**Probing a Ruthenium Coordination Complex at the Ionic Liquid-Vacuum Interface with Reactive-Atom Scattering, X-Ray Photoelectron Spectroscopy, and Time-of-Flight Secondary Ion Mass Spectrometry**

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**Abstract**

The speciation, conformation, and reactivity of transition metal complexes at the gas-liquid interface is poorly understood, yet the potential is high for observing chemistry unique to this anisotropic interface and leveraging interfacial structure to control the state and environment of the complex. If transition metal complexes can be designed to populate a liquid-vacuum interface preferentially, then it may be possible explore catalytic behavior by delivering reactants to the interface with a molecular beam and monitoring the scattering dynamics of reaction products to obtain detailed information on the reaction mechanism. In this initial experimental study, we have used reactive-atom scattering (RAS) with a hyperthermal F-atom probe, as well as X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (TOF-SIMS), to explore the interfacial composition and structure of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in perdeuterated 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (d11-[C2mim][Tf2N]). These data provide strong evidence that a Ru complex is present at the extreme liquid-vacuum interface with a number density that is higher than expected from the bulk concentration (2-3% vs. 0.04%). The experimental data also inform the chemical nature and environment of the Ru complex that resides at or near the extreme liquid-vacuum interface.

**1. INTRODUCTION**

The concept, science, and practice of chemical catalysis with organometallic compounds has been recognized by several recent Nobel prizes (asymmetric hydrogenation,1 metal-catalyzed alkene metathesis,2-4 palladium-catalyzed cross coupling reactions,5 etc.), and the field of homogeneous organometallic catalysis is vitally important to the fine chemical industry.6 As the name implies, “homogeneous catalysis” is typically focused on the behavior of transition metal complexes that are solutes in the bulk phase of a solvent. However, relatively little is known about the behavior and catalytic activity of these transition metal complex solutes at interfaces, such as the liquid-liquid and gas-liquid interfaces. This paucity of knowledge is primarily a result of experimental difficulties associated with probing the composition, structure, and reactivity of a fluctuating interface with high sensitivity and interfacial specificity. The investigation of a gas-liquid interface by vacuum surface science methods is particularly challenging because most common solvents have vapor pressures that make them incompatible with high-vacuum (10-6 to 10-9 Torr) or ultra-high vacuum (UHV, <10-9 Torr) environments without the use of special methods (e.g., liquid microjet7 technology). In this context, room-temperature ionic liquids (RTILs), which are widely used as solvents for homogeneous catalysis, offer interesting advantages.8-14 RTILs are molecular salts that are liquid at or near room temperature.8-9 They have solvation properties that are typically comparable to common molecular solvents, but the strong Coulomb interactions between ions in the liquid result in extremely low vapor pressures. RTILs are thus typically stable in UHV environments, permitting the use of a wide range of powerful surface science methods that can provide information on liquid-vacuum interfacial composition, structure, and reactivity. Examples of vacuum surface science methods that can be applied to ILs include sum frequency generation (SFG),15-19 low-energy ion scattering (LEIS),20 high-resolution Rutherford backscattering (HRBS),21-22 X-ray photoelectron spectroscopy (XPS),23-26 time-of-flight secondary ion mass spectrometry (TOF-SIMS),27 and reactive-atom scattering (RAS).28-33

Among these methods, reactive-atom scattering with mass spectrometric detection (RAS-MS)29, 33 is uniquely able to deliver a wide variety of gaseous reactants to the liquid-vacuum interface under controlled conditions with a molecular beam. In addition, the velocity and angular distributions of specific reaction products that promptly scatter (<1 μs) from the liquid-vacuum interface can be monitored with high sensitivity. These distributions can provide insight into the *nature* of the reaction mechanism and strong *dynamical* evidence for the interfacial specificity of the reaction. If transition metal complexes can be engineered to populate the extreme RTIL-vacuum interface, RAS-MS studies can be designed to probe transition metal complex reactivity at this interface. The ability to observe catalytic reaction products originating from the extreme liquid-vacuum interface opens up the possibility of observing reaction intermediates, as desorption into the vacuum should be an important loss pathway that can preserve unstable or highly reactive intermediates. For example, highly reactive D-atom intermediates produced by interfacial solvated electrons were detected by delivering sodium atoms to the liquid-vacuum interface of glycerol with a molecular beam.34 Also, a variety of reaction intermediates from the surfactant-promoted reactions of Cl2 and Br2 with Br– in glycerol were detected with the use of beam-surface scattering techniques.35

In extensively studied liquids such as water, the extreme anisotropy of the liquid-vacuum interface has been demonstrated to modify the chemical and physical properties of the interface relative to the liquid bulk. For RTILs, the anisotropy of the liquid-vacuum interface is known to cause the ions that are exposed to the vacuum to order, resulting in a liquid-vacuum interfacial structure that is dramatically different from the bulk liquid structure.36 The chemical consequences of this ordering are, in general, poorly understood. However, for highly reactive gases that attack atoms of the ionic liquid ions, ion orientation has been demonstrated to control the location of the reaction site by regulating the accessibility of different functional groups to the reactive gas.33 In addition, ILs are *tunable* in the sense that the interfacial structure and other chemical and physical properties of the liquid can be modified by changing the identity of the constituent ions. Provided that transition metal complexes can be designed to populate the extreme liquid-vacuum interface with sufficiently high concentration, it may be possible to leverage the tunable RTIL interfacial structure to modify the position, orientation, local environment, and reactivity of a transition metal complex at or near the liquid-vacuum interface.

