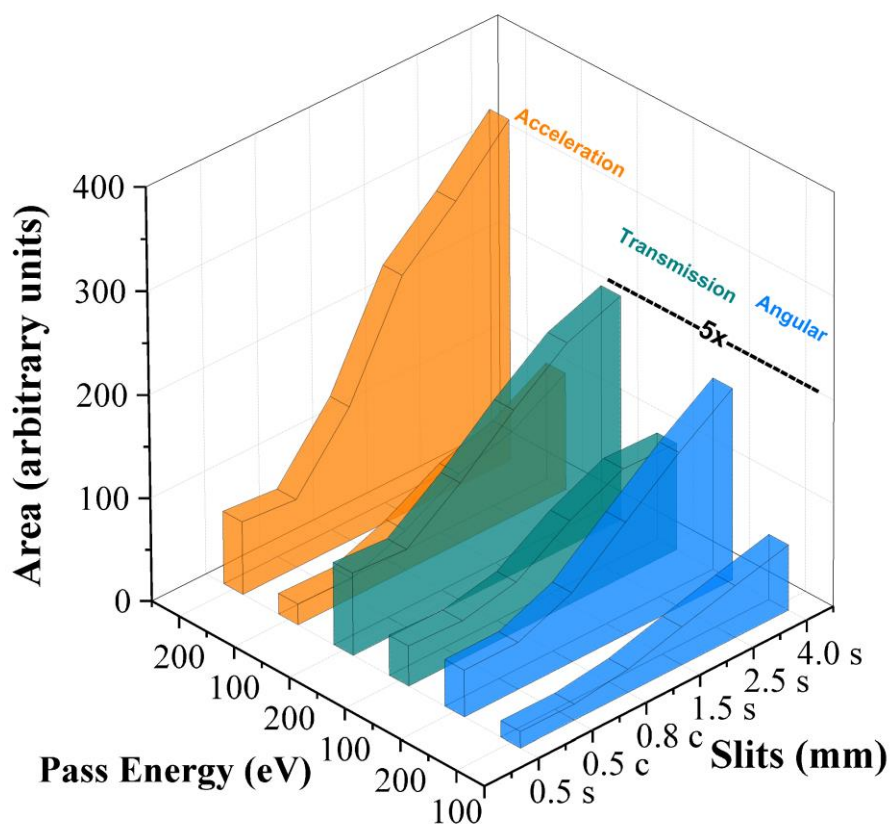


Figure 1.8: The effect of Pass energy (eV) and slit width (mm) on the area of Ag 3d from a Ag foil substrate. Transmission and Angular data were multiplied by a factor of 5.

The raw areas of the transmission and angular data were multiplied by five to compare data effectively. It is worth noting that the signal ratio between 200 and 100 eV for pass energy is approximately three times for acceleration and angular. Meanwhile the effect of the slit width is more dramatic across all three modes of operation. An approximate fivefold increase in signal is noted between the 0.5 mm slit and the 4.0 mm in acceleration while a fourfold and threefold increase was noted for angular and transmission, respectively.

1.3 Ionic Liquids Introduction

Ionic Liquids are salts comprised of a cation and anion with a melting point below a 100 °C. Applications of ionic liquids have reached several areas of science including catalysis,¹⁴ separation¹⁵ and renewable energy technologies such as fuel cell and dye sensitized photovoltaic cells.¹⁶ Ionic liquids have garnered significant attention in recent years. Much of the interest in these mobile salts stem from their unique properties such as negligible vapor pressure and unique structural behavior.¹⁷ Deetlefs, et al.¹⁸ presented the number of publications related to ionic liquids from 1980 to 2014 (Figure 1.9) and contrasted it with other areas of general interest such as Bucky balls and superconductivity. It is clear that ionic liquids have garnered significant attention, surpassing 6000 individual publications in 2010 and continuously rising.

Multiple disciplines have fueled this surge in interest towards ionic liquids. Those disciplines include chemistry, chemical engineering environmental science and material science. Broadly speaking, ionic liquids are known for their stability and conductivity.¹⁹ Until relatively recently they have been labelled generally as having flame retarding properties and negligible vapor pressure. However, with 10¹⁸ different

possible combinations there is large variability of key properties of ionic liquids. Some ionic liquids are flame resistant while others can be used as rocket propellants.²⁰ Similarly, many ionic liquids are vacuum compatible while others are relatively volatile and unfit for vacuum applications.²¹

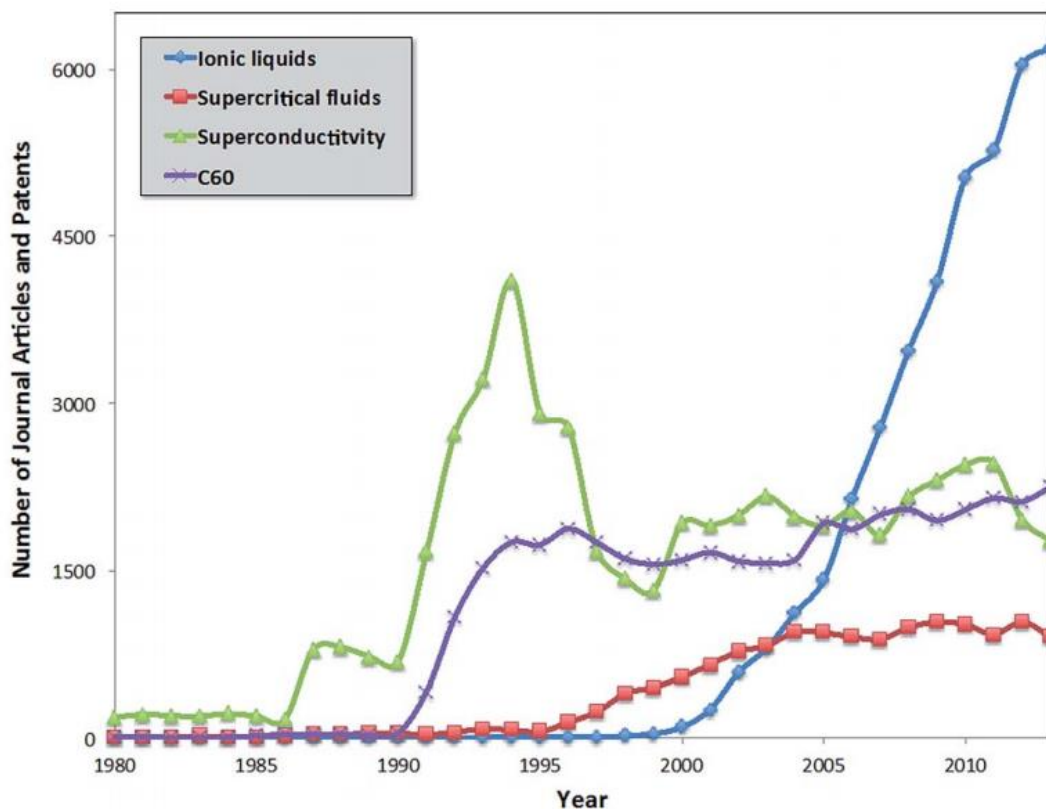


Figure 1.9: Number of publications of Ionic Liquids compared to other important scientific interests of the century as a function of years. Reprinted with permission from Deetlef, et al.¹⁸

Due to the endless combinations, ionic liquids are referred to sometimes as designer solvents as it enables the tuning of desired physical properties possible. Several types of ionic liquids can be classified such as task-specific ionic liquids,

supported ionic liquid membranes, ionic liquids supported on metal-organic frameworks are just a few examples.²² The cations of ionic liquids are usually an organic structure with low symmetry. While there is a variety of cation structures such as ammonium, pyrazolium and phosphonium, most studies employ an asymmetric dialkylimidazolium cation. Anion choices on the other hand vary significantly more in the ionic liquid literature and is picked for being weakly basic with a hard or diffuse negative charge.²³ Some examples of commonly found ionic liquids in the literature are depicted in Figure 1.10.

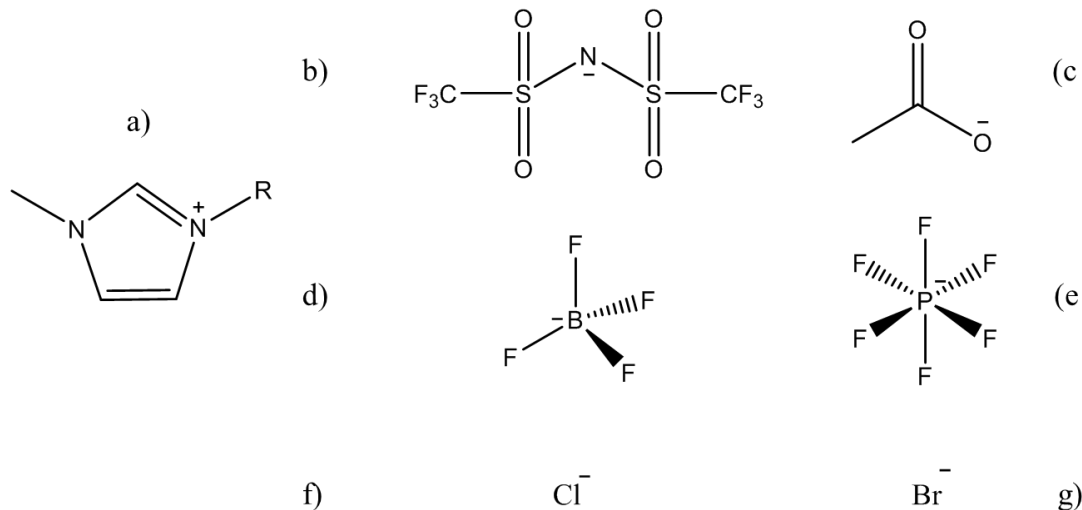


Figure 1.10: Typical ionic liquid components such as a) 1-alkyl-3-methylimidazolium cation where $R = C_xH_{2x+1}$, $[XMIM]^+$. Common anions include but are not limited to b) Bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$, c) Acetate $[OAc]^-$, d) Tetrafluoroborate $[BF_4]^-$, e) Hexafluorophosphate $[PF_6]^-$, f) Chloride $[Cl]^-$ and g) Bromide $[Br]^-$.

1.3.1 Interface of Ionic Liquids

Many applications of ionic liquids mentioned above are dependent on interface properties of ionic liquids. The negligible vapor pressure of many imidazolium based

ionic liquids permits use of techniques that typically require UHV conditions. Generally speaking there are two inter-related categories of information that is extracted from these surface sensitive studies, namely, surface composition and molecular orientation.²⁴ There are numerous studies of the ionic liquid-vacuum interface utilizing surface sensitive techniques such as low energy ion scattering,²⁵ neutral impact collision ion scattering spectroscopy (NICISS),²⁶ metastable induced electron spectroscopy (MIES),²⁷ direct recoil spectroscopy,²⁸ sum-frequency generation,²⁹⁻³⁴ neutron reflectometry³⁵ and X-ray reflectivity.^{29,36} Generally speaking, ionic liquids with high basicity and smaller molecular radii tend to have the cation closer to the surface, while ionic liquid that are larger tend to layer on the top layer with the imidazolium cation underneath.³⁷ Several XPS and AR-XPS studies³⁸⁻⁴¹ examining the degree of enhancement of the alkyl chain for imidazolium based ionic liquids have been conducted on ionic liquids in the past few years.

It is important to note that a significant portion of the literature studying the interface of ionic liquids do so in vacuum conditions. In-situ studies are generally limited to SFG.⁴² These SFG studies showed the dependency of the cation structure of the outer surface of the ionic liquid on the presence of minute amounts of water present.⁴³⁻⁴⁵ Two NICISS studies conducted on mixtures of water and imidazolium chloride ionic liquid (utilized in Chapter 3) had contradictory conclusion on the [Cl]⁻ anion migrating towards⁴⁶ or away⁴⁷ from the vacuum interface illuminating the need for further investigation of the effect of water on the interface of ionic liquids. From ultrahigh vacuum XPS and dosing of water the heat of adsorption onto the surface of 1-butyl-3-methylimidazolium tetrafluoroborate⁴⁸ ([EMIM][BF₄]) was determined,

highlighting the thermodynamic information available to be extracted through temperature dependent studies.

While the information gathered from these techniques is meaningful, studies done in the presence of atmospherically relevant conditions, such water as vapor, are very limited.

1.4 Scope of the Dissertation

The primary focus of this thesis is to probe the interface of several ionic liquids and ionic liquid mixtures via AP-XPS to understand the interaction of the ionic liquid surface with gas phase water and any consequential effects that may arise from such interaction.

Experimental parameters including details regarding ionic liquids utilized in this thesis is presented in Chapter 2. Chapter 3 illustrates the utility of the hydrophobic ionic liquid [EMIM][Tf₂N] to calculate the total electron scattering cross-section of gas phase water at several different kinetic energies without the need to access synchrotron radiation. In contrast to the previous chapter, Chapter 4 explores water interaction with [HMIM][Cl] and provides quantitative insights into the water enhancement relative to bulk results. Mixture of ionic liquids (discussed in Chapter 5), particularly ones that contrast each other in terms of hydrophilicity such the [EMIM][Tf₂N][OAc] are explored via AR-XPS and AP-XPS to examine the surface segregation behavior of [Tf₂N]⁻ and the effects of water vapor has on the surface composition. Chapter 6 provides a summary of the findings presented in Chapters 3 through 5 and highlights some potential future directions.

Chapter 2

EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

2.1 Samples of Ionic Liquids.

1-hexyl-3-methyl-imidazolium chloride, [HMIM][Cl] (Sigma Aldrich, 97%), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][Tf₂N] (Iolitec, 99%) and 1-Ethyl-3-methylimidazolium acetate, [EMIM][OAc] (Iolitec, 95%), were purchased and used without further purification. The ionic liquids were stored in a vacuum desiccator and used as received.

For the [HMIM][Cl] and [EMIM][Tf₂N] AP-XPS experiments, a droplet of the relevant ionic liquid (< 1 mm thick) was deposited onto a polycrystalline gold foil that was placed into the AP-XPS analysis chamber and pumped on for three days prior to experiments.

Regarding the ionic liquid mixture, a batch composed of [EMIM][OAc] and [EMIM][Tf₂N] with $X_{\text{Tf}_2\text{N}} = 0.1$ was prepared gravimetrically and carefully loaded into the indents of the aluminum stub.

2.2 Substrate Preparation

Au substrates are cleaned via acetone, annealed and allowed to cool down prior to dropping the ionic liquid for analysis. Al stub utilized for Chapter 5's work was always sonicated in acetone for 20 minutes prior to loading with the ionic liquid mixture.

2.3 AP-XPS Experimental Details

For AP-XPS analysis of the ionic liquids [HMIM][Cl], [EMIM][Tf₂N] and the [EMIM][Tf₂N][OAc] mixture a gold polycrystalline foil (Alfa Aesar, 0.25 mm thickness, 99.9975% purity) was used to contain the droplet of the ionic liquid of interest (< 1 mm thick). All experiments utilizing AP-XPS were done at room temperature. Figure 2.1 shows [EMIM][Tf₂N] placed on the Au foil stabilized by a clip inside of the chamber, which supplies a connection for ground (Figure 2.1).

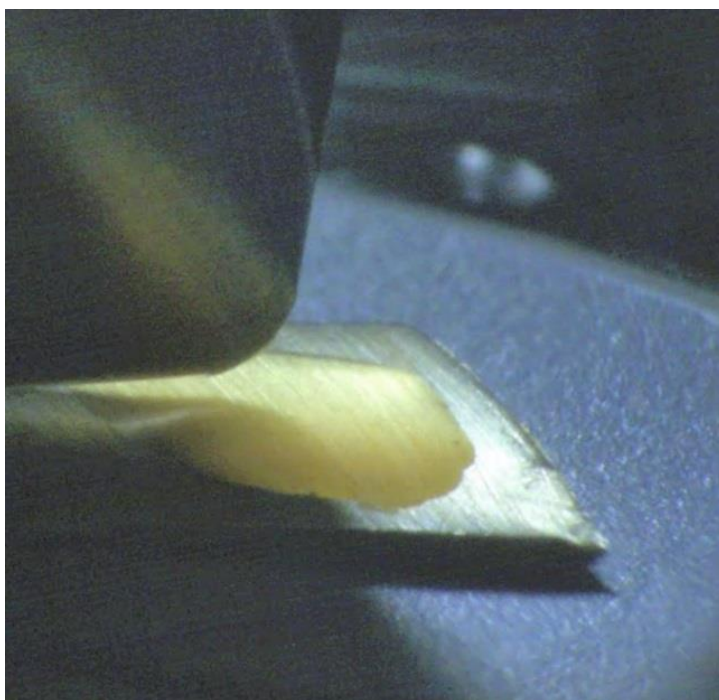


Figure 2.1: Picture inside the XPS chamber. The ionic liquid droplet on a polycrystalline Au substrate is shown.

AP-XPS were conducted using a Scienta HIPPI-2 photoelectron analyzer and monochromatic Al K α ($h\nu = 1486.6$ eV) X-rays source (Scienta MX650) operated at 20 mA and 10 kV and the 700c slit. The details of this setup are discussed in Chapter 1

and in Newberg, et al.¹² Electrons were captured at 20° relative to the surface normal. Survey spectra were collected at 200 eV pass energy, while high resolution spectra were collected at 100 eV pass energy. Energy step setting for survey and high-resolution spectra were 1 eV and 0.02 eV with a dwell time of 100 ms and 700 ms, respectively.

2.3.1 Water Exposure Details

Water was introduced into the APXPS analysis chamber using a variable leak valve, behind which was a glass bulb containing MilliQ water (18.2 MΩ cm⁻¹). The water was freeze degassed three times prior to the start of experiments. When changing the water vapor pressure between spectra acquisitions, irradiation by the X-ray source temporarily ceased by cutting the high voltage power supply to reduce the total X-ray exposure time. For all experiments, there was no evidence of X-ray induced beam damage, which is known to manifest itself as a low binding energy shoulder in the N 1s region for imidazolium based ionic liquids.⁴⁸

2.4 AR-XPS Experimental Details

To take advantage of the non-destructive nature of AR-XPS without access to beamline synchrotron radiation, the tilting of the sample surface cannot be avoided. This is typically not problematic for solid samples most commonly used in XPS. The tilting of a liquid such as ionic liquids can provide some experimental challenges, however, this problem is easily circumvented by taking advantage of the high viscosity of the ionic liquids. A stub is punched out of an aluminum sheet and four shallow wells were punched (in a straight line) into the stub to create space for a small

reservoir of ionic liquid. Below (Figure 2.2) is a picture of the aluminum substrate containing an ionic liquid mixture.