The strong Coulomb interactions between RTIL ions result in relatively high liquid viscosities compared to conventional solvents, which can have a negative impact on some practical catalytic applications of RTILs. Supported ionic liquid phase (SILP) systems have been developed to minimize transport issues, in addition to facilitating catalyst recycling and to reducing the costs associated with using bulk ILs as solvents. SILP catalysts can be prepared by anchoring a metal complex to a porous solid support and coating the support with a RTIL thin-film, or by dissolving a catalyst in a RTIL prior to coating the support.12, 37-49 Ruthenium complexes are active catalysts for a range of reactions including the cyclopropanation of olefins,50 alkene metathesis,51-56 alkyne functionalization,57 hydrogenation,58-60 and others.61-62 For the present study, the relative stability of [RuCl2(*p*-cymene)PR3] complexes was a particularly desirable characteristic, while still representing a catalytically relevant system. A perdeuterated variant of the common RTIL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) or d11-[C2mim][Tf2N], was selected as the solvent so that deuterium-atom abstraction from d11-[C2mim]+ by incident F atoms to form DF could be distinguished from hydrogen-atom abstraction from the Ru complex to form HF. We have found that a Ru complex is present at the liquid-vacuum interface and is oriented to expose the *p*-cymene group and/or the P(C8H17)3 (trioctylphosphine) group to the vacuum. When the liquid-vacuum interface is continually refreshed in high vacuum with a scraper and allowed ~1 second to restructure before exposure to a reactant gas, the Ru complex number density is on the order of ~2-3% of the total number density of the Ru complex, d11-[C2mim]+, and [Tf2N]– at the interface. These observations on liquid-vacuum interfacial composition and structure are expected to inform future studies of catalyst reactivity at the liquid-vacuum interface.

**2. EXPERIMENTAL METHODS**

**2.1. Sample Preparation.** Samples of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C2mim][Tf2N]) and 1-(D5)ethyl-3-(D3)methyl(D3)imidazolium bis(trifluoromethylsulfonyl)imide (d11-[C2mim][Tf2N]) were prepared and purified as described previously (see **Figure 1**).31 [RuCl2(*p*-cymene)P(C8H17)3] was synthesized using a modified literature procedure, as described in the Supporting Information (**SI**).63 Magic-angle spinning (MAS) NMR spectroscopy was used to probe speciation of the complex in the bulk liquid when it was dissolved in [C2mim][Tf2N] (see **Figures S5 and S6**). MAS NMR reduces the peak broadening that often occurs in IL solutions as a result of the high viscosity if ILs compared to conventional solvents. A single resonance at 16.9 ppm was found in the 31P NMR spectrum of [RuCl2(*p*-cymene)P(C8H17)3] in [C2mim][Tf2N], which is similar to that of the complex in CDCl3 (12.1 ppm). This relatively small change in chemical shift could arise from a simple solvent effect, inaccuracies in referencing, or a small change in speciation (see discussion below). There is no evidence of free P(C8H17)3, suggesting that the phosphine ligand remains coordinated upon dissolution in the IL. The FWHM is not particularly large (6 Hz), suggesting no phosphine ligand exchange on the NMR timescale. For the RAS-MS, XPS, and TOF-SIMS experiments, a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] was prepared by adding 0.0080 g of [RuCl2(*p*-cymene)P(C8H17)3] to 4 mL of d11-[C2mim][Tf2N] and repeatedly stirring and sonicating the mixture at room-temperature until a majority of the solid dissolved. The resulting solution was an orange-red color. A few flakes of the Ru complex did not dissolve. The homogeneous solution was pipetted off, leaving the flakes behind.

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**Figure 1.** Molecular structures, with names and abbreviations, of the ruthenium coordination complex and two ionic liquid ions prepared for this study.