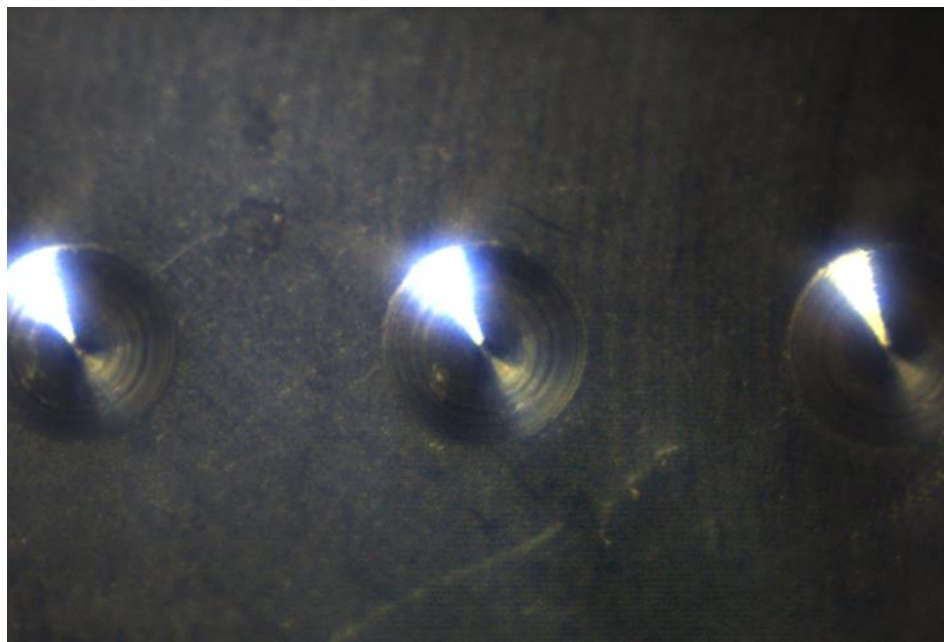


Figure 2.2: Snapshot of aluminum stub containing four shallow wells (the 4th is out of view) containing the ionic liquid mixture [EMIM][Tf₂N]/[EMIM][OAc] inside of the XPS system.

AR-XPS was performed on all four liquid [EMIM][Tf₂N][OAc] samples at 0° and 80° relative to the sample normal using a Thermo Scientific K-alpha X-ray photoelectron system via the angle resolved module. At both 0° and 80° sample height optimization based on signal was made. The X-ray source utilizes an aluminum K α micro-focused monochromator with an analysis spot size of 200 μ m. Survey spectra were collected at a pass energy of 100 eV with a dwell time of 10 ms and a step size of 1.0 eV (averaged over 3 scans). High resolution spectra were collected with a 20 eV pass energy at both 0° and 80° with a step energy of 0.10 eV and a dwell time of 50 ms.

averaged over 10 scans (the number of scans were tripled for the 80° spectra). A flood gun was utilized with a current of 125 μ A.

2.5 Calibration and Fitting

All XPS spectra were analyzed using peak fitting software (CasaXPS, v2.3.1.6) with Gaussian-Lorentzian (70%-30%) peak fits and linear or Shirley background subtraction. All binding energies are referenced to the imidazolium alkyl carbon, C_{alkyl} , at 285.0 eV.⁴⁰ In regard to [EMIM][Tf₂N], The full width at half maximum (FWHM) of the C 1s imidazolium peaks were constrained to within a 0.06 eV window, while leaving the BEs unconstrained. For S 2p spectra the S 2p(1/2) spin was constrained to the known separation of 1.18 eV from the S 2p(3/2) spin. All other peaks (F 1s, N 1s, O 1s) were unconstrained. For [HMIM][Cl], the C 1s spectra were fit with three components by constraining the full width at half maximum (FWHM) between 1.0 and 1.1 eV while N 1s, O 1s and Cl 2p FWHM were left unconstrained. Finally for [EMIM][Tf₂N][OAc], all species were left unconstrained, except for C 1s, where position constraints were placed for the C_{ox} and C_{ring} species (see Figure 5.6 for more details).

Chapter 3

TOTAL ELECTRON SCATTERING CROSS-SECTION OF H₂O(g) FROM [EMIM][Tf₂N]

3.1 Introduction

Electron collision events with gas phase molecules are ubiquitous in the atmosphere. Those events play an important role in applied science and the physics and chemistry of planetary atmospheres⁴⁹ in addition to radiation induced damage in biological specimen.⁵⁰ Collisions of electrons with H₂O are of vital importance to understand since water is the third most abundant molecule in the universe. It makes up a significant fraction of our troposphere and is an important greenhouse gas.⁵¹ The strength of electron-molecule interactions in the gas phase can be assessed by the total electron scattering cross-section (σ_e). The value is a function of the kinetic energy of the e⁻.⁵² In the latter half of the 20th century, multiple groups were able to experimentally determine σ_e of a variety of gases. Table 3.1 shows all the studies used to determine the σ_e of H₂O(g) from a kinetic range of 0 up to 10,000; however, it is worth noting that a significant portion of those studies focus on the lower kinetic energy regime. In all of the studies shown in Table 3.1 (apart from Bluhm, et al.¹¹) the transmission of e⁻ through a gas cell containing H₂O(g) is measured by utilizing a Faraday cup or a Time-Of-Flight detector.

Table 3.1: Calculated total electron scattering cross-section of H₂O(g)

Paper	Kinetic Range (eV)	Reference
2010 Bluhm	105-700	11
2008 Khakoo	0-100	53
2007 Munoz	10-10,000	50
2005 Itkawa	1-1000	54
1998 Straub	10-1000	49
1990 Saglam	25-300	55
1988 Djuric	15-150	56
1988 Nishimura	7-500	57
1987 Zecca	10-3000	58
1986 Sueoka	1-400	59

3.2 Results and Discussion

3.2.1 Utilizing AP-XPS to Calculate Total Electron Scattering Cross-Section

The signal intensity of photoelectrons can be described by Eq. 3.1 below:

$$\ln \frac{I}{I_0} = -\frac{\sigma_e d_{\text{eff}} c}{kT} p = -mp \quad (\text{Eq. 3.1})$$

Where I is signal intensity for a given element pressure (p) measured in Torr, I_0 is signal intensity under vacuum, $c = 133.322$ is the conversion from Pascal to Torr, σ_e is the total electron scattering cross section at different kinetic energies,⁶⁰ d_{eff} is the effective path length through the gas phase, T is temperature in K and k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$).

Bluhm, et al,¹¹ calculated the σ_e of gas phase water by utilizing the highly hydrophobic quality of a highly ordered pyrolytic graphite sample in a synchrotron-based AP-XPS. This was made possible by monitoring the varying kinetic energy (made possible via synchrotron radiation) of the C 1s signal as a function of increasing

pressures, of $\text{H}_2\text{O}(\text{g})$. This is shown in Figure 3.1. The inset shows the extraction of σ_e at multiple kinetic energies compared to previously published results.

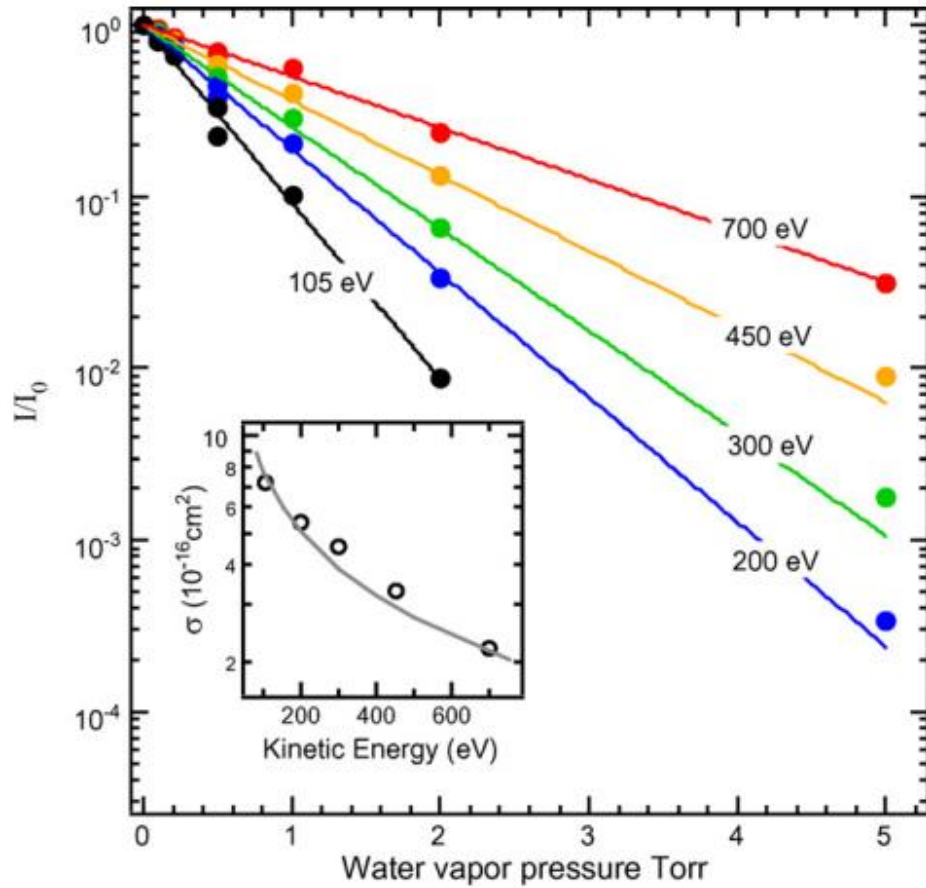


Figure 3.1: Experimentally determined attenuation of C 1s electrons from HOPG substrate as a function of water vapor pressure and kinetic energy. Data were normalized to vacuum signal (I_0). Inset shows the total electron scattering cross section (σ_e) obtained from the slope of the fits and compared to Munoz, et al.⁵⁰ Reprinted with permission from Bluhm, et al.¹¹

A value of $d_{\text{eff}} = 0.81$ mm has been previously determined for our instrument in transmission mode.¹² Plots of $\ln(I/I_0)$ versus pressure allows for the extraction of σ_e

from the experimental slope (m). By multiplying out the constants, σ_e can be extracted.

While our lab-based AP-XPS system does not have the capability of changing the kinetic energy of C 1s signal due to the fixed energy of the Al K α X-ray source, this problem can be quickly overcome by utilizing a different substrate. In the following sections the viability of using a hydrophobic ionic liquid rich in elements as a probe for the σ_e parameter is discussed.

3.2.2 Surface Characterization of [EMIM][Tf₂N]

The chemical structure of 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][TF₂N] is shown in Figure 3.2.

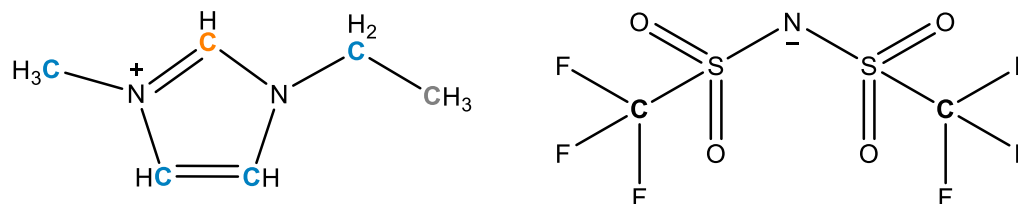


Figure 3.2: The chemical structure of [EMIM][Tf₂N].

An initial survey spectra of the [EMIM][Tf₂N] is shown in Figure 3.3. Characterization spectra were conducted at 4×10^{-8} Torr prior to water exposure. The ionic liquid-vacuum interface is made up of the expected elements of F, S, N, C and O seen in the molecular structure. This indicates the absence of any foreign elemental impurities in the interface. It is worth while recognizing the wide range of binding

energy [EMIM][Tf₂N] components cover. All spectra were calibrated to the C 1s alkyl component at 285 eV.

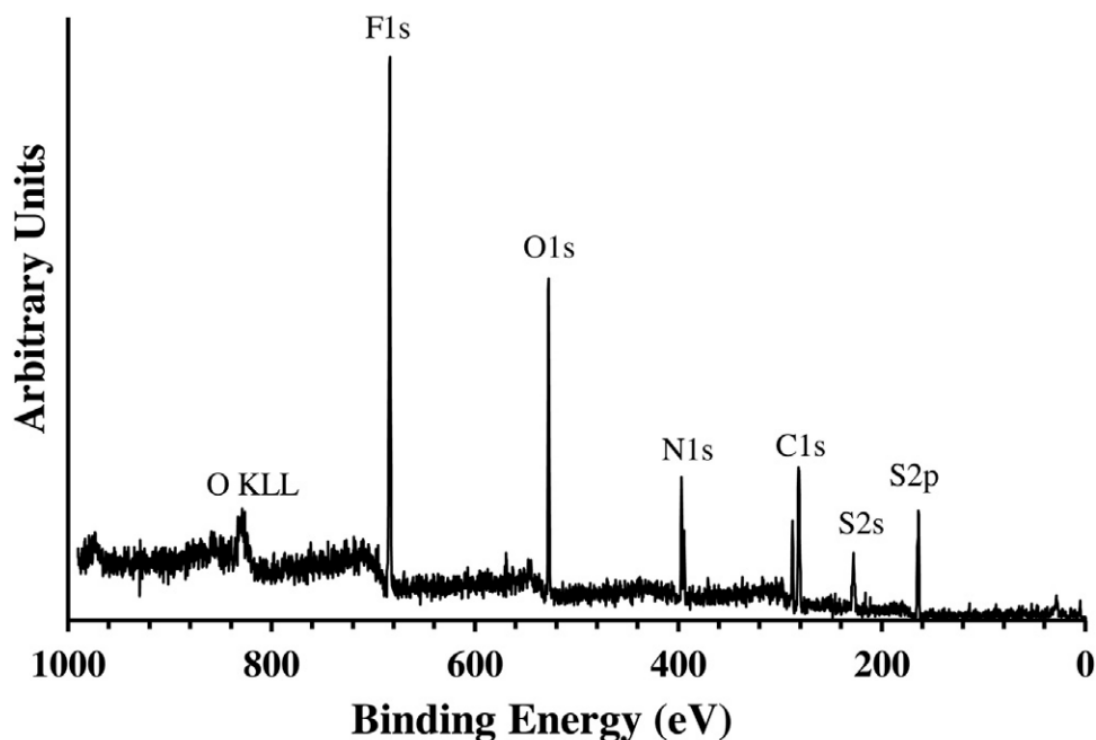


Figure 3.3: Survey spectrum of [EMIM][Tf₂N] prior to water exposure.

Figure 3.4 shows high resolution spectra of F 1s (a), and S 2p (b) under vacuum conditions at 4×10^{-8} Torr. F 1s shows one symmetric peak with a binding energy of 688.4 eV for the six fluorine atoms present in the [Tf₂N]⁻ anion. The sulfur present in the anion shows an expected doublet with an S 2p (3/2) binding energy of 168.5 eV.

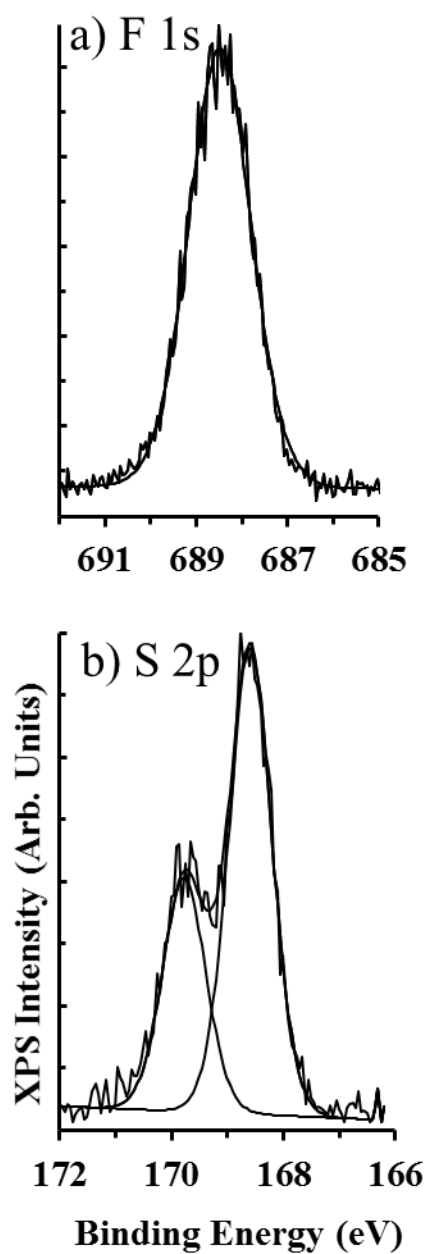


Figure 3.4: High resolution spectra of a) F 1s, b) S 2p prior to water exposure.

N 1s (Figure 3.5) presents two well resolved peaks associated with the $[\text{EMIM}]^+$ cation and $[\text{Tf}_2\text{N}]^-$ anion representative of the imide functional group at 401.6

eV and 399.0 eV, respectively. We see the expected stoichiometric ratio of 2:1 of $I_{[\text{EMIM}]^+} : I_{[\text{Tf}_2\text{N}]^-}$, which shows that there is no preference for either cation or anion on the surface at this collection angle.

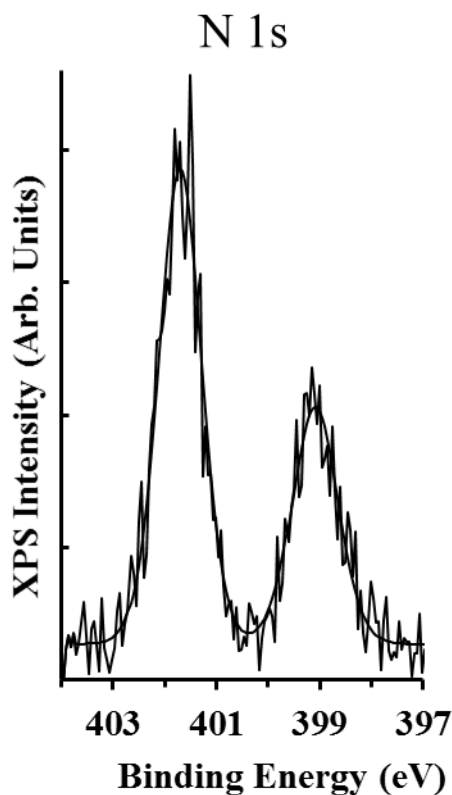


Figure 3.5: High resolution N 1s prior to water exposure.

The purity of the $[\text{EMIM}][\text{Tf}_2\text{N}]$ is further confirmed by looking at the high-resolution C 1s and O 1s (Figure 3.6). In regards to C 1s four distinctive peaks arise. At 292.4 eV one peak corresponding to the carbon on the $[\text{Tf}_2\text{N}]^-$ anion. Centered on 286.2 eV are three convoluted components which are reflective of the $[\text{EMIM}]^+$ carbons in different chemical environments. The three species (color coded in Figure

3.2) belong to C_{ox} (orange): C_{ring} (blue): C_{alkyl} (grey) showing up at 287.1 eV, 286.2 eV and 285.0 eV, respectively, with the expected stoichiometry ratio of 1:4:1 (see Figure 3.2 for color coded carbon assignments).