**2.2. Reactive-Atom Scattering (RAS)**.All RAS data were collected with the use of a crossed-beams apparatus configured for beam-surface scattering.29, 34, 64-67 A hyperthermal beam of F-atoms was prepared with a laser-detonation source that employed SF6 as a precursor gas. A 7 J pulse of 10.6 μm light from a CO2 TEA laser was directed though a ZnSe window into a “source” vacuum chamber pumped by a 2400 L/s turbomolecular pump to a base pressure of ~2.0 🞨 10-7 Torr. Inside the source chamber, this laser pulse was simultaneously redirected and focused into the throat of a copper cone with the use of a concave gold mirror. In the throat of the copper cone, the focused laser radiation encounters the SF6 gas pulse that was injected into the nozzle cone by a custom piezoelectric pulsed valve (stagnation pressure of 210 psig). Laser-induced breakdown of the SF6 gas near the apex of the copper cone initiates a detonation event that evolves into a blast wave that propagates through the remaining gas in the cone. The gas dynamics inside the copper cone promote charge-charge recombination but discourage atom-atom recombination, resulting in a spatially well-defined pulse of high-velocity, neutral atomic fluorine and sulfur. This hyperthermal gas pulse travels through the source vacuum chamber before encountering a skimmer and aperture that permit the central portion of the gas pulse to exit the source chamber and enter a “main” vacuum chamber as a collimated beam (approximately 1.3 mm x 2.0 mm). In the main vacuum chamber (base pressure ~2.0 🞨 10-7 Torr), a synchronized chopper wheel is used to selectively transmit F and S atoms that have velocities that lie within a narrow velocity range. After the chopper wheel, the F-atom translational energy distribution had an average of ~384 kJ mol-1 and a FWHM of ~50 kJ mol-1. This sequence of events was executed with a repetition rate of 2 Hz to create a pulsed hyperthermal beam of F and S atoms.

After velocity selection with the chopper wheel, F and S atoms in the pulsed hyperthermal beam collide with molecules at the liquid-vacuum interface of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. This liquid-vacuum interface was prepared by rotating a polished stainless-steel wheel through a temperature-controlled reservoir of the ionic liquid mixture and scraping the resulting film to a uniform thickness of 102 μm. The liquid temperature was held at 295 ± 1 K. The rotation frequency of the reservoir wheel was fixed at 0.25 Hz to ensure that every pulse of the hyperthermal F/S-atom beam encountered a freshly prepared liquid-vacuum interface free from the reaction products of the previous gas pulse. The entire liquid reservoir assembly can rotate about an axis, , that (1) passes through a point, **P**, at the center of the circular or elliptical area of the liquid-vacuum interface that is exposed to the pulsed hyperthermal beam, (2) passes through a point, **Q**, at the center of the front face of the rotating wheel, and (3) is perpendicular to the axis of the pulsed hyperthermal beam, . Thus, the incident angle, *θi*, of the F and S atoms in the pulsed hyperthermal beam with respect to the macroscopic interfacial normal of the liquid film, , can be adjusted by rotating the reservoir assembly about . Note that, under the conditions of this experiment, the liquid interface receives approximately F atoms cm-2 pulse-1 or approximately 10% of a monolayer per pulse.

It is important to note that S atoms in the pulsed hyperthermal beam are a *byproduct* of the process of producing F atoms. However, S atoms are not expected to interfere with F-atom chemistry at the liquid-vacuum interface because the flux is low (from stoichiometry, the S-atom flux is 1/6th the F-atom flux), so it is very unlikely for more than a single F or S atom to encounter the same local interfacial region. In addition, the rotating wheel of the liquid reservoir ensures that every pulse of the hyperthermal beam encounters a freshly prepared liquid-vacuum interface that is free from the radicals and reaction products from the previous pulse. Furthermore, most of the hyperthermal F and S atoms are expected to scatter from the liquid-vacuum interface without reacting (e.g., nonthermal F-atom flux was approximately 71% of the combined F and HF flux from the liquid-vacuum interface of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at *θi* = 60° and *θf* = 70°33). While both F and S atoms in the pulsed hyperthermal beam can react with atoms at the liquid-vacuum interface, we focused on the reactive and nonreactive scattering of F atoms because S-atom reactive scattering is complicated by the isotopes of sulfur and dissociative ionization of the SH, SD, H2S, HDS, and D2S products (see **Section 3** below).

F, HF, and DF that scattered from the liquid-vacuum interface at a final angle *θf* with respect to were detected after they passed through the entrance aperture of a mass spectrometer that can independently rotate about in a plane defined by and . Negative values of *θf* indicate that the pulsed hyperthermal beam and the rotatable mass spectrometer are on the same side of . Positive values of *θf* indicate that the pulsed hyperthermal beam and the rotatable mass spectrometer are on opposite sides of . The rotatable mass spectrometer contains an electron-bombardment ionizer68 coupled to a quadrupole mass filter and a Daly-type ion counting system.69 In this experiment, the rotatable mass spectrometer was used to collect number density distributions *N*(*t*) (also referred to as time-of-flight or TOF distributions) as a function of product flight time from the liquid-vacuum interface to the electron-bombardment ionizer.

Products that promptly scatter from the liquid-vacuum interface (<1 μs residence time after the arrival of the incident hyperthermal pulse of F atoms) typically yield bimodal TOF distributions.70 The TOF peak at shorter flight times is produced by impulsive scattering (IS) trajectories where the incident atom or reaction product undergoes one or only a few71 collisions with interfacial atoms before scattering into the vacuum. IS atoms or molecules do not attain thermal equilibrium with the liquid-vacuum interface before exiting the interface. Also, IS atoms or molecules retain some “memory” of the pre-collision conditions after exiting the interface, and their scattering dynamics generally vary with *θi*, *Ei*, collision site, etc. The TOF peak at longer flight times is produced by thermal desorption (TD) trajectories where the incident atom or reaction product undergoes a sufficient number of collisions at the interface to lose all “memory” of the pre-collision conditions before exiting the interface, often with a Maxwell-Boltzmann (MB) velocity distribution at the temperature of the liquid interface. Assuming that there is no barrier to adsorption/desorption and trapping is not dependent on *θi*, TD atoms or molecules exit the interface with an angle-randomized, integrated flux angular distribution that is proportional to cos(*θf*).

Bimodal TOF distributions for F, HF, and DF scattering from the liquid-vacuum interface of the ionic liquid mixture were decomposed into the component IS and TD number density distributions. The TD component was isolated by fitting the appropriate peak or shoulder of the total TOF distribution to a number density distribution that corresponds to a MB velocity distribution at the temperature of the liquid interface. The IS component was isolated by subtracting the TD component from the total TOF distribution. The intensities of the IS and TD components were calculated by converting each number density distribution to a flux distribution and integrating the resulting peak. The average energy of the IS component was calculated by converting the IS number density distribution to a flux distribution, applying a coordinate transformation to change the dependent variable from time to translational energy, and computing the average value of the resulting translational energy probability density distribution, *P*(*ET*). Binary-encoded TOF data were exported in an ASCII format and processed by custom data analysis functions composed in Igor Pro 7 (WaveMetrics, Inc., Lake Oswego, OR, USA).

In general, RAS experiments can be carried out with a wide variety of gaseous probe atoms or molecules. In this study, hyperthermal F atoms were selected as the ideal probe of ionic liquid-vacuum interfacial composition and structure. There are several reasons that justify this selection. First, F atoms are known to form a simple, terminal, and stable monohydride product in high yield when interacting with hydrocarbons. Also, F atoms only have one stable isotope (19 Da). Thus, H-atom abstraction from the liquid-vacuum interface by an F atom should only produce scattered HF with a mass of 20 Da and a signal in the mass spectrometer detector at a mass-to-charge ratio of *m*/*z* = 20 (HF+). Similarly, abstraction of a D atom from the liquid-vacuum interface by an F atom should only produce scattered DF with a signal at *m*/*z* = 21 (DF+). Second, HF and DF are expected to show little to no dissociative ionization in the electron-bombardment ionizer,72 simplifying the interpretation of the scattered F-atom signal at *m*/*z* = 19 (F+) because there is no component of this signal that originates from scattered HF or DF. The ability to detect all three relevant products (F, HF, and DF) uniquely increases data collection efficiency and simplifies the interpretation of TOF distributions collected at *m*/*z* = 19, 20, and 21. Third, F atoms are extremely reactive, with <4 kJ mol-1 H-atom abstraction barriers for aliphatic C-H bonds, and should show little bias between equally accessible aliphatic C-H reaction sites. Low bias between equally accessible reactive sites is helpful in quantifying relative interfacial composition. In addition, the high reactivity of the F-atom probe should improve the reactive scattering yield and the overall sensitivity of the method. Also, there is some evidence that the high reactivity of the probe may increase the interfacial specificity of the TD channel.33 Fourth, for an individual collision at the interface, hyperthermal translational energies for the incident atom tend to promote short and highly localized collisions. In this “structural scattering” regime,73 gas-liquid collisions should follow trends that are qualitatively consistent with the predictions of a hard-sphere scattering model that has been extended to include inelastic translational energy transfer (a “soft-sphere” model).71 Also, in the structural scattering regime, increasing the translational energy of the incident atom tends to increase the probability of IS at the expense of TD. These trends are desirable because (1) the defining characteristics of IS provide strong *dynamical* evidence of the extreme surface specificity of this scattering pathway and (2) highly localized IS can permit the association of scattering observables, such as translational energy transfer and flux angular distributions, with properties of the reaction site. As the fifth and final justification for the selection of a hyperthermal F-atom beam in the RAS experiments performed in this study, the high velocity of the incident F atom improves the flight time separation between IS and TD TOF distributions. The physical origin of this effect is rooted in the properties of structural scattering. In this scattering regime, increasing the translational energy of the incident atom should increase the translational energy of IS, which is equivalent to reducing the flight time of the associated IS TOF peak. As the TD TOF peak is only a function of the surface temperature, increasing the hyperthermal F-atom velocity improves the flight-time resolution between the IS and TD TOF distributions.

**2.3. X-Ray Photoelectron Spectroscopy (XPS).** X-ray photoelectron spectra were collected with the use of a Physical Electronics 5600 X-rayphotoelectron spectrometer with AugerScan software (**RBD Instruments, Inc.,** Bend, OR, U.S.A.). This instrument uses a focused,monochromatic Al Kα source to deliver a 2 mm diameter beam of soft X-rays with a photonenergy of 1486.6 eV to the sample. The X-ray power was fixed at 250 W. The angle ofincidence of the monochromatic X-rays was 45° with respect to sample interfacial normal.Unless otherwise noted, electron emission from an 800 μm diameter region of the sample was monitored at an exitangle of 45° with respect to the interfacial normal. Note that the Physical Electronics 5600instrument makes use of a hemispherical electron energy analyzer and a multichannel plate detector.