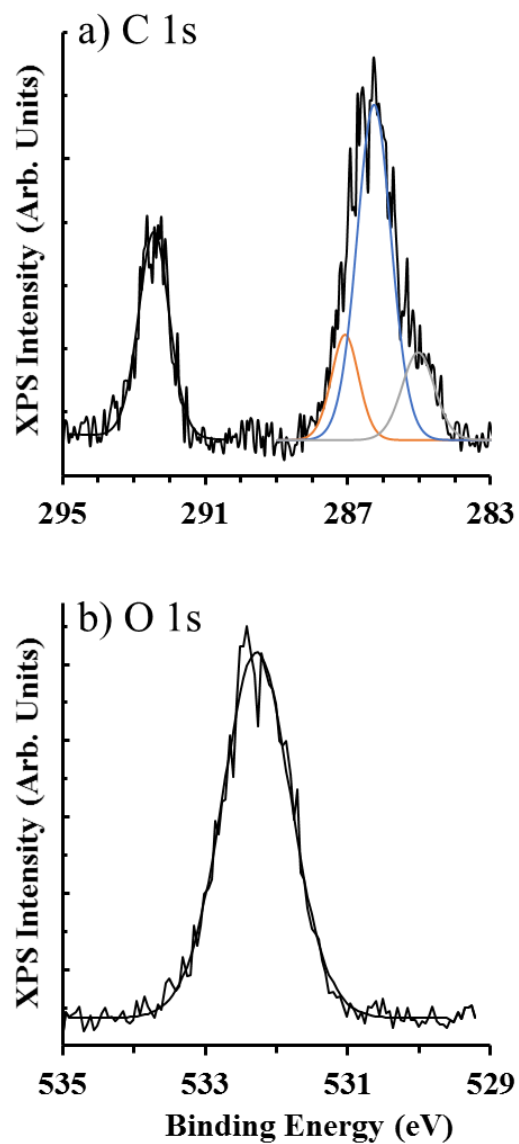


Figure 3.6: High resolution spectra of a) C 1s and b) O 1s prior to water exposure.

In regard to the O 1s spectrum, the four isoelectronic oxygens of the anion show up as a symmetric peak at a binding energy of (532.2 eV). All reported BEs of the components that make up [EMIM][Tf₂N] at the vacuum level spectra show excellent agreement with previously published data.³⁸

3.2.3 Exposure of [EMIM][Tf₂N] to Water.

The effect of water on the vacuum-liquid interface of [EMIM][Tf₂N] has been examined.⁶¹ The pressure was raised from 4×10^{-8} Torr systematically by an order of magnitude up to 0.1 Torr via a leak valve, where the pressure was changed in smaller increments up to a maximum of 2.0 Torr. At each pressure high resolution spectra of the elements that make up [EMIM][Tf₂N] were collected and shown in Figure 3.7. All non-vacuum spectra were calibrated in a similar fashion by setting the C 1s alkyl component to 285 eV. At 0.1 Torr, the emergence of a vapor phase peak at 534.9 occurs and it continues to rise as the density of gas increases. It is important to note that no changes to peak position were observed at any of the water exposure pressures. A horizontal line is drawn at each set of spectra to aid in the confirmation of negligible shifting. More specifically all binding energies were within ± 0.15 eV (± 2 standard deviations) over the entire isotherm. Additionally, no significant changes in the FWHM of the peaks were detected, which would be indicative of a chemical change, occurring as all values were within ± 0.06 eV (± 2 standard deviations). The only apparent change in the high-resolution spectra as a result of increasing vapor pressure in the sample chamber is the signal attenuation that becomes noticeable at higher pressures.

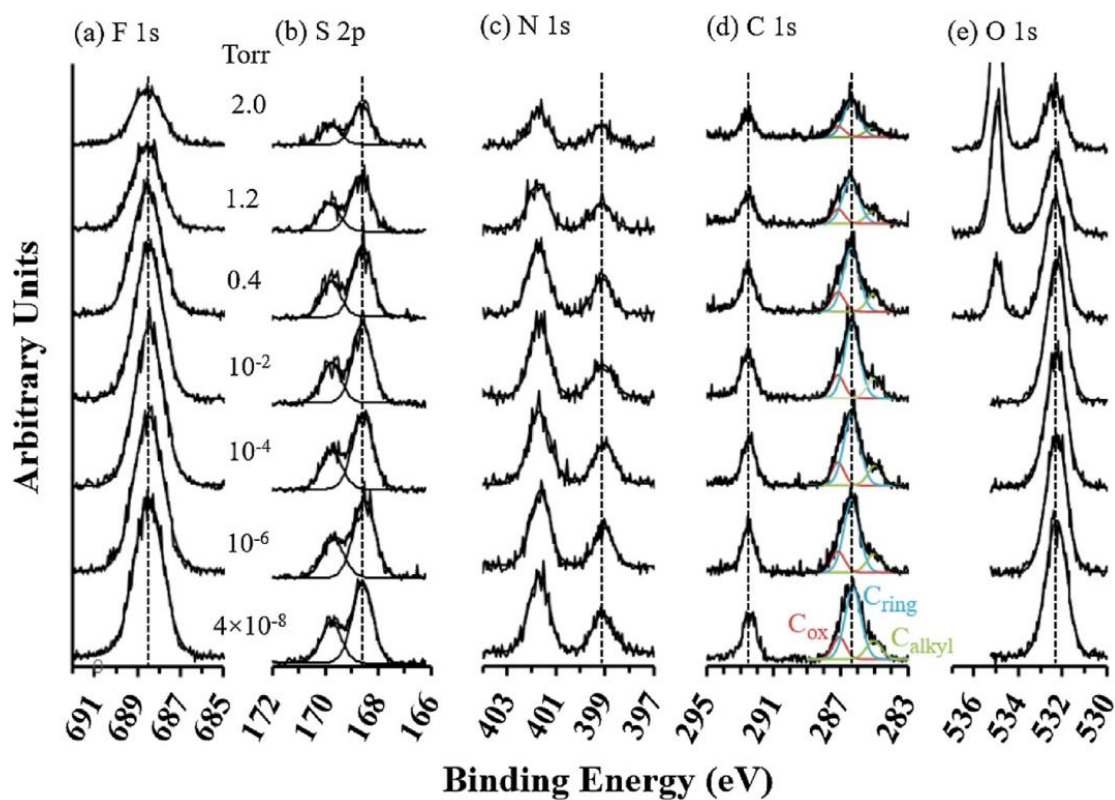


Figure 3.7: APXPS spectra of [EMIM][Tf₂N] as a function of increasing water vapor pressure in the (a) F 1s, (b) S 2p, (c) N 1s, (d) C 1s, (e) O 1s regions. Bottom spectra is taken prior to the introduction of water vapor into the analysis chamber. Vertical line guides placed to confirm lack of shifting. Reprinted with permission from Khalifa, et al.⁶¹

Furthermore, analysis of the C 1s and N 1s overlays at high vacuum shown in blue and at 2.0 Torr allows us to exclude any structural changes in the [EMIM][Tf2N] environment (Figure 3.8). Both high resolution spectra allow us to probe if either cation or anion is enriched at the interface as a result of water exposure. Figure 3.8 shows that there is no significant changes at the ionic liquid-water interface. It is worth noting, however, that a probe depth of approximately 13 monolayers prevents us from observing any subtle changes occurring at the top ionic liquid-vacuum layer. It has been established previously by Rubero, et al.⁴⁴ using sum frequency generation (SFG) that the imidazolium ring of the [BMIM][Tf2N] ionic liquid-gas interface of [BMIM][Tf2N] undergoes a reorientation in the presence of water vapor. Additionally, it should be stated that previous ARXPS studies of [EMIM][Tf2N] did not change as a function of electron emission angle of 0° and 70°. It is therefore appropriate to assume that no water is interacting with the sample surface, which would be evidenced by a separate peak, a shoulder or a change in FWHM of the native oxygen of the [Tf2N] anion. These findings are consistent with the hydrophobic nature of the [EMIM][Tf2N] ionic liquid and its immiscibility with water.⁶²

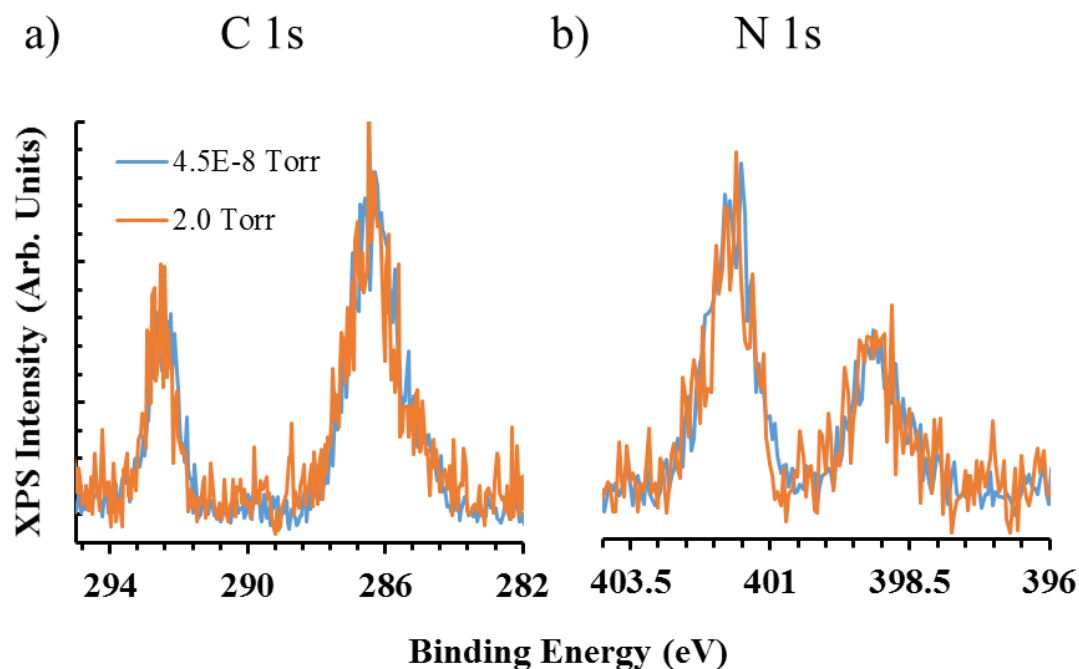


Figure 3.8: a) C 1s and b) N 1s spectra at high vacuum (blue) and 2.0 Torr (orange) showing no significant changes to the ionic liquid structure.

3.2.4 [EMIM][Tf₂N] as a Total Electron Scattering Cross-section Probe.

The lack of water adsorption or water film on the interface of the ionic liquid means that any signal attenuation is strictly due to the effects of the gas phase. By monitoring the signal attenuation $\ln(I/I_0)$ of the different elements and taking advantage of the range of kinetic energies they cover we can examine the attenuation slopes of the different elements.

In Figure 3.9, one can see that the slope of attenuation for the F 1s signal (purple line) is significantly more negative than the slope of attenuation of S 2p or C 1s (blue and red, respectively). Electrons emanating from F 1s orbitals arrive at the analyzer with a kinetic energy of 793.5 eV, which, in contrast to S 2p electrons arrive

at 1313 eV. Extraction of attenuation slopes from the different elements allowed for σ_e to be calculated at different kinetic energies which is shown in Figure 3.10.

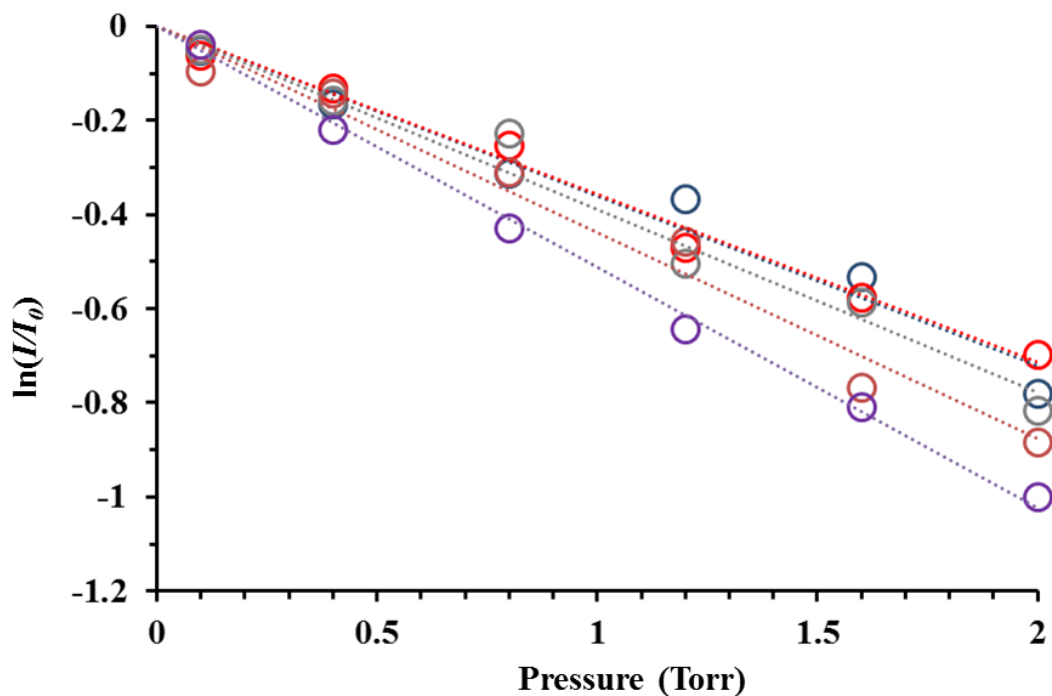


Figure 3.9: Attenuation of intensity as a function of pressure for the five elements that make up [EMIM][Tf₂N], F 1s (purple), O 1s (maroon), N 1s (grey), C 1s (red) and S 2p (blue). Reprinted with permission from Khalifa, et al.⁶¹

These results are compared with Bluhm, et al.¹¹ and compliments the kinetic energy range (Figure 3.10). At higher kinetic energies, the probability of electron-water molecule interaction becomes sufficiently small to be considered negligible. This becomes advantageous when attempting to quantify a material at an interface where there is no native element to compare adsorbate to.

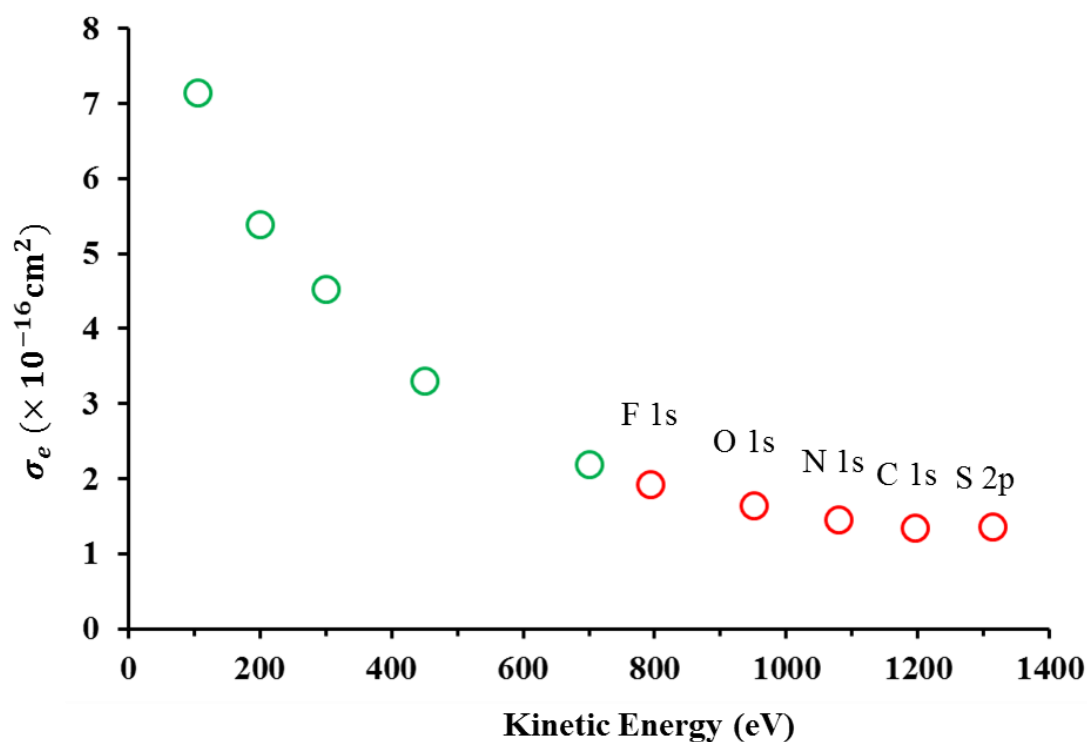


Figure 3.10: Calculation of total electron scattering cross-section of water as a function of kinetic energy. Red data are extracted from attenuation slopes using Eq. 3.1, blue data are extracted from Bluhm, et al.¹¹

3.3 Conclusions

Characterization of the [EMIM][Tf₂N] gas-liquid interface showed a pure surface. This surface was exposed to water vapor from high vacuum up to 2.0 Torr (10% relative humidity at room temperature). No evidence of molecular water was found at the interface from analysis of O 1s. The elemental diversity of [EMIM][Tf₂N] and its highly hydrophobic character allowed us to extract the total electron scattering cross-section of water vapor in the at five different kinetic energies in the range of 793 eV to 1,313 eV. These results nicely compliment previously published results from synchrotron-based AP-XPS and show the capability of lab-based APXPS and ionic

liquid's to calculate σ_e at different kinetic energies without access to a synchrotron facility, where the X-ray energy can be manipulated. This study can be extended to different gases of interest provided the gas phase does not absorb into the ionic liquid.

Chapter 4

WATER INTERACTION WITH THE INTERFACE OF [HMIM][Cl]

4.1 Introduction

The efficacy of ionic liquids in applications such as flue gas separation is sensitive to their ambient environmental condition where dissolved gases can alter their physical properties.⁶² One ambient parameter that has significant effects on ionic liquid physical properties is relative humidity. Water is ubiquitous in imidazolium-based ionic liquids, and the anion plays a primary role in the degree of hydrophilicity.⁶³ The presence of minute amounts of water has been shown to change fundamental ionic liquid characteristics.⁶⁴ These characteristics include, but are not limited to, viscosity,⁶⁵ conductivity,⁶⁶ electrochemical window⁶⁷ and surface tension.⁶⁸ Many of the applications of ionic liquids that utilize these mentioned properties are dependent on the nature of the ionic liquid gas interface.³⁷ Consider Blanco, et al.,⁶⁹ who found using molecular dynamic simulations that water mostly associates with the anion and to some extent with other water molecules, essentially slowing down the diffusion of both ionic liquid and dissolved CO₂. As a result, it is becoming increasingly recognized that water influences the interfacial structure and chemistry of ionic liquid-solid and ionic liquid-gas interfaces.⁴²

While the number of studies done on the interfaces of ionic liquid-vacuum are considerable, the number of studies that focused on water effects at the interface are limited. Water interactions on the surface of ionic liquids have been studied via

molecular dynamics simulations⁷⁰⁻⁷³ and experimental surface techniques such as temperature programmed desorption,⁷⁴ X-ray reflectivity,⁷⁵ sum frequency generation^{43-45,76} and neutral impact-collision ion spectroscopy (NICISS).^{46,47} Ridings, et al.⁴⁶ utilized NICISS to measure the effects of liquid water in the ppm range (premixed prior to analysis) on the surface structure of 1-hexyl-3-methyl-imidazolium chloride, [HMIM][Cl]. The results they obtained point towards an interface dominated by the alkyl chain character of the [HMIM]⁺ cation at low water concentrations with increasing chloride anion migration to the surface, as a function of increasing water content. Scattering results from Reichelt, et al.⁴⁷ looking at carbon and chlorine in [HMIM][Cl] reveal a layering of the interfacial region with the cation closest to the vacuum interface and the chloride anion present as an adjacent layer beneath the cation.⁴⁷ For ionic liquid-water mixtures with water mole fractions ranging from 0.43 to 0.71 (prepared ex-situ), an enhanced water layer relative to the bulk is observed at ~1 nm from the vacuum interface, located beneath the top [HMIM]⁺ cation layer. Because these experiments were performed under vacuum (a requirement of NICISS), it is still unclear to what extent water is present in the interfacial region as a function of variable water vapor pressures.

A number of ultra-high vacuum (UHV) XPS studies have examined the interfacial structure and chemistry of imidazolium-based chloride ionic liquids.^{38,40,41,77-80} Additionally, Lovelock, et al.⁴⁸ studied monolayer water adsorption onto a frozen ionic liquid and determined the heat of adsorption for water by performing temperature dependent XPS experiments.

In this study we utilize lab-based APXPS to quantitatively examine the interaction of water at the vapor-liquid interface of [HMIM][Cl] up to a maximum pressure of 5 Torr at room temperature. The results are compared to bulk uptake measurements of water into [HMIM][Cl] to assess the propensity for water to reside at the ionic liquid-vapor interface.

4.2 Results and Discussion

4.2.1 Surface Characterization of [HMIM][Cl]

Initial XPS spectra of [HMIM][Cl] (structure shown in Figure 4.1) were captured under a base pressure of 1.4×10^{-8} Torr. Figure 4.2 shows a survey spectrum in the binding energy range of 0 to 1100 eV. Detected elements include chlorine, carbon and nitrogen, consistent with the elemental composition of [HMIM][Cl]. These results indicate that there is no evidence of detectable surface contamination for the ionic liquid sample as received from the vendor.

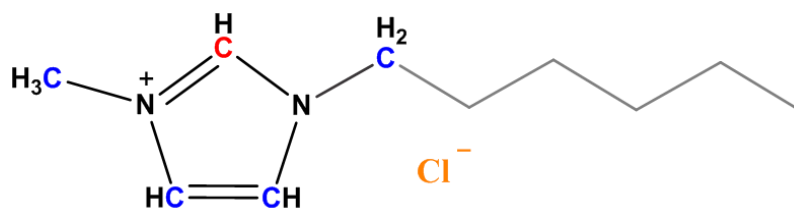


Figure 4.1: Chemical structure of [HMIM][Cl].

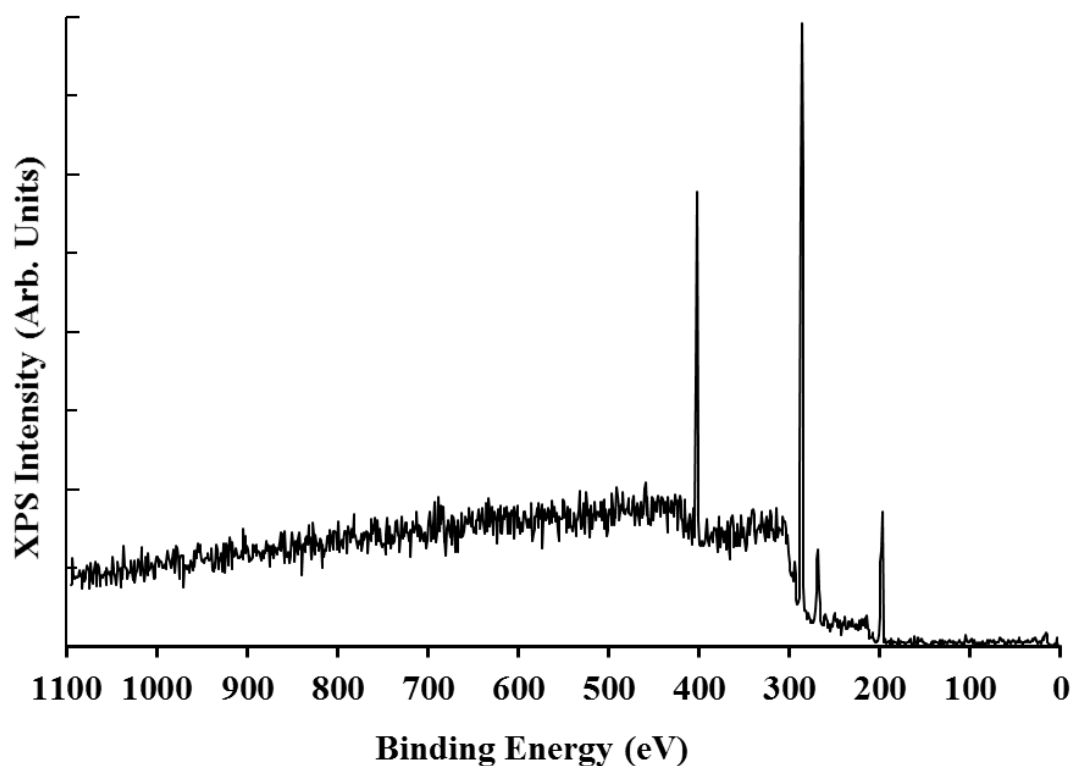


Figure 4.2: XPS survey, N 1s, C 1s and Cl 2p spectra of [HMIM][Cl] taken at a base pressure of 1.4×10^{-8} Torr. The structure of [HMIM][Cl] is shown at the top.

Initial XPS spectra in the C 1s, N 1s and Cl 2p regions were also taken under vacuum (Figure 4.3 and 4.4). The C 1s spectra were fit with three components by constraining the full width at half maximum (FWHM) between 1.0 and 1.1 eV. The N 1s, O 1s and Cl 2p FWHM were left unconstrained. The C 1s spectrum is composed of three peaks corresponding to the imidazolium cation alkyl chain (C_{alkyl} , grey tail, 285.0 eV), ring carbons (C_{ring} , blue, 286.2 eV) and the most oxidized carbon found on the ring in between the two nitrogen atoms (C_{ox} , red, 287.0 eV). The three C 1s peak areas are consistent with the 5:4:1 stoichiometry for $C_{\text{alkyl}}:C_{\text{ring}}:C_{\text{ox}}$, respectively. The

N 1s spectrum shows a single peak for the two nitrogen atoms on the imidazolium ring (N_{ring}) with a BE of 401.7 eV.

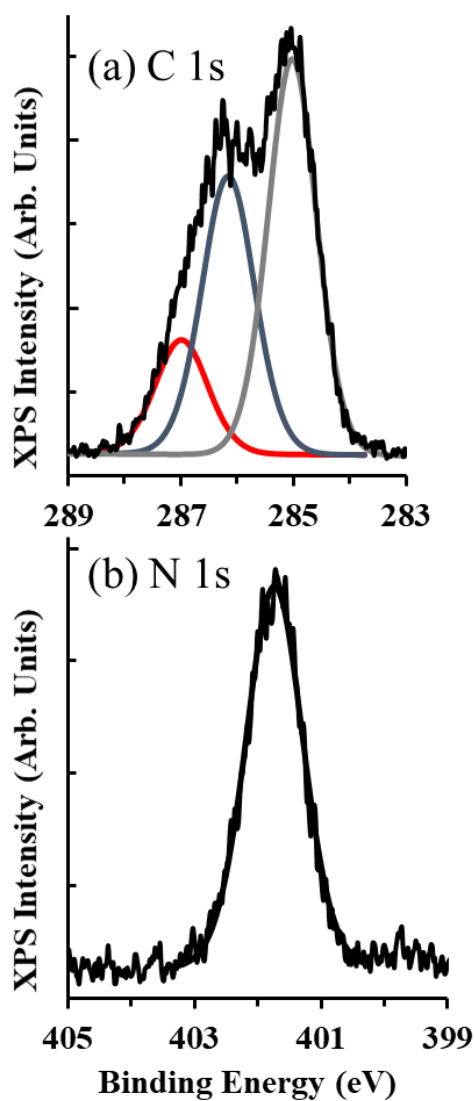


Figure 4.3: High resolution spectra of (a) C 1s, (b) N 1s

The Cl 2p spectrum due to chloride shows an expected doublet for the 2p(3/2) and 2p(1/2) spins, with a separation of 1.6 eV.⁷ The Cl 2p(3/2) binding energy is 197.1

eV. These observed BEs under vacuum are consistent with (≤ 0.1 eV) previous UHV XPS binding energy measurements of [OMIM][Cl], which also used $C_{alkyl} = 285.0$ eV as the internal reference.⁴⁰

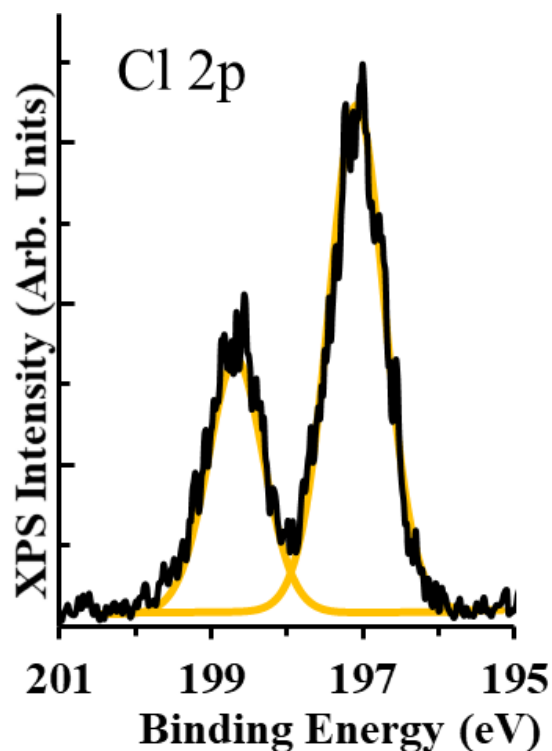


Figure 4.4: High resolution spectrum of Cl 2p.

4.2.2 [HMIM][Cl] – Water Isotherm

Next the [HMIM][Cl] ionic liquid sample was exposed to increasing water vapor pressures in the APXPS analysis chamber. Figure 4.5 shows representative offset O 1s spectra taken as a function of increasing pressure from 10^{-6} to 5.0 Torr. From 10^{-6} to 10^{-2} Torr no oxygen species are detected at the interface. At 0.1 Torr two peaks appear, one at 532.4 eV due to the presence of water at the ionic liquid-vapor

interface (O_w) and another peak at a higher binding energy of 535.9 eV due to gas phase water (O_g).⁸¹

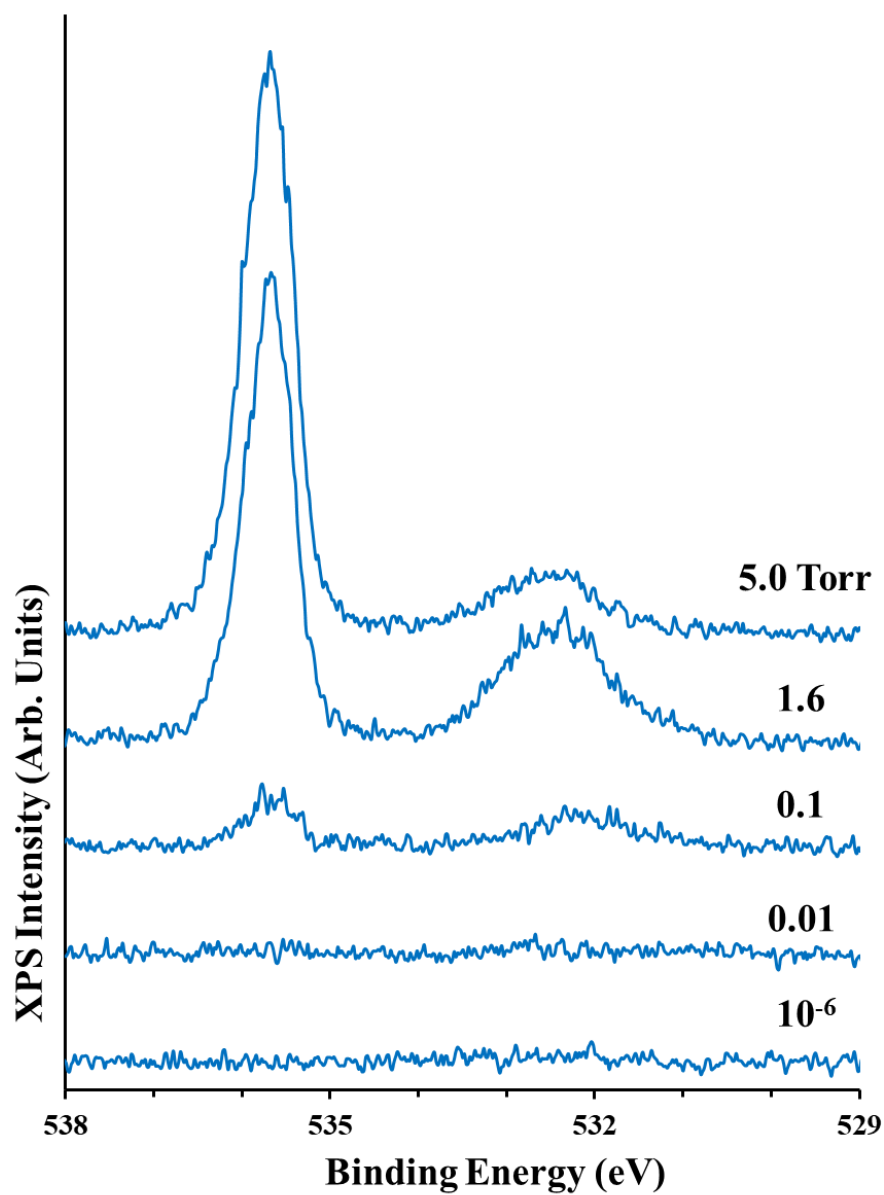


Figure 4.5: O 1s spectra taken as a function of increasing water vapor pressure in the chamber showing the presence of gas phase water (O_g) and condensed phase water (O_w) at the [HMIM][Cl]-vapor interface.

To assess whether the uptake of water was changing as a function of time, two O 1s spectra were taken back-to-back. Figure 4.6 shows results of two spectra taken immediately after the analysis chamber reached 0.4 Torr. When comparing the first spectrum (blue) with the second spectrum (black), it is seen that the spectra perfectly overlap, indicating that the uptake of water into the interfacial region has not changed.

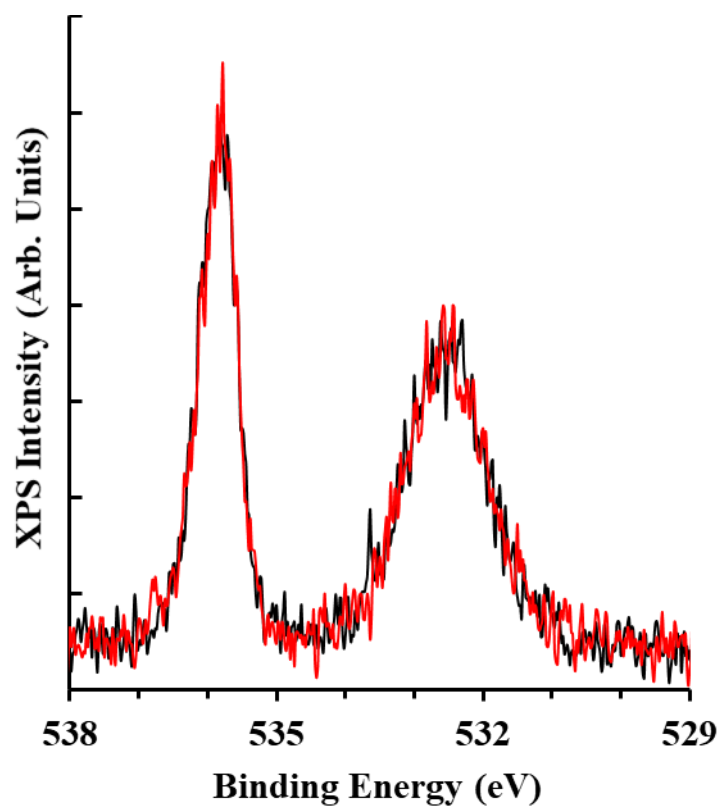


Figure 4.6: Two consecutive O 1s spectra taken back-to-back at 0.4 Torr showing no evidence of time dependent changes at the [HMIM][Cl]-vapor interface.

These results show that water in the interfacial region already reached equilibrium with the gas phase upon acquiring the first spectrum. Thus, the uptake

kinetics are more rapid than the time it takes to acquire an O 1s spectrum (~8 min.). We found this to be the case for all pressures, as the O 1s spectra were collected in duplicate during the experiment. These results indicate that under our experimental conditions, water uptake into the interfacial region is much more rapid than water uptake into the bulk. For example, absorption studies using an analytical balance^{62,82} or ATR-IR⁸³ show that the uptake of water into the bulk occurs on the order of many hours for hydrophilic and hydrophobic imidazolium-based ionic liquids. The results herein are consistent with our previous study, which showed that the bulk absorption of water into [BMIM][OAc] was much slower than of water uptake at the interface.⁸¹

Figure 4.7 shows the APXPS peak areas for C_{alkyl} (black), N_{ring} (green), Cl^- (red), O_g (blue, solid) and O_w (blue, open) as a function of increasing pressure. The C_{alkyl} , N_{ring} and Cl^- peak areas all decrease monotonically as a function of increasing pressure. This decrease is due to two contributing factors. The first is gas phase attenuation. As the pressure above the sample increases, there is an increase in the scattering of electrons by the gas phase leading to less signal making it to the electron energy analyzer.⁶¹ The second contribution is the dilution of the ionic liquid as water increases in the interfacial region. As the pressure increases from 0.1 to 5 Torr both O 1s peak areas O_w and O_g initially increase, followed by a decrease at higher pressure. The gas phase water peak initially increases due to the increase in pressure up to a maximum at 4 Torr, above which the intensity decreases due to self-attenuation of the photoelectrons being emitted by the gas phase molecules themselves. The O_w peak area increases initially due to an increase in the amount of water at the ionic liquid-gas interface, reaching a maximum intensity at 1.2 Torr. Above this pressure, gas phase

attenuation becomes significant and the overall O_w peak area decrease with increasing pressure.