Pure [C2mim][Tf2N] and [RuCl2(*p*-cymene)P(C8H17)3] were studied, as well as a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. Samples were prepared by spreading ~50 μL ona fresh silicon wafer (Silicon Inc., Boise, ID, U.S.A.). The samples were stable in the UHV environment of the XPSinstrument (base pressure of 10-9 Torr with the sample present in the chamber). Surveyspectra were collected from a binding energy of 0 to 1400 eV with a 0.4 eV increment and apass energy of 46.95 eV. High-resolution spectra of specific photoelectron peaks werecollected with an increment of 0.1 eV and a pass energy of 23.50 eV. As discussed in theliterature,25 the ionic conduction of RTILs is sufficient to prevent severecharging of the liquid-vacuum interface and extreme distortion of the XPSpeak shape without applying electrons to the liquid-vacuum interface with an electron gun.However, ion conduction in RTILs is insufficient to completely preventthe liquid-vacuum interface from developing a small positive charge under the conditions ofthis experiment. This small positive charge at the liquid-vacuum interface uniformly increasesthe binding energy of all XPS peaks detected from the ionic liquid. To correct for thisoffset, the binding energy axis was shifted to ensure that the N 1s photoelectron peak from[C2mim]+ or d11-[C2mim]+ was centered at 402.1 eV. Note that this N 1s reference value was derived inthe literature by correcting the aliphatic C 1s photoelectron peak from [C8mim][Tf2N] to 285.0 eV.25

AugerScan was used to export all spectra as ASCII files containing the associated binding energy and an amplitude proportional to electron count. These ASCII files were plotted and processed using custom and built-in functions in Igor Pro 7. The background in the X-ray photoelectron spectra was fit to a linear or Shirley background depending on the shape of the background. All peaks were fit with a Gaussian/Lorentzian product line shape

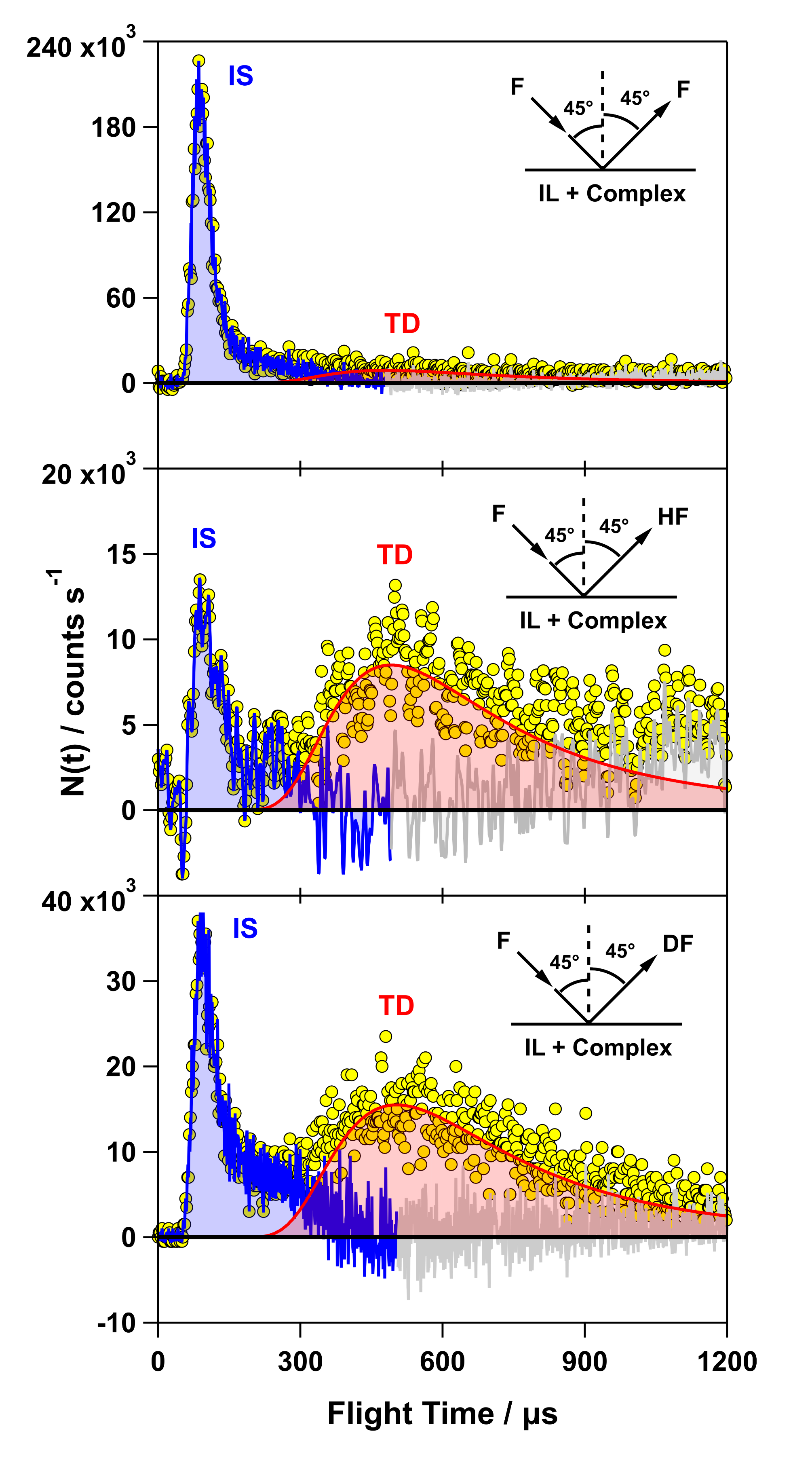
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where *m* is fixed at 0.30 (30% Lorentzian), *E*0 is the peak position in eV, *F* is the FWHM of the peak in eV, and *E* is the binding energy in eV. Atomic sensitivity factors were obtained from the *Handbook of X-Ray Photoelectron Spectroscopy*.74 Note that the sensitivity factors for Ru, Cl, and P were validated by confirming that the relative number densities of Ru, Cl, and P calculated from integrated XPS signals from solid RuCl2(*p*-cymene)P(C8H17)3 (1.0:1.9:0.97) were in good agreement with the expected relative number densities from stoichiometry (1:2:1).

Identical atoms in chemically distinct environments display small shifts in the core-electron binding energies relative to those that would be observed in vacuum. When these *chemical shifts* are large enough to resolve the presence of multiple peaks in an X-ray photoelectron spectrum, they can facilitate spectral decomposition schemes that can be used to estimate the relative abundances of elements in specific chemical states. In this study, favorable chemical shifts allow C atoms in [Tf2N]–, N atoms in [Tf2N]–, and N atoms in [C2mim]+ or d11-[C2mim]+ to be distinguished and independently quantified.

The most intense XPS peaks for ruthenium and carbon are associated with electron ejection from the 3d and 1s orbitals, respectively. Both Ru 3d and C 1s peaks must be carefully integrated to quantify the relative number densities of ruthenium and carbon in the liquid volume probed by XPS. Unfortunately, the Ru 3d5/2 peak is partially obscured and the Ru 3d3/2 peak is completely obscured by the intense C 1s peaks associated with aliphatic carbon, aromatic carbon, carbon shifted by bonding with nitrogen, and carbon shifted by bonding with phosphorous. The procedure used to separate the Ru 3d peaks from the C 1s peaks is as follows. Two Shirley75 backgrounds were used in the C 1s/Ru 3d region of the XPS spectrum. The first Shirley background removes inelastic electron scattering from the C 1s peak associated with carbon atoms in the [Tf2N]– anion. The second Shirley background removes the inelastic electron scattering from the remaining C 1s peaks and the Ru 3d peaks. After background removal, the Ru 3d5/2 peak was fit to a Gaussian/Lorentzian product function (see **Equation 1**). To predict the position, intensity, and width of the Ru 3d3/2 peak, we made use of several expectations. First, the Ru 3d3/2 peak should be observed at a higher binding energy than the Ru 3d5/2 peak. Second, the Ru 3d splitting should have the value of 4.17 eV, which has been measured for a large number of ruthenium compounds in a wide variety of oxidation states.76 Third, the peak area of the Ru 3d3/2 peak should be two-thirds the peak area of the Ru 3d5/2 peak.23 With this information, the Ru 3d3/2 peak was predicted from the position and area of the Ru 3d5/2 peak. Both Ru 3d peaks were then subtracted from the XPS spectrum (see **Figure S4**). The remaining C 1s signal was integrated numerically.

**2.4. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS).** Positive and negative TOF-SIMS spectra were collected with the use of a Phi-Evans TRIFT I instrument with WinCadence software (Physical Electronics, Inc., Chanhassen, MN, U.S.A.). Approximately 50 μL of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] was used to prepare an ionic liquid film on the TOF-SIMS sample mount. This liquid film was introduced into the TOF-SIMS chamber and found to be stable under UHV conditions (base pressure ~1.0 x 10-9 Torr). Depending on the polarity of the TOF-SIMS spectrum, this sample was held at a bias of ± 3 keV. A pulsed beam of Ga+ was prepared with a primary kinetic energy of 15 keV, a repetition rate of 10 kHz, and a pulse width <14 ns. This ion beam was directed onto an area smaller than 1 μm2 at the liquid-vacuum interface of the ionic liquid mixture. To ensure static SIMS conditions, the primary ion dose was kept below 1013 ions cm-2. To prevent charging of the sample, low-energy (<20 eV) electrons were intermittently applied to the sample. A multi-stop time-to-digital converter was used to record time-of-flight spectra of secondary ions emitted from the liquid-vacuum interface with a time precision of 138 ps and a mass resolution (*m*/*Δm*) of approximately 2000. Both positive and negative ion TOF-SIMS spectra were recorded in the range, *m*/*z* = 0-3000. All spectra were exported from WinCadence as ASCII files containing the number of ion counts associated with all detected *m*/*z* ratios. These data were binned and plotted using custom functions composed in Igor Pro 7.