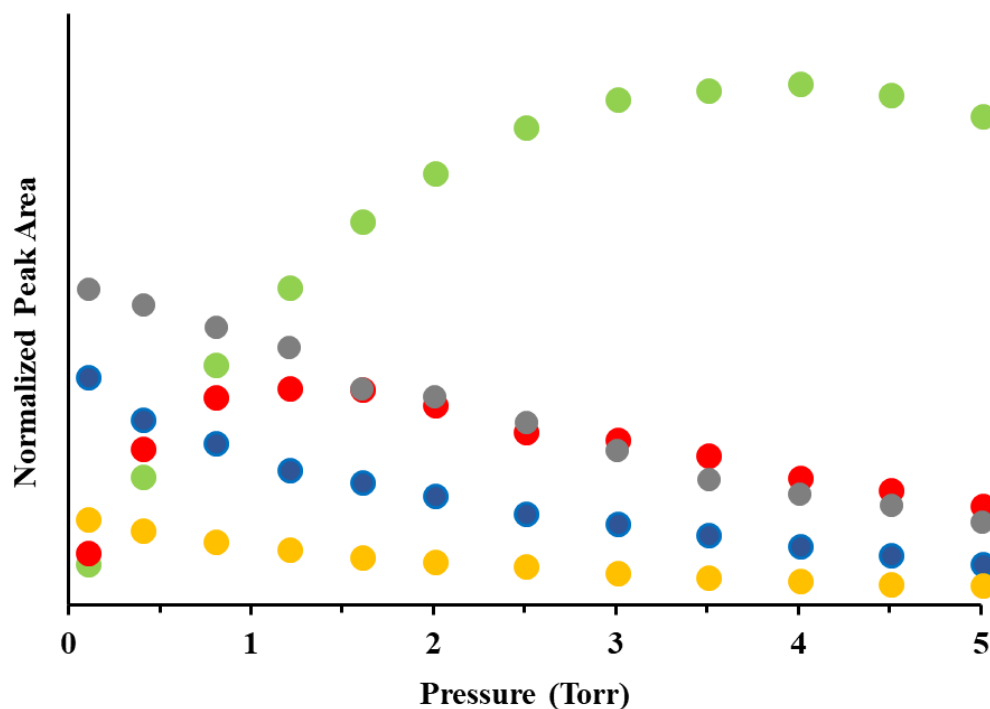


Figure 4.7: APXPS peak area as a function of increasing pressure for C 1s C_{alkyl} (grey), N 1s (blue), Cl 2p(3/2) (yellow), O 1s gas phase (green), O 1s interfacial water (red).

4.2.3 Quantitative Assessment of Water on [HMIM][Cl] Interface.

It is difficult to assess the amount of water present at the ionic liquid-vapor interface by solely using the O_w peak area. In order to quantitatively assess the amount of interfacial water we need to separate out the aforementioned effects of gas phase signal attenuation. This is accomplished by taking the ratio of the O 1s O_w peak to a different photoemission peak with a similar kinetic energy. Ideally, we would like to use an O 1s peak from the ionic liquid itself. However, given [HMIM][Cl] does not

have an oxygen moiety in its structure, an ionic liquid peak with a binding energy that is close to the O 1s is utilized. As seen from Figure 4.3b, the N 1s photoemission peak with a binding energy of ~ 402 eV is the closest element to the O 1s region at ~ 532 eV for O_w . The measured KEs for the O 1s and N 1s peaks in the presence of water vapor are ~ 950 and ~ 1080 eV, respectively, a difference of ~ 130 eV in kinetic energy. At these high KEs near ~ 1 keV we have shown that the electron scattering cross-section increases only by a factor of ~ 1.1 in going from ~ 1050 to ~ 950 eV.⁶¹ Thus, the gas phase attenuation for O 1s and N 1s is similar, which allows for a quantitative assessment of water in the interfacial region of [HMIM][Cl]. Figure 4.8 shows the ratio of the peak areas of O_w/N_{ring} as a function of increasing pressure. These results show that the amount of water in the interfacial region increases as a function of pressure.

The inelastic mean free path (λ) of electrons escaping from the [HMIM][Cl] surface with 1015 eV kinetic energy (the average kinetic energy for O 1s and N 1s orbitals) is calculated to be 3.39 nm using NIST software with the Gries predictive formula.⁸⁴ The thickness of one monolayer of ionic liquid is approximated⁸⁵ using $\rho^{-1/3}$, which is 0.69 nm for [HMIM][Cl]. Defining the probing depth to be $3\lambda\cos(20^\circ) = 9.6$ nm, which accounts for 95% of the signal from unscattered photoelectrons⁶, this corresponds to a probing depth of ~ 14 layers of ionic liquid. However, it should be noted that all 14 layers do not contribute equally to the overall XPS spectral intensity. Given that this is an exponentially decreasing relationship of XPS intensity versus ionic liquid depth (Beers Law),⁶ the first ionic liquid layer at the ionic liquid-vacuum interface is contributing significantly more to the XPS intensity than the fourteenth ionic liquid layer.

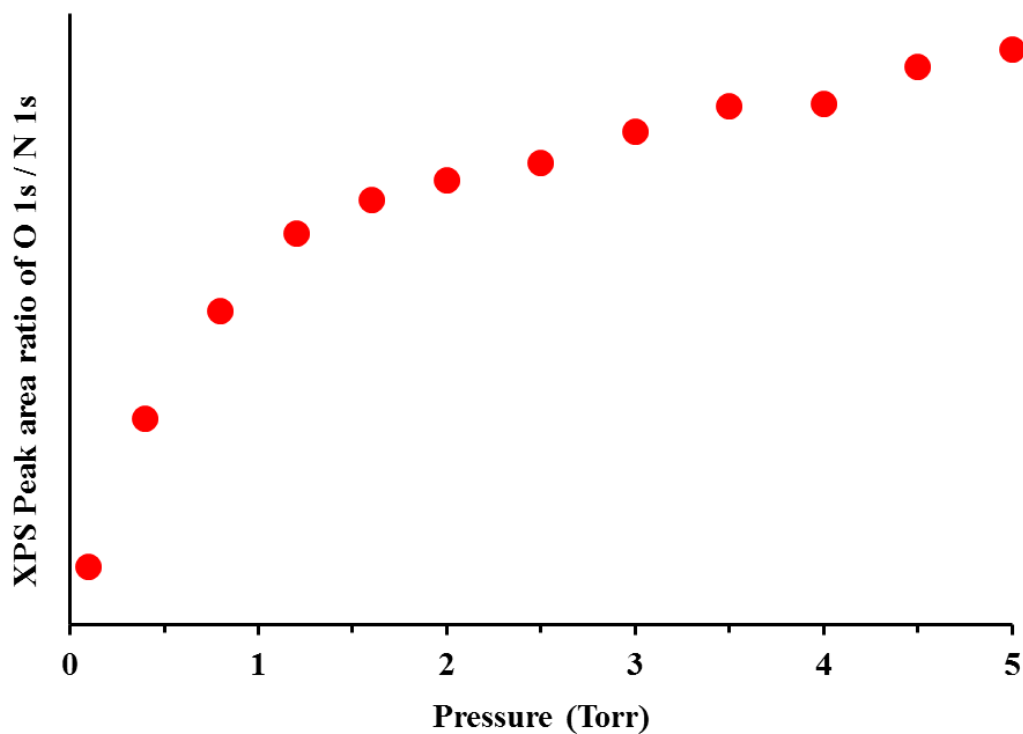


Figure 4.8: APXPS peak area ratio of O 1s O_w to N 1s vs. pressure.

The XPS peak area ratio is converted to a mole ratio via Equation 1 (E1).⁷ The ratio intensity of O_w peak area (I_w) to the N 1s peak area due to the imidazolium ring (I_{IL}) show the relationship to n_w and n_{IL} which are the number of moles per unit volume of water and ionic liquid, and where S_{O1s} and S_{N1s} are the O 1s and N 1s sensitivity factors, respectively. The ratio S_{O1s}/S_{N1s} in Equation (E1) was measured to be 1.87 for our instrument using [BMIM][Ac], which contains both oxygen and nitrogen in the pure ionic liquid. The factor of two in Equation (E1) is from the two moles of nitrogen per imidazolium cation.

$$\frac{n_{IL}}{n_w} = \frac{I_{IL}/2}{I_w} \left(\frac{S_{O1s}}{S_{N1s}} \right) \quad (\text{Eq. 4.1})$$

$$x_w = \frac{1}{1 + \frac{n_{IL}}{n_w}} = \frac{1}{1 + \frac{I_{IL}}{2 * I_w^{1.87}}} \quad (\text{Eq. 4.2})$$

Using Equation (4.2), the results of Figure 4.8 are then converted to x_w and then plotted as a function of pressure using linear (blue) and log (black) x-axes. From 10^{-6} to 10^{-2} Torr (on the log scale), there is no measurable amount of water in the interfacial region. Above 10^{-2} Torr, there is a sharp onset in water uptake at the ionic liquid-vapor interface. From 0.1 to 0.4 Torr, there is a steep increase (on the linear scale) in x_w , which levels off to a maximum of $x_w = 0.72$ at 5.0 Torr. By comparison, we have observed from APXPS data for [BMIM][OAc] that $x_w = 0.85$ at 5.0 Torr at room temperature.⁸¹

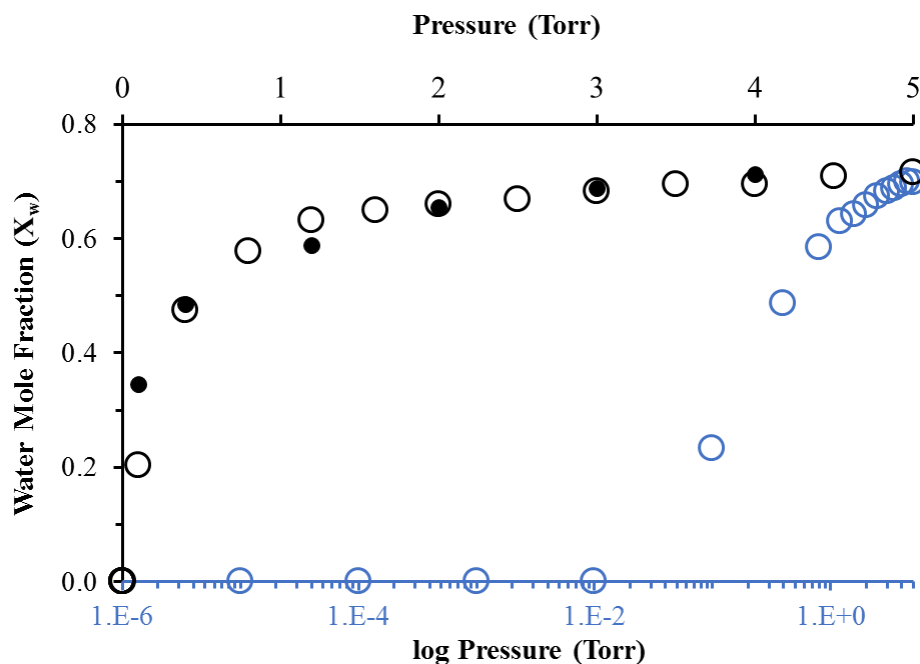


Figure 4.9: APXPS results of water mole fraction (x_w) as a function of increasing pressure on a log scale (black) and linear scale (blue, open symbols) and as a function of decreasing pressure (blue, closed symbols).

Cao, et al.⁶² have shown via gravimetric analysis studies that the amount of water uptake into the bulk is predominantly driven by the ionic liquid anion, and they also observed more water in the bulk for imidazolium [OAc]⁻ versus [Cl]⁻. Thus, the larger amount of water associated with [OAc]⁻ compared to [Cl]⁻ seems to occur both in the interfacial region (as observed via APXPS) and within the ionic liquid bulk (as observed gravimetrically). The open symbols of Figure 4a (blue, linear scale) are data captured as a function of increasing pressure while the closed symbols show the reverse experiment, captured as a function of decreasing pressure. The overlap of these two isotherms (forward and reverse) indicates that there is no significant hysteresis, and the uptake of water at the ionic liquid-vapor interface is reversible.

4.2.4 Interface vs Bulk Water Content.

MacMillan, et al.⁸⁶ investigated the bulk uptake of water into [HMIM][Cl] using tandem nanodifferential mobility analysis (TDMA).⁸⁶ To our knowledge, these are the only experiments exploring the bulk uptake of water into [HMIM][Cl] under thermodynamic equilibrium. These experiments involved generating dry monodisperse ionic liquid aerosol droplets with an average diameter of 27 nm. The dry droplets of ionic liquid were then exposed to humidified air at room temperature. Upon interaction with water vapor, the droplets grew in size due to water absorption, and hygroscopic growth factors (GFs) were measured as a function of increasing relative humidity (RH) ranging from 10 to 90 %. The GFs were quantitatively converted to equilibrium water mole fractions allowing for the assessment of x_w versus RH. Using WebPlotDigitizer version 3.9, the TDMA data of x_w versus RH was extracted and is displayed in Figure 4.10 (red data). For comparison, the APXPS data in Figure 4.9 were converted to RH and displayed in Figure 4.10 (black data). When

comparing the APXPS data with the TDMA data, it is apparent that the top few nanometers of the ionic liquid-gas interface of [HMIM][Cl] are significantly enriched in water compared to the ionic liquid bulk under low RH conditions. For example, at 20 % RH, $x_w \approx 0.3$ within the bulk while $x_w \approx 0.7$ at the ionic liquid-gas-interface.

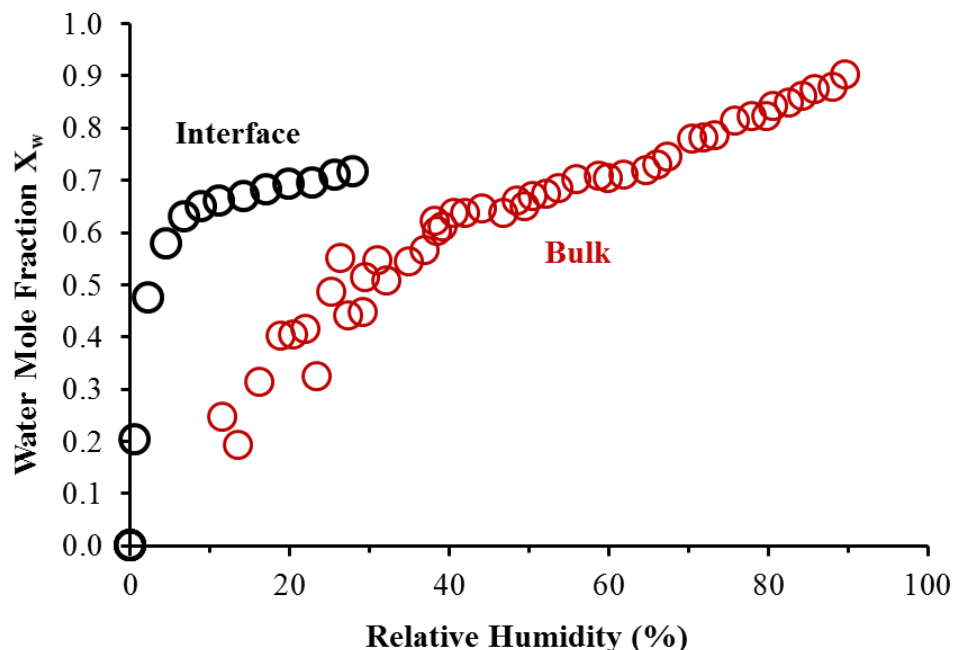


Figure 4.10: Comparison of APXPS (black) results for interfacial water uptake versus TDMA results of bulk water uptake obtained from Macmillan, et al.⁸⁶ (shown in red) as function of relative humidity (RH).

While these results clearly show a difference between APXPS (surface) and TDMA (bulk) water uptake, it should be noted that the two experiments were performed under different absolute pressures. The APXPS experiments were performed in a vacuum chamber under fixed absolute water vapor pressures, while the TDMA studies were performed at atmospheric pressure with partial pressures of water

at a given RH. Future gravimetric analyses exposing [HMIM][Cl] to absolute pressures of water, similar to those performed by Takamuku, et al.⁸⁷ for [EMIM][BF₄], would be useful to compare to these APXPS and TDMA results to disseminate any changes in uptake of water between partial pressures and fixed absolute pressures.

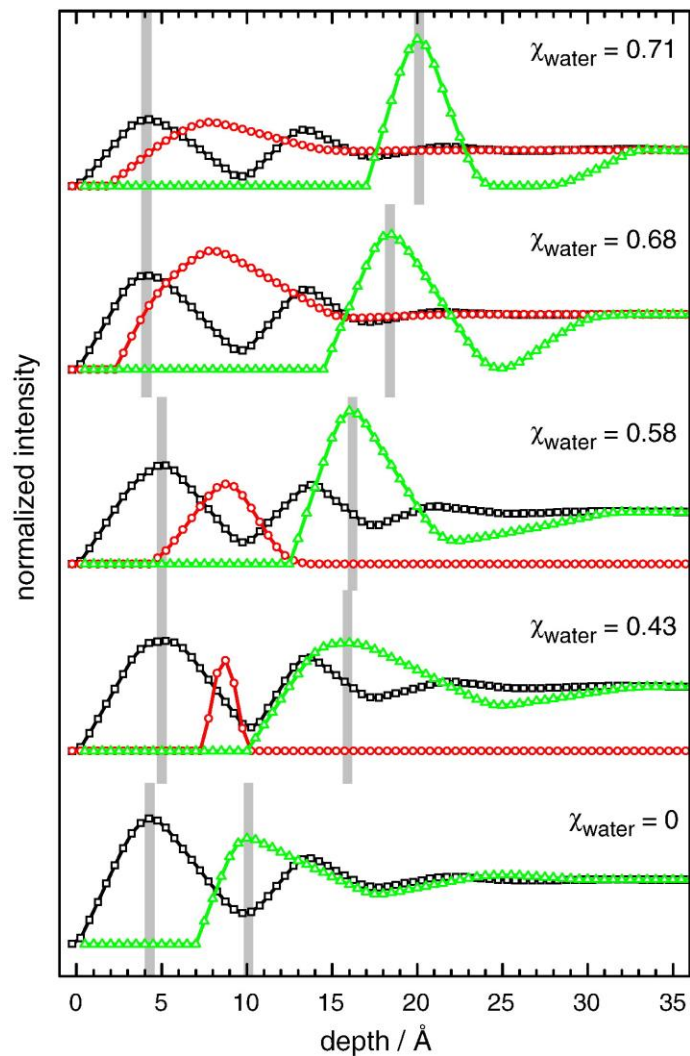


Figure 4.11: Concentration depth profiles of carbon (black squares), oxygen (red circles) and chlorine (green triangles) for [HMIM][Cl] and mixtures at different x_w . Grey lines show maximum position of carbon and chlorine respectively. Reprinted with permissions from Reichelt, et al.⁴⁷

Previously published concentration depth profile results using NCISS in the same mole fraction range also confirm that the water layer is enhanced relative to the bulk⁴⁷, as seen in Figure 4.11. This picture of water being enhanced at the ionic liquid-vacuum interface is also consistent with molecular dynamic simulation studies of water and dimethyl imidazolium chloride.⁷¹

These results add to the growing body of evidence that compared to the pure ionic liquid, water at the ionic liquid-gas interface can significantly change its structure and chemical nature.⁴² Given the ubiquity of water in both laboratory and industrial settings, it is important to take into consideration the effects of water on the interfacial chemistry of ionic liquids under ambient conditions, which in turn may significantly alter the kinetics and/or thermodynamics by the ionic liquid.