**Figure 2.** Representative time-of-flight (TOF) distributions of scattered F, HF, and DF are shown in yellow. F atoms traveling at ~6300 m s-1 were directed toward the liquid-vacuum interface of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] at *θi* = 45°, and the products were detected at *θf*= 45°. The TOF distributions have been separated into components corresponding to products that were impulsively scattered (IS) and thermally desorbed (TD).

**3. RESULTS AND ANALYSIS**

**3.1. Reactive-Atom Scattering.** **Figure 2** shows representative TOF distributions that were collected at *m*/*z* = 19, 20, and 21, which correspond to scattered F, HF, and DF. Clear IS signals were observed in all the TOF distributions for these products. The observation of IS HF is unambiguous evidence that C-H bonds are accessible to the F-atom probe at the continually-refreshed liquid-vacuum interface of the ionic liquid mixture. Clear IS signals were also observed at *m*/*z* = 32, 33, and 34. Detailed analysis of these sulfur products was not conducted because of complications resulting from the isotopic distribution of sulfur (94.99% 32S, 0.75% 33S, 4.25% 34S, and 0.01% 36S), the mono- and dihydrides of sulfur, and the multiple dissociative ionization pathways that are possible in the electron bombardment ionizer (SH → S+ + H, H2S → SH+ + H, HSD → SD+ + H, etc.). Because the IL-ruthenium complex mixture contains a Cl– ligand, it might be possible for an incident F atom to form the mixed halide molecule FCl. The observation of IS or TD FCl would prove that this reaction can occur. Also, the observation of IS FCl would unambiguously demonstrate that Cl is accessible to the vacuum in the ionic liquid mixture. As Cl has two isotopes, 76% percent of the FCl should be produced at *m*/*z* = 54 and 24% at *m*/*z* = 56. However, no clear IS or TD signal was observed at *m*/*z* = 54 or 56. Thus, we found no evidence that could be used to prove that hyperthermal F atoms can form FCl or that Cl is exposed to the vacuum at the liquid-vacuum interface.

In general, reactive and nonreactive products will scatter anywhere within the 3D hemisphere above the macroscopically flat liquid-vacuum interface. It is common to quantify the direction of a 3D scattering trajectory with the angular variables of a spherical polar coordinate system: the polar angle, *θf*, and the azimuthal angle, *φf*. Consider a typical situation where the incident beam is not aligned with the macroscopic interfacial normal (*θi* ≠ 0). The in-plane forward scattering direction defines *φf* = 0°. *θf* = 0° defines a scattering trajectory that exits the interface along macroscopic interfacial normal. For *φf* = 0°, negative values of *θf* correspond to a situation where the incident beam and the scattering trajectory are on the same side of the interfacial normal. Similarly, for *φf* = 0°, positive values of *θf* correspond to a situation where the incident beam and the scattering trajectory are on opposite sides of the interfacial normal. The most rigorous method for quantifying the *yield* of a specific product would require integrating the scattered flux over *θf* and *φf* across the full 2π steradians of the hemisphere. This integration is straightforward for the TD channel because the 3D flux angular distribution should follow a cos(*θf*) angular distribution for all values of *θf* and *φf*. In principle, a single flux measurement over an infinitesimal solid angle centered around a specific value of *θf* is enough to predict the full 3D flux angular distribution and the total TD flux that is emitted from the surface. However, other scattering channels may have more complex 3D flux angular distributions. For example, in many hyperthermal beam-surface scattering experiments, IS has a lobe that is directed at or near the in-plane specular direction (i.e., centered about *φf* = 0° at or near *θf* = *θi*). This lobe is particularly narrow for grazing incident angles. Although it is common for engineering models to parameterize the shape of the IS flux angular distribution,77 there is no general 3D analytical model for this scattering pathway.

In this study, we only measure in-plane scattering (*φf* = 0°) across a limited range of final angles that primarily sample forward scattering trajectories (positive *θf*). Geometry restrictions in the beam-surface scattering machine result in a different range of accessible *θf* angles for each *θi*. Because IS represents a significant fraction of the total scattered flux for all scattering geometries reported in this paper, we are unable to calculate the full 3D scattering yield for F, HF, and DF. Given the nature of the experimental scattering data sets collected in this study, we have decided to adopt a convention for quantifying scattering yield that integrates the corresponding in-plane flux angular distribution across the largest *θf* range that is common to all measured incident angles – i.e., *θf* = 20° to *θf* = 80°.