4.3 Conclusions

The gas-liquid interface of the [HMIM][Cl] was probed via APXPS in the presence of water vapor. The amount of water in the interfacial region was assessed quantitatively by comparing the oxygen to nitrogen XPS signal. An increase in interfacial water was observed as a function of increasing water vapor pressure. . Experiments performed as a function of decreasing pressure revealed that interfacial water uptake is completely reversible and free of hysteresis effects. Our APXPS findings indicate that water was enhanced at the ionic liquid-gas interface when compared to previously published bulk uptake experiments using TDMA. This study reveals the importance of understanding the effects of atmospherically relevant gases on the surface chemistry of ionic liquids, providing insight in the future design of task-specific ionic liquids with careful consideration for the potential impact of ambient water on the ionic liquid-gas interface.

Chapter 5

SURFACE SEGREGATION IN [EMIM][Tf₂N][OAc] MIXTURES

5.1 Introduction

While a dominant portion of the literature has focused on the interface of pure ionic liquids,^{34,37,88-93} much less attention has been given to the interfacial properties and structure of ionic liquid mixtures. A number of experimental techniques have been utilized to study the ionic liquid mixture-vacuum interface including X-ray photoelectron spectroscopy (XPS),⁹⁴⁻⁹⁶ angle resolved X-ray photoelectron spectroscopy (AR-XPS),⁴¹ time of flight secondary ion mass spectrometry (ToF-SIMS),⁹⁷ high resolution Rutherford backscattering (HRBS),^{2,98-100} low-energy ion scattering,¹⁰¹ reactive atom scattering,¹⁰² small angle X-ray scattering and neutron scattering.¹⁰² Maier, et al.⁴¹ examined the surface of a 9:1 mixture of 1-ethyl-3-methylimidazolium, [EMIM]⁺, to 1-dodecyl-3-methyl-imidazolium, [DMIM]⁺ with bis(trifluoromethanesulfonyl) imide, [Tf₂N]⁻, as a common anion using AR-XPS. The study showed that there is no preferential enrichment of the dodecyl alkyl chain to the outer surface. This was in contradiction with the findings of Bruce, et al.¹⁰² who utilized small-angle X-ray and neutron scattering experiments (in addition to molecular dynamics (MD) simulations) to show enrichment of the [DMIM]⁺, at the liquid-vacuum interface with varying [EMIM][Tf₂N] mole fractions. Additionally, in the same mixtures with low mole fraction of [DMIM][Tf₂N] in [EMIM][Tf₂N], it was found that the alkyl pockets in the bulk of [DMIM]⁺ appear at a mole fraction of ~0.25 and increase further with increasing [DMIM][Tf₂N] content. These pockets eventually

form long range bi-continuous networks, which have a clear effect on physical properties such as density, viscosity, and conductivity.

Mixtures that utilize two different anions with a common cation have also been shown to have certain structuring. Using ToF-SIMS, Souda, et al.⁹⁷ showed the surface segregation preference of the $[\text{Tf}_2\text{N}]^-$ anion relative to its counterpart hexafluorophosphate ($[\text{PF}_6]^-$). Nakajima, et al. utilizing HRBS⁹⁸⁻¹⁰⁰ also found similar enhancement of the $[\text{Tf}_2\text{N}]^-$ anion relative to other anions on the interface such as $[\text{BF}_4]^-$,¹⁰⁰ $[\text{PF}_6]^-$,^{98,100} $[\text{Cl}]^-$,^{98,99} and $[\text{TfO}]^-$.⁹⁹ Additionally, Villar-Garcia, et al.¹⁰¹ studied several mixture interfaces using LEIS two of which involves $[\text{Tf}_2\text{N}]^-$ anion mixed with halides. The authors noted a significant increase in $[\text{Tf}_2\text{N}]^-$ at the surface relative to the bulk accompanied by a dramatic depletion of halide anions. Villar-Garcia, et al.⁹⁴ using XPS also explored the electronic behavior of ionic liquids that have a common cation (i.e., $[\text{OMIM}]^+$) and different anions such as $[\text{Tf}_2\text{N}]^-$ and $[\text{Cl}]^-$. The study highlighted the corresponding effects these varying electronic environments have on the catalytic efficiency of a ionic liquid mixture/palladium catalyst. It is important to note that a quantitative determination of anion enhancement using XPS on ionic liquid mixture has been lacking in the literature.

While there have been a number of experimental⁹⁷⁻¹⁰¹ and MD^{103,104} studies examining the structure of the ionic liquid-vacuum interface of ionic liquid mixtures, the body of literature combining both experimental and theoretical work is limited. This approach has been explored previously with aqueous solutions containing halide salts.^{105,106} Recent efforts by Shimizu, et al. have compared and combined MD and ARXPS to study the surface composition of different pure imidazolium cations with $[\text{Tf}_2\text{N}]^-$ counter ion. Specifically, the authors were able to get quantitative agreement

of the ratio of alkyl chain to carbons on the imidazolium head group. The authors used this structural information derived from both techniques to help understand and predict trends in surface tension.

Combining both ARXPS with MD is a powerful tool to examine ionic liquid surface structure. With regards to binary ionic liquid mixtures, these combined techniques can examine surface enrichment of ions relative to others. In the current study, we report the quantitative concentration of the surface structure of a binary ionic liquid mixture containing 0.1 mole fraction [EMIM][Tf₂N] ($X_{\text{Tf}_2\text{N}} = 0.1$) and 0.9 mole fraction [EMIM][OAc] ($X_{\text{OAc}} = 0.9$) using a combination of MD simulations and AR-XPS. The alignment of each molecule was also studied in terms of vector orientation distribution to better understand the surface structure of the [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} mixture. The structure of the ionic liquid mixture components is shown in Figure 5.1 (see section 5.3.2 for carbon species assignment).

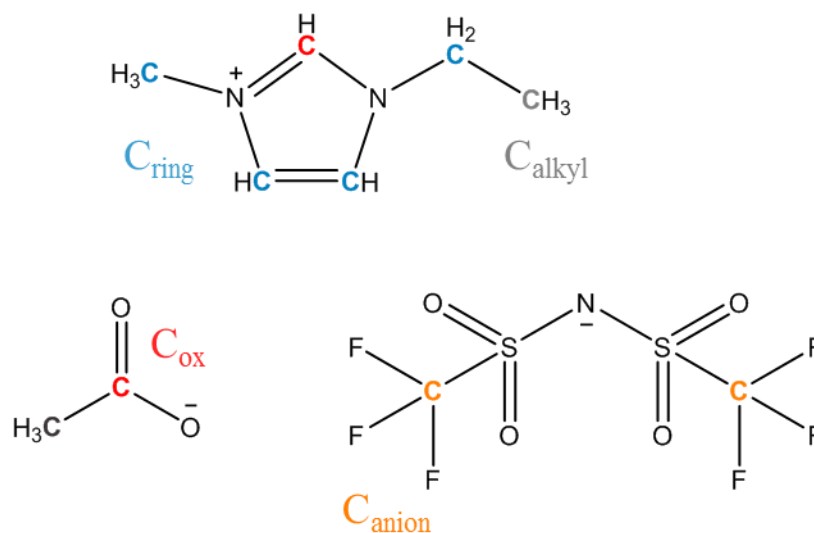


Figure 5.1: Chemical structure of the components of the ionic liquid mixture [EMIM][Tf₂N]_{0.1}[OAc]_{0.9}.

5.2 Experimental Considerations

Samples were constrained in four shallow wells. The wells were made sufficiently small to restrict movement of the viscous ionic liquid mixture during angle resolved XPS measurements. The ionic liquid laid flat to the naked eye inside of the wells (cartoon representation on Figure 5.2). The wells were purposefully mounted directly above the tilting axis of the AR module such that distance of the sample from the acceptance aperture is not altered. At both 0° and 80° sample height optimization based on signal was made. Raw spectra of O 1s and N 1s at both 0° and 80° are shown in Figure 5.2 illustrating the repeatability of those measurements.

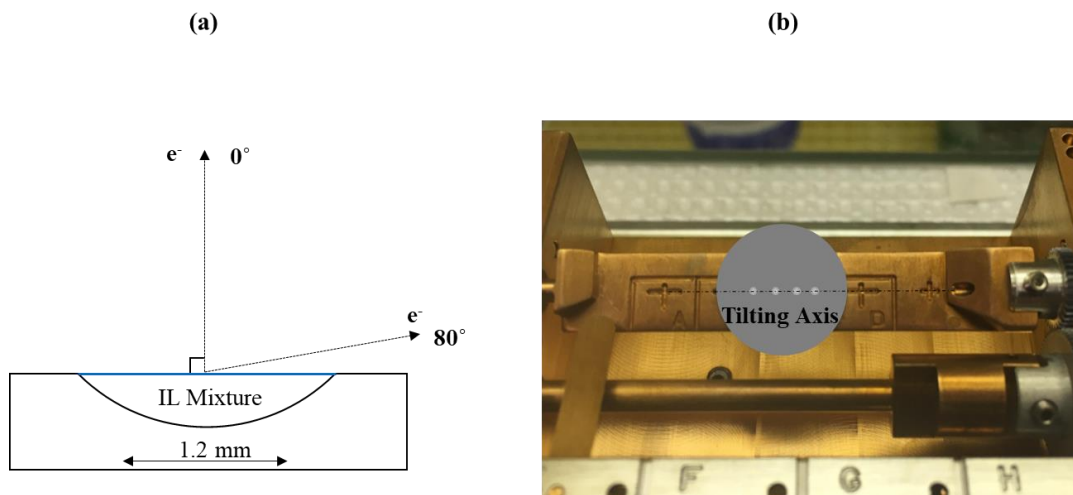


Figure 5.2: Side view cartoon depiction illustrating ionic liquid mixture inside of wells on aluminum stub (top). Wells mounted directly over tilting axis of angle resolved module (bottom).

5.3 Results and Discussion

5.3.1 Precision of Measurements

The results of the analysis at 0° and 80° (Figure 5.3 and 5.4) show the precision of the measurements, giving confidence in the repeatability of these experiments.

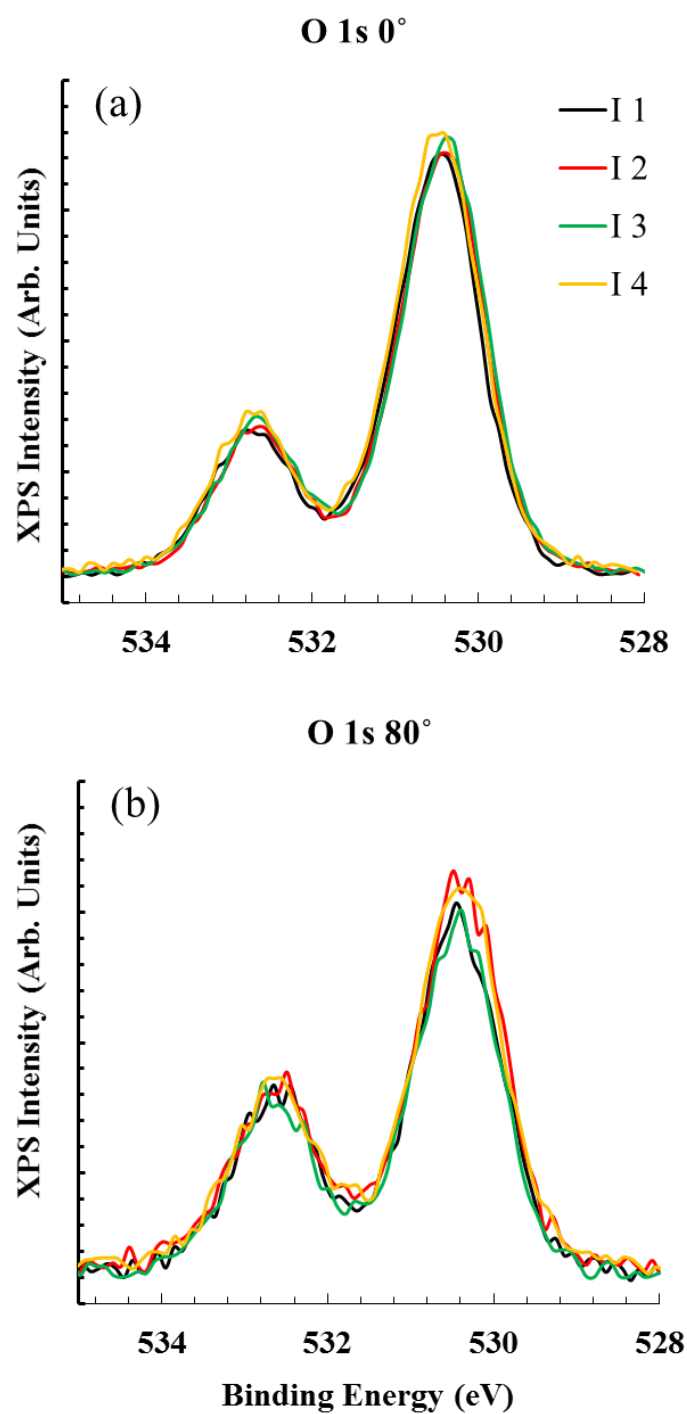


Figure 5.3: Raw O 1s spectra of the ionic liquid mixture [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} measured in four indents (labeled I) of aluminum substrate at 0° (top) and 80° (bottom).

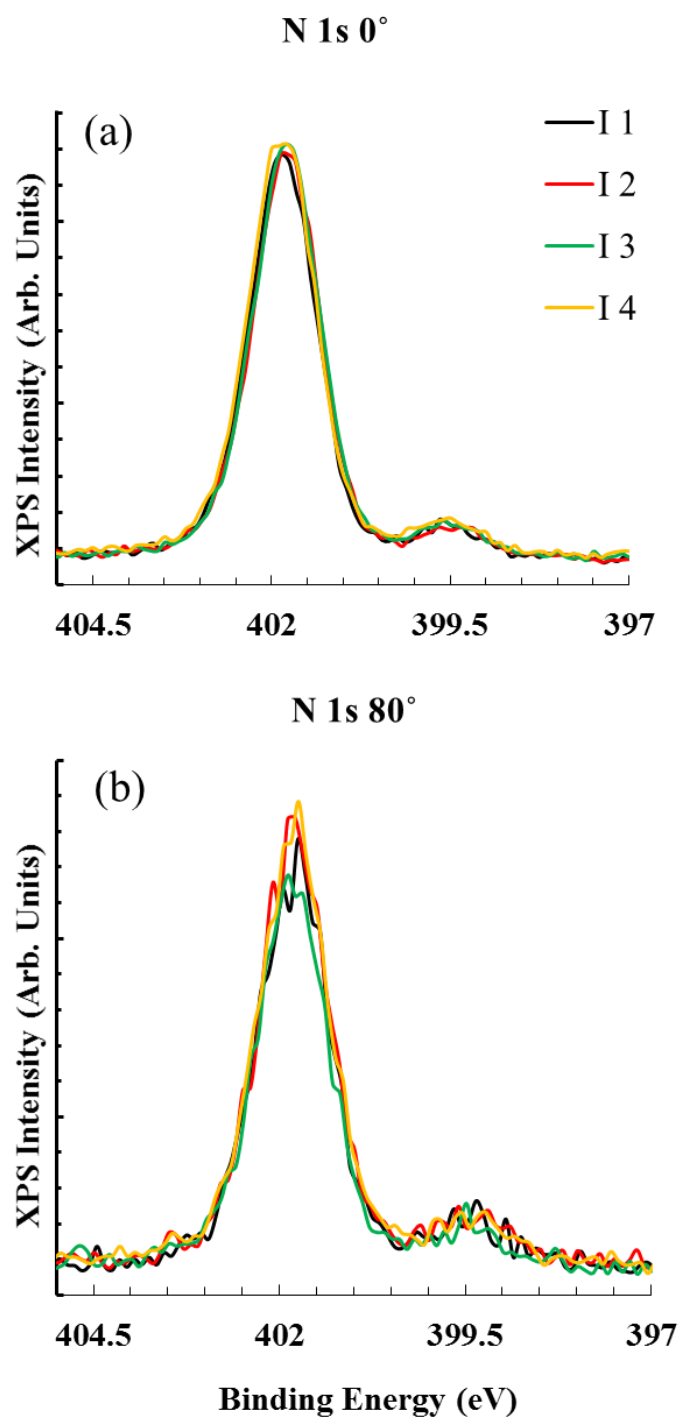


Figure 5.4: Raw N 1s spectra of the ionic liquid mixture [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} measured in four indents of aluminum substrate at 0° (top) and 80° (bottom).

5.3.2 [Tf₂N]⁻ Interface Enhancement from MD

Survey spectra (Figure 5.5) show the expected elements with no trace of the aluminum peaks at both 0° and 80°, indicating that the X-ray spot size was within the 1.2 mm diameter droplets so as to only probe the ionic liquid-vacuum interface, not capturing the aluminum edges. Additionally, the survey spectra show no indication of halide contamination.