The IS and TD F, HF, and DF scattering yields largely follow expected trends as a function of *θi*. The IS F, HF, and DF scattering yields are calculated by integrating the IS flux angular distributions shown in **Figure 3**. Similarly, the TD F, HF, and DF scattering yields are calculated by integrating the corresponding TD flux angular distributions (not shown). For all products, the integrated IS flux angular distributions between *θf* = 20° and *θf* = 80° increase as *θi* increases (see **Table 1**). For F and DF, the integrated TD flux angular distributions between *θf* = 20° and *θf* = 80° decrease as *θi* increases (see **Table 2**). Despite an interesting insensitivity of the TD HF flux to *θi* (see **Table 2**), the ratio of the IS flux angular distribution integrated between *θf* = 20° and *θf* = 80° to the TD flux angular distribution integrated between *θf* = 20° and *θf* = 80° increases as *θi* increases for F, HF, and DF (see **Table 3**). This increase of the IS/TD ratio with increasing *θi* is commonly observed in hyperthermal RAS experiments and is a consequence of several factors. For example, in the structural scattering regime, larger incident angles produce lower deflection angles (*χ* = 180° – *θi* – *θf*), which results in lower average collisional energy transfers (e.g., see **Figure 4**).78 Also, at larger *θi*, a larger range of forward-scattering trajectories is not directed toward the liquid, reducing the probability of secondary collisions. Lowering the average collisional energy transfer and reducing the number of secondary collisions increases IS at the expense of TD, increasing the IS/TD ratio.

Although the relationship between product yields and composition of the liquid-vacuum interface depends on the details of the liquid-vacuum interfacial structure and gas-liquid scattering dynamics, we can obtain a crude but purely experimental estimate of the concentration of the Ru complex at the interface with a few simple assumptions. We assume that (1) IS HF and DF yields are proportional to the respective number densities of C-H and C-D bonds accessible to the vacuum, (2) each d11-[C2mim]+ cation at the liquid-vacuum interface contributes 8 alkyl C-D bonds to the interface, (3) each Ru complex can be associated with a charge of +1 (justified below) and contributes 61 aliphatic C-H bonds to the liquid-vacuum interface, and (4) cations and anions are present at the extreme liquid-vacuum interface in equal numbers. If these assumptions are roughly correct, the IS HF and IS DF yields suggest that the number density of the Ru complex is ~2-3% of the total number density of the Ru complex, d11-[C2mim]+, and [Tf2N]– at the interface. As discussed below, our data are unable to identify unambiguously the precise speciation of the Ru complex at the liquid-vacuum interface. Specifically, it is unclear if the Ru complex is best described by (*i*) [RuCl(*p*-cymene)P(C8H17)3]+, (*ii*) [RuCl(*p*-cymene)P(C8H17)3(Tf2N)], or (*iii*) [(RuCl(*p*-cymene)P(C8H17)3)2]2+. It is important to note that a surface concentration of ~2-3% is correct if the Ru complex at the extreme liquid-vacuum interface is best described by *i*, *ii*, or a mixture of *i* and *ii*. However, if the Ru complex is best described by the dimer *iii*, our surface concentration estimate could be incorrect by as much as a factor of two. A surface concentration of ~2-3% is much larger than expected from bulk stoichiometry (~0.04%) and has the same order of magnitude as the estimate obtained from the XPS data described below (see **Section 3.2**). It is also important to note that the liquid-vacuum interface had approximately one second to reorganize and restructure as the rotating wheel of the liquid reservoir moved the liquid film past the scraper into a position where it was exposed to the hyperthermal F-atom beam pulse.

The branching between IS and TD, the IS angular distributions, and the IS translational energy transfer trends are dynamical RAS observables. Although the dynamical RAS observables in this study can be correlated with qualitatively similar observations on different chemical systems in the literature, the trends are complex and do not support a simple, consistent interpretation without extending the study beyond the scope of this preliminary investigation. For example, the data in **Table 3** demonstrate that the IS/TD flux ratio is larger for DF scattering compared to HF scattering at *θi* = 30°, 45°, and 60°. Although the physical origin of this effect is not entirely clear, our observations are qualitatively consistent with the results of a study by Nathanson and coworkers79 where molecular DCl was scattered from the liquid-vacuum interface of pure glycerol and a solution of 0.03 M tetrahexylammonium bromide in glycerol (THABr-glycerol). Prompt and nonreactive DCl scattering from the THABr-glycerol had a lower IS flux and a higher TD flux relative to analogous fluxes obtained from pure glycerol. The authors suggested that the decrease in IS flux is a consequence of THA+ hexyl groups deflecting IS DCl over a broader angular range (presumably both in-plane and out-of-plane). Although our angular distributions (**Figure 3**) show that IS DF from d11-[C2mim]+ scatters over a broader range than IS HF from the Ru complex, it is still possible that the full 3D angular distribution of IS HF is broader than that of IS DF. In the experiment of Nathanson and coworkers, the increase in TD DCl flux was attributed to a THA+-induced