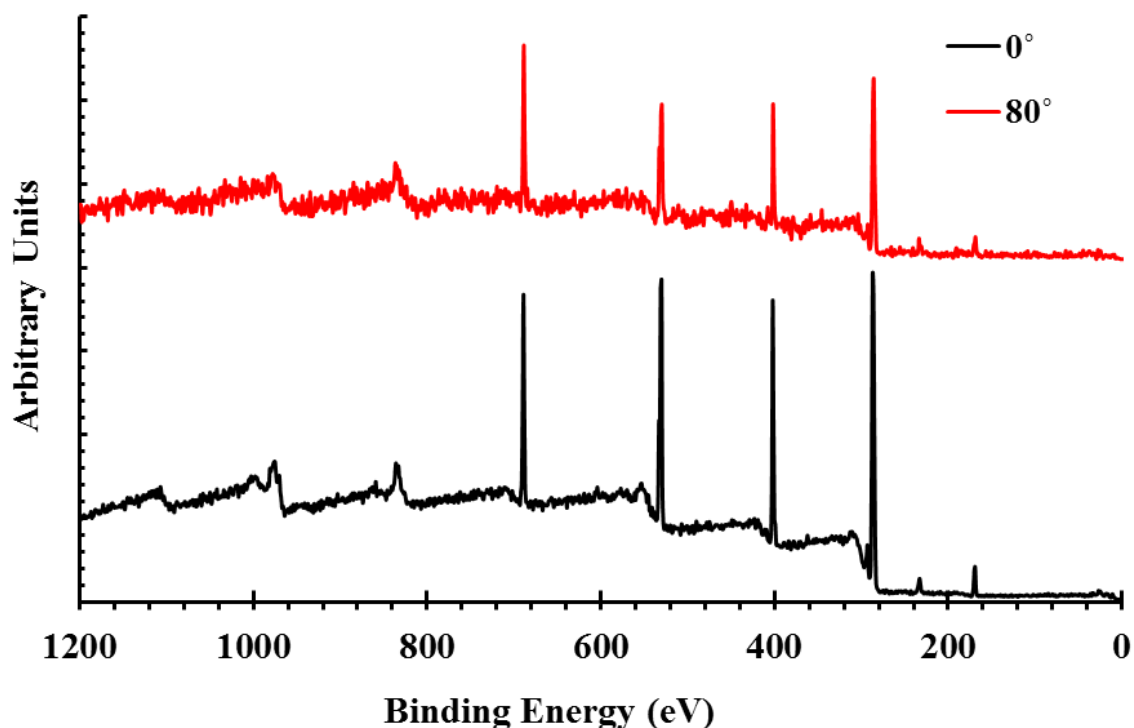


Figure 5.5: Survey spectra depicting the ionic liquid mixture [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} at 0° and 80°.

In regard to C 1s measured at 0° (Figure 5.6), three components are fitted to the broad peak encompassing the [EMIM]⁺ and [OAc]⁻ ions with position constraints. We expect the ratio between $C_{alk}:C_{ring}:C_{ox}$ to be roughly 1:2.1:1 for a mixture of

approximately 0.1 $X_{\text{Tf}_2\text{N}}$. Our experimental findings come up to be 1:2.3:1.1, reasonably close to the expected stoichiometry.

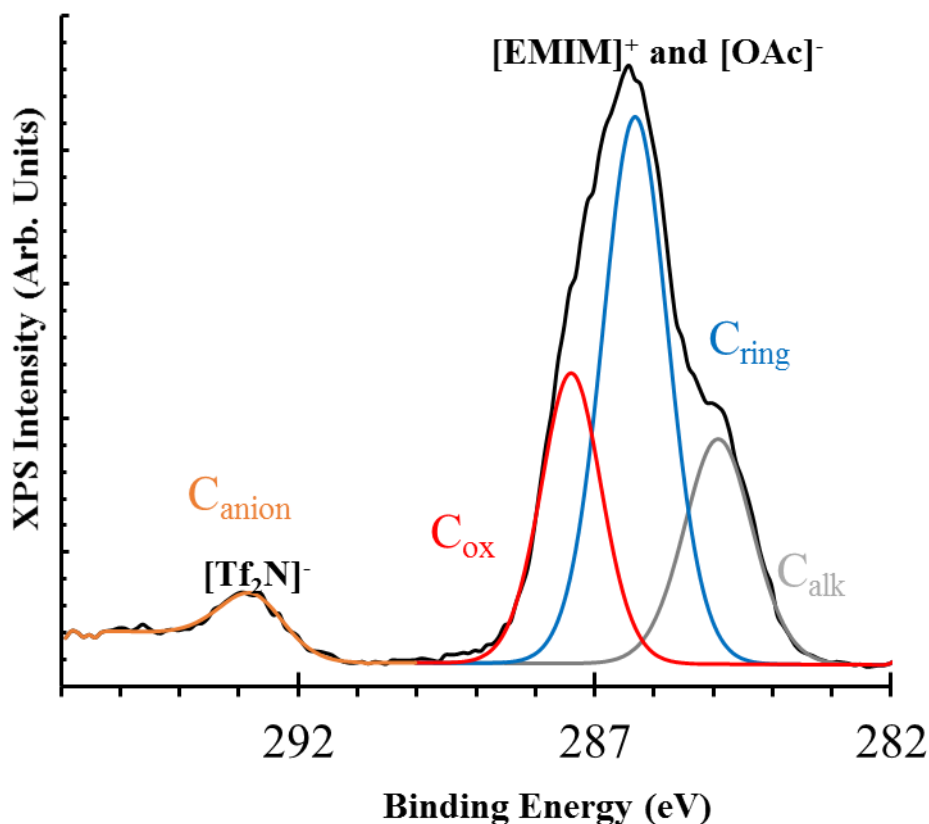


Figure 5.6: C 1s analysis of $[\text{EMIM}][\text{Tf}_2\text{N}]_{0.1}[\text{OAc}]_{0.9}$.

Next we compare simulated oxygen concentration profiles from MD results and experimentally obtained XPS data. The extent of enhancement of $[\text{Tf}_2\text{N}]^-$ at the interface can be investigated in relation to the $[\text{OAc}]^-$ anion, since oxygen is part of both moieties. To compare the enhancement observed in the MD simulations with the AR-XPS results, the density profile from MD (supplied by our collaborators Dr. Yong Zhao and Dr. Ed Maginn) was converted into an exponentially decreasing signal

intensity from the interface going into the bulk. The raw concentration profiles were simulated from the perspective of AR-XPS ratios by utilizing an adaption of the convolution integral equation¹⁰⁵:

$$\int_0^d e^{-\frac{z}{\lambda \cos \theta}} \rho(z) dz \quad (\text{Eq. 5.1})$$

where d is the commonly defined probing depth in XPS $3\lambda \cos \theta$, z is the liquid depth, $\rho(z)$ is the ion concentration as a function of z (from the MD simulation) and λ is the inelastic mean free path of photoelectrons with a given kinetic energy emitted at angle θ from the sample normal. λ was calculated to be 32 Å for O 1s (35 Å for N 1s) using the Gries predictive formula from NIST Electron Inelastic-Mean-Free-Path Database (v. 1.2)⁸⁴ based on a weighted average of the density of the material. The concentration profiles of oxygen atoms as a result of applying the exponentially attenuating function in Eq. (1) are displayed in Figure 5.7, where the solid red and blue lines represent $[\text{Tf}_2\text{N}]^-$ and $[\text{OAc}]^-$, respectively, when the sample is probed at a sample normal collection angle of 0° . The dashed red and blue lines are of the same elements at a more surface sensitive grazing angle of 80° . It is important to note that at 0° the probing depth is estimated to be $3\lambda \cos 0^\circ \sim 96$ Å which accounts for 95% of the signal.⁶ The curves in Figure 5.7 show an O(Tf_2N) peak concentration at shallow liquid depth, which drops off at deeper depth due to the exponentially decaying factor.

Below the top layer, for the dashed lines, a sharper drop off in signal is observed due to the enhanced surface sensitivity. By restricting the signal from deeper

layers at 80° , it can be seen that the $[\text{Tf}_2\text{N}]^-$ anion further dominates the interface due to the probing depth being reduced to $\sim 17\text{\AA}$ ($3\lambda \cos 80^\circ$). The integrated area (obtained via Eq. 1) under each of the concentration profiles in Figure 3a are proportional to measured XPS intensities, allowing for a direct comparison to XPS experiments.

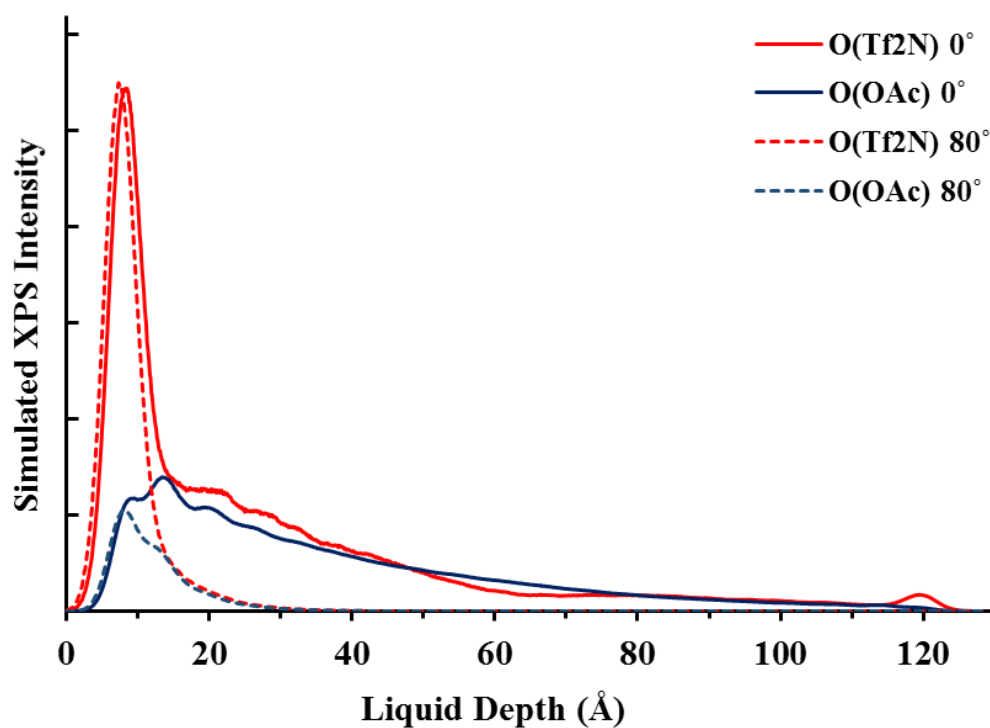


Figure 5.7: Simulated XPS of oxygen concentration profiles after applying Eq. 5.1 to density profile. Red solid and dashed lines represent the $[\text{Tf}_2\text{N}]^-$ component at 0° and 80° , respectively, while blue solid and dashed are of $[\text{OAc}]^-$ oxygen profile. Data were normalized to the height of the $[\text{Tf}_2\text{N}]^-$ oxygen intensity.

5.3.3 [Tf₂N]⁻ Interface Enhancement from AR-XPS

The experimental acquisition of high resolution AR-XPS O 1s spectra (Figure 5.8) provides experimental evidence of similar enhancement of the [Tf₂N]⁻ anion between 0° (shown in solid black) and 80° (dashed black). The four and two iso-electronic oxygen atoms belonging to [Tf₂N]⁻ (red) and [OAc]⁻ (blue) arise at 532.6 eV and 530.4, respectively. The spectra at 80° show a clear decrease in [OAc]⁻ intensity as we probe more of the surface, indicating the enrichment and partitioning of the [Tf₂N]⁻ anion at the interface relative to [OAc]⁻.

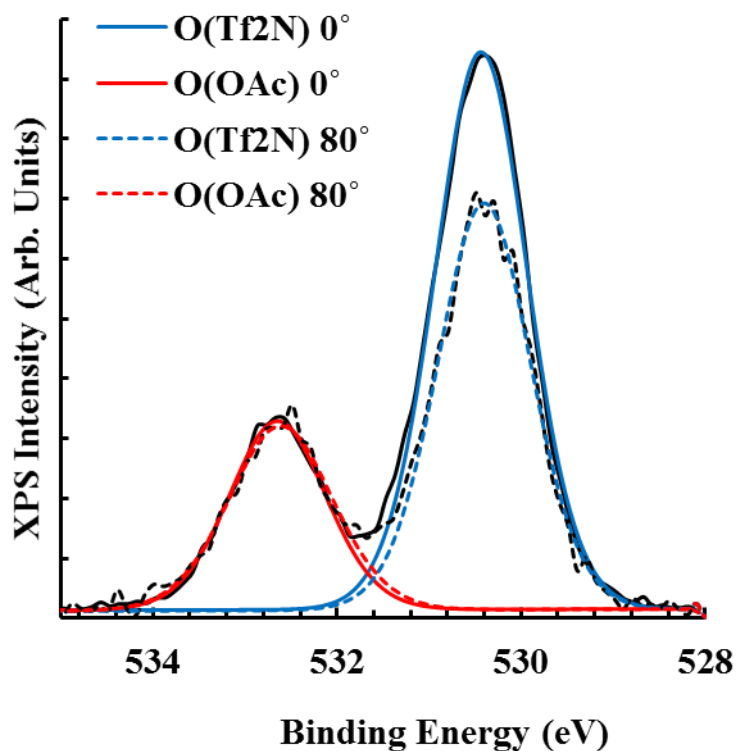


Figure 5.8: Experimental AR-XPS data of the ionic liquid mixture collected at 0° (solid black) and 80° (dashed black). Both plots have been normalized by height to the [Tf₂N]⁻ component showing the enhancement at the interface.

In regard to N 1s (Figure 5.9) the two peaks at 401.8 eV and 399.5 eV correspond to the nitrogen atoms on the cation and the imide nitrogen on the $[\text{Tf}_2\text{N}]^-$ anion. The decrease in intensity of $[\text{EMIM}]^+$ nitrogen signal at 80° signifies the enhancement of $[\text{Tf}_2\text{N}]^-$ at the interface relative to the cation.

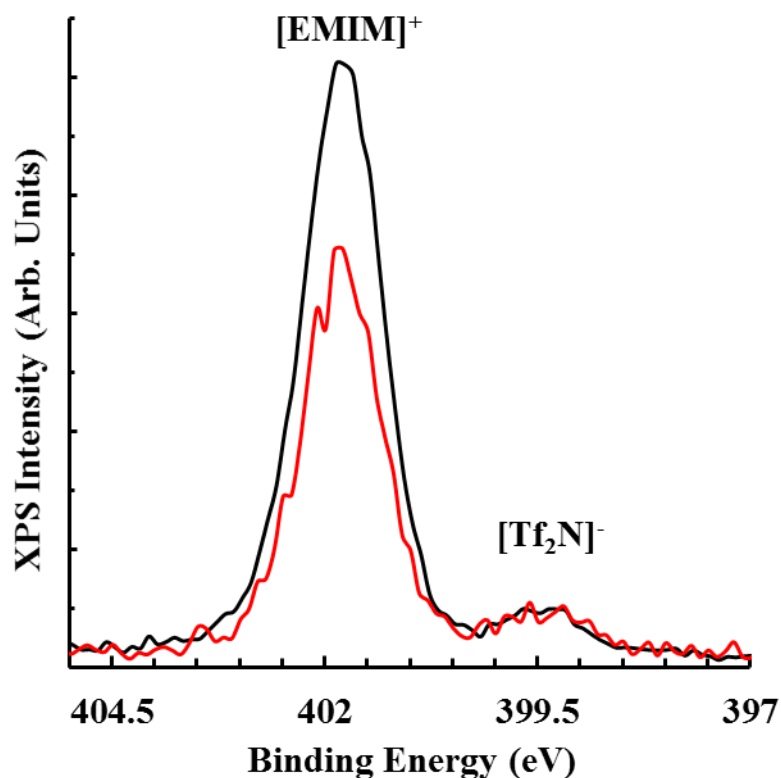


Figure 5.9: N1s spectra containing the $[\text{EMIM}]^+$ cation at 401.8 eV and 399.5 for the $[\text{Tf}_2\text{N}]^-$ anion.

For C 1s (Figure 5.10), the noticeable decrease in signal from the broad peak encompassing the $[\text{OAc}]^-$ and $[\text{EMIM}]^+$ cation shows just how dominant is the presence of $[\text{Tf}_2\text{N}]^-$ on the interface. It is interesting to note how the different elements

tell the same story from different perspectives. In regard to O 1s, it is a direct comparison between the $[\text{OAc}]^-$ and the $[\text{Tf}_2\text{N}]^-$ anions. The N 1s peak allows us to compare the $[\text{Tf}_2\text{N}]^-$ anion versus all $[\text{EMIM}]^+$ cations. C 1s on the other hand allows for a direct comparison of $[\text{Tf}_2\text{N}]^-$ and all other ions in the system.

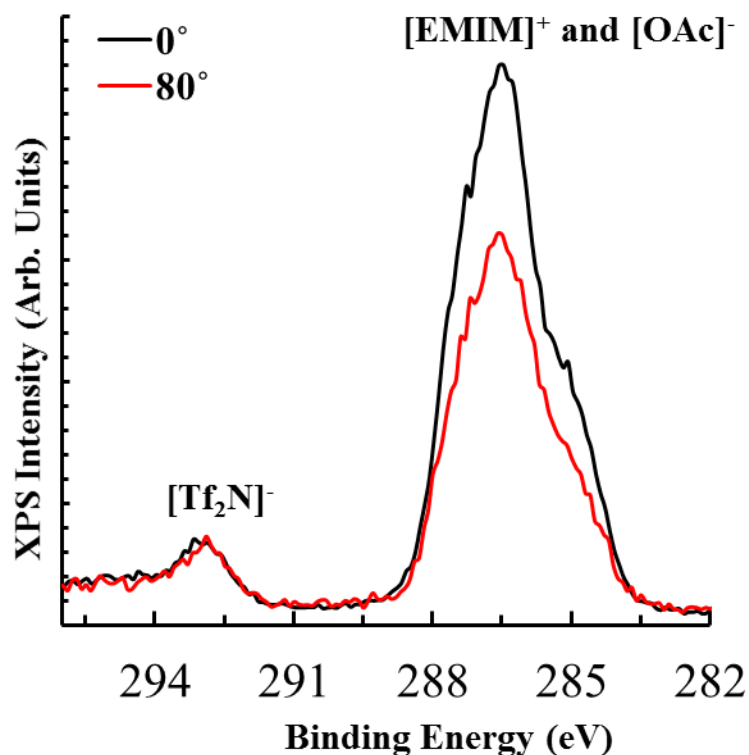


Figure 5.10: AR-XPS C1s at 0° and 80° showing peaks for the $[\text{EMIM}]^+$ cation and $[\text{OAc}]^-$.

5.3.4 $[\text{Tf}_2\text{N}]^-$ Anion Quantification

The integrated component areas (I) from O 1s and N 1s spectra are proportional to the moles of material (n). Recognizing that there are 4 moles of oxygen, 1 mole of nitrogen per mole of $[\text{Tf}_2\text{N}]^-$ and 2 moles of oxygen per $[\text{OAc}]^-$ in

addition to 2 moles of nitrogen per mole of $[\text{EMIM}]^+$, the mole ratio of $[\text{Tf}_2\text{N}]^-$ to $[\text{OAc}]^-$ and $[\text{EMIM}]^+$ based on I can be reduced to:

$$\frac{n_{\text{TFSI}}^{O\ 1s}}{n_{\text{OAc}}^{O\ 1s}} = \frac{I_{\text{TFSI}}^{O\ 1s}}{2 \times I_{\text{OAc}}^{O\ 1s}} \quad (\text{Eq. 5.2})$$

$$\frac{n_{\text{TFSI}}^{N\ 1s}}{n_{\text{EMIM}}^{N\ 1s}} = \frac{2 \times I_{\text{TFSI}}^{N\ 1s}}{I_{\text{EMIM}}^{N\ 1s}} \quad (\text{Eq. 5.3})$$

The mole ratios determined from the four independent spots is shown in Table 5.1 below:

Table 5.1: Mole ratios of $[\text{Tf}_2\text{N}]^-$ of the same mixture at different spots (I).

		0°	80°
$n_{\text{TFSI}}^{O\ 1s}/n_{\text{OAc}}^{O\ 1s}$	I 1	0.182	0.252
	I 2	0.175	0.256
	I 3	0.181	0.247
	I 4	0.177	0.251
$n_{\text{TFSI}}^{N\ 1s}/n_{\text{OAc}}^{N\ 1s}$	I 1	0.170	0.264
	I 2	0.172	0.250
	I 3	0.171	0.230
	I 4	0.175	0.257

The experimental mole fraction of $[\text{Tf}_2\text{N}]^-$ ($X_{\text{Tf}_2\text{N}}$) was calculated from oxygen and nitrogen based on the following equations:

$$\text{For O } 1s \text{ } X_{\text{Tf}_2\text{N}} = \frac{1}{1 + \frac{2 \times I_{\text{OAc}}^{O 1s}}{I_{\text{TFSI}}^{O 1s}}} \quad (\text{Eq. 5.4})$$

$$\text{For N } 1s \text{ } X_{\text{Tf}_2\text{N}} = \frac{1}{1 + \frac{I_{\text{EMIM}}^{N 1s}}{2 \times I_{\text{TFSI}}^{N 1s}}} \quad (\text{Eq. 5.5})$$

It is worth noting that these experimental mole fractions were determined by averaging the results of four replicate, independent spots. $X_{\text{Tf}_2\text{N}}$ from simulation results have been calculated by integrating the anion components along the z coordinate (Eq. 1). The results comparing experiments and simulations are shown in Table 5.2. According to oxygen, a nominal ratio of 0.100 is expected, as there should be one $[\text{Tf}_2\text{N}]^-$ for every one $[\text{OAc}]^-$ molecule. At 0° $X_{\text{Tf}_2\text{N}}$ is 0.152 ± 0.005 (2σ) and 0.118 based on experimental AR-XPS and MD simulation, respectively. This illustrates that $[\text{Tf}_2\text{N}]^-$ species dominates the interface at 0° , which probes deeper into the sample. At a grazing angle of 80° $X_{\text{Tf}_2\text{N}}$ for AR-XPS and MD is 0.201 ± 0.005 (2σ) and 0.252, this further demonstrates the enrichment of $[\text{Tf}_2\text{N}]^-$. The nominal $X_{\text{Tf}_2\text{N}}$ according to nitrogen species is 0.091, as there is one $[\text{Tf}_2\text{N}]^-$ molecule for every ten $[\text{EMIM}]^+$. At 0° we calculated a $X_{\text{Tf}_2\text{N}}$ value of 0.147 ± 0.003 (2σ) and 0.103 from XPS and MD simulations respectively, both extending beyond the nominal value of 0.91. Both methods show further increase of $X_{\text{Tf}_2\text{N}}$ at 80° of 0.200 ± 0.023 (2σ) and 0.210 for XPS and MD. In general, both XPS and MD show that the mole fraction of $[\text{Tf}_2\text{N}]^-$ increase significantly when going from 0° to 80° . Numerical deviation between both techniques can be inherent error due to force fields utilized in the simulation, and some water adsorbed to the hydrophilic ionic liquid $[\text{EMIM}][\text{OAc}]$ during gravimetric preparation.

Table 5.2: Interfacial mole fraction of $[\text{Tf}_2\text{N}]^-$ for a sample with bulk $X_{\text{Tf}_2\text{N}} = 0.1$ calculated based on experimental AR-XPS and MD simulation at 0° and 80° .

		Mole fraction $X_{\text{Tf}_2\text{N}}$	
		0°	80°
O1s	Nominal ^a	0.100	-
	MD	0.118	0.252
	AR-XPS	0.152	0.201
N1s	Nominal ^b	0.091	-
	MD	0.103	0.210
	AR-XPS	0.147	0.200

^a Based on anion ratio of 1:10, ^b based on anion to cation ratio of 1:11

The precise reason behind the enrichment of $[\text{Tf}_2\text{N}]^-$ at the surface has been a point of contention among the ionic liquid community. Souda, et al.⁹⁷ and Nakajima, et al. argue that anion size is the driving force for surface enrichment of anions relative to other anions. It is also argued that partitioning of $[\text{Tf}_2\text{N}]^-$ to the surface reduces the overall surface energy due to better screening of the electric field.⁹⁸ On the other hand, Villar-Garcia, et al.¹⁰¹ contends with this hypothesis, arguing that the driving force of surface segregation lies in cation-anion interaction. It is interesting to note that this system is analogous to aqueous solutions containing organic compounds with perfluoro functionalities, which display high surface activity.¹⁰⁷

5.3.5 Exposure of [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} to 1.0 Torr of Water.

The same ionic liquid mixture was introduced into the AP-XPS chamber. An isotherm exposing the sample to 1.0 Torr of water allowed us to examine the behavior of the ionic liquid mixture sample. The O 1s profile of [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} at 5.8×10^{-8} Torr (Figure 5.11) shows the expected peaks at 530.5 eV for the [OAc]⁻ anion and 532.7 eV for the [Tf₂N]⁻ anion. Upon exposure to 1.0 Torr of water we see two changes, the first is the emergence of the expected vapor phase peak and another species, which we attribute to interfacial water at 532.2 eV. The second change is the significant increase in the [Tf₂N]⁻ peak component. Utilizing Eq. 5.4, above we are able to calculate to the $X_{\text{Tf}_2\text{N}}$ and found it to be 0.18 and 0.30 at 5.8×10^{-8} Torr and 1.0 Torr of water respectively. The mole fraction of water $x_{\text{H}_2\text{O}}$ was calculated to be 0.62, which is slightly less water on the interface when compared to the pure analog [BMIM][OAc] which showed $\sim 0.70 x_{\text{H}_2\text{O}}$ at the same pressure. It should be noted that vacuum spectra from the APXPS shows a 0.03 increase in $X_{\text{Tf}_2\text{N}}$ relative to the mole fraction calculated from the AR-XPS results. This slight increase can be attributed due to the collection angle inside APXPS (22° vs 0°). Additionally, there could have been residual water in the chamber that absorbed into the sample surface, which led to accumulation of [Tf₂N]⁻ on the interface.

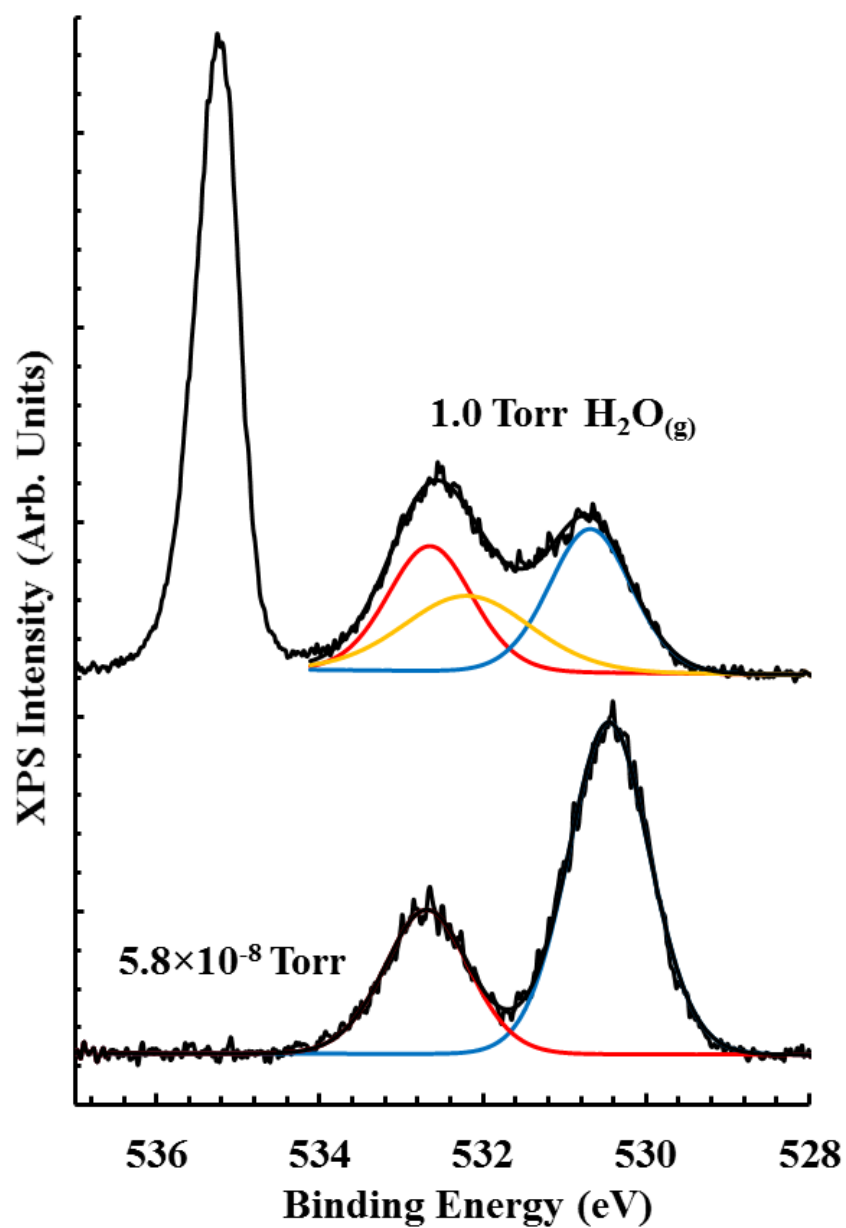


Figure 5.11: High resolution O 1s spectra of [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} at vacuum and 1.0 Torr of water, showing the [Tf₂N]⁻ component (red), [OAc]⁻ (blue) and interfacial water (orange).

With regards to the N 1s (Fig. 5.12), we see the two characteristic peaks of the [EMIM]⁺ two nitrogen atoms on the cation (401.8 eV) and the [Tf₂N]⁻ imide nitrogen (399.5 eV) this is within 0.1 eV of results obtained in the ARXPS data. While at UHV O 1s and N 1s gave consistent results for the $X_{\text{Tf}_2\text{N}}$ values both at 0 ° and 80 ° results from APXPS deviate interestingly. It was found that the mole fraction of [Tf₂N]⁻ at high vacuum yielded a value of 0.15 a value similar to what is expected. This value only increased to 0.22 upon addition of water to the chamber.

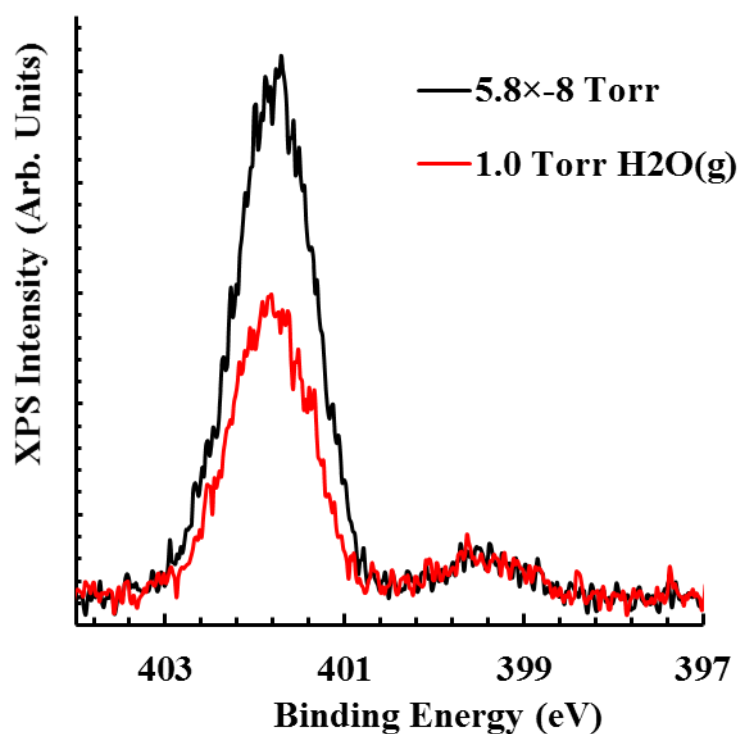


Figure 5.12: High resolution N 1s spectra of [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} at vacuum and 1.0 Torr of water.

5.4 Conclusions

A quantitative analysis of the structure of the ionic liquid mixture [EMIM][OAc] and [EMIM][Tf₂N] (9:1 molar ratio) was examined using both MD simulations, ARXPS and APXPS experiments. From MD and ARXPS we showed a consistent portioning behavior of the large [Tf₂N]⁻ anion relative to both [EMIM]⁺ and [OAc]⁻ ions by comparing the 0° data to 80°, based on measurements at four independent spots. At 0° the $X_{\text{Tf}_2\text{N}}$ surpassed the theoretical value of 0.1, showing a clear portioning of the [Tf₂N]⁻ at the surface of the mixture. At 80° the enhancement of $X_{\text{Tf}_2\text{N}}$ increases further by 0.2. Water exposure of 1.0 Torr to the [EMIM][Tf₂N]_{0.1}[OAc]_{0.9} increased the [Tf₂N] content on the surface two folds. These results show how sensitive ionic liquids can be to their ambient environment, which allows for the development and tuning of smart materials.

Chapter 6

SUMMARY AND FUTURE WORK

6.1 Future Work

6.1.1 The Effects of Temperature and Sputtering

Many more mixtures containing ions with different properties can be examined via the same methodology as described in Chapter 5. For example, preliminary AR-XPS data done on equimolar mixtures of [BMIM][Cl] and [BMIM][OAc] showed no preference of either anion on the interface, which is an interesting contrast to the [EMIM][Tf₂N][OAc] system. Similar work can be performed with systems involving three halides such as [Br]⁻, [Cl]⁻ and [I]⁻. A system like that is likely to segregate based on halogen atomic radius. Furthermore, the effects of water vapor on that interface would be interesting to observe. This exploratory direction is possible due to the fact that those three halogens have a separation of approximately 150 eV between reasonably high signal intensity peaks in the higher kinetic energy regime, allowing us to assume a very similar rate of attenuation for the three species from the gas-phase.

Temperature effects are also worth exploring, as it is evident that temperature has significant effects on bulk properties such as density, surface tension, viscosity and refractive index.^{108,109} Kolbeck, et al.¹¹⁰ showed the degree of alkyl enrichment is inversely proportional with increasing temperature for varying alkyl chain imidazolium cations with [Tf₂N]⁻. Varying temperature in AP-XPS is an established method to calculate thermodynamic properties involved with water or absorbates in

general on the interface of ionic liquids. Furthermore, varying temperature during AR-XPS analysis of ionic liquid mixtures and examining enhancement effects is particularly interesting as it provides another “knob” to fine-tune ionic liquid interfaces for a desired application.

Another worthwhile exploration concerns sputtering of ionic liquids. When ionic liquid surface structures were initially explored, impurities such as silicon oxide, were common to find.^{38,79} Many of these impurities were specifically surface active due to their lack of charge. Non-charged molecules tend to be rejected to the interface to minimize the disruption of long range electrostatic attraction between cations and anions. Sputtering of ionic liquids to obtain a clean surface for analysis is not extensively studied. Kolbeck, et al.¹¹¹ showed depletion of contaminants on the surface as a result of sputtering using Ar^+ ions. With carbonaceous signal typically showing up at 285 eV, it becomes typical to see a pronounced carbon species at that particular binding energy where it is not part of the ionic liquid moiety and therefore considered un-intentional contamination. During the scope of the work in this thesis, contaminated samples have been encountered. Typically the sample had to be evacuated and a fresh drop was placed on the substrate to carry out the study. Utilizing sputtering sources to understand the effects of Ar^+ ions with varying energies has on the ionic liquid surface-active contaminants and the stoichiometric makeup of the ionic liquid is critical for the development of rigorous cleaning methods that do not affect the natural profile of ionic liquid interfaces. Furthermore, using the sputter source to induce substrate dissolution would be interesting to study metal ion interactions with ionic liquids.

6.2 Summary

6.2.1 Total Scattering Cross-Section of H₂O(g) From [EMIM][Tf₂N]

The highly hydrophobic surface of the ionic liquid [EMIM][Tf₂N] showed no measurable level of interaction with water (up to 2.0 Torr).⁶¹ The absence of an aqueous layer on the interface essentially reduces the attenuation contribution that of the gas phase species. From the attenuation slopes information about the total electron scattering cross-section can be extracted at five different kinetic energies. This is possible due to the presence of five different elements with inner core binding energies spanning approximately 500 eV. Data obtained from [EMIM][Tf₂N] were used to supplement values obtained by Bluhm, et al.¹¹. This study can be extended to different gases, such as oxygen and nitrogen, as a spectroscopic probes for the total electron scattering cross section. Additionally, the total electron scattering cross-section of gas phase water at kinetic energies beyond 1 keV do not vary significantly.

6.2.2 Water Interaction with [HMIM][Cl] Interface

The structure of [HMIM][Cl] is free of an oxygen moiety in its structure allowing for a heightened sensitivity to oxygen species. The vapor-liquid interface of [HMIM][Cl] was probed via APXPS up to a maximum pressure of 5.0 Torr. Reverse isotherms were done by decreasing the pressure systematically. It was found that the water uptake is reversible and the system is free of hysteresis effects. By taking advantage of the negligible change in the total electron scattering cross-section at the kinetic energies of ~530 eV and ~400 eV (representative of signal coming from O 1s and N 1s respectively), we are able to calculate a mole fraction uptake of water on the interface. Furthermore, the quantitative determination of the mole fraction of water on the interface of [HMIM][Cl] showed a preference to water when compared to bulk

measurements made on nanoparticles via tandem differential mobility analysis. These quantitative findings highlight the importance of understanding the effects of atmospherically relevant gases on the interface chemistry of ionic liquids for better design of task specific applications of ionic liquids.

6.2.3 Surface Segregation in [EMIM][Tf₂N][OAc] Mixture

A mixture of the hydrophilic ionic liquid [EMIM][OAc] and hydrophobic [EMIM][Tf₂N] in a molar ratio of 9:1 was investigated using MD, AR-XPS and AP-XPS. MD density profiles were transformed to simulate XPS intensity. From AR-XPS and MD at 0° it was realized that the $X_{\text{Tf}_2\text{N}}$ on the interface was higher than the theoretical value of 0.10. At a grazing angle of 80° the amount of [Tf₂N]⁻ on the interface increases to above 0.20 further illustrating the dominance of [Tf₂N]⁻ on the top layer. The same ionic liquid mixture was examined via AP-XPS and showed significant [Tf₂N]⁻ anion migration to the water vapor-ionic liquid interface at 1.0 Torr when compared to vacuum. The sensitivity of the interface structure to ambient conditions should serve as a guideline in development of smart materials that utilize Ionic liquids.

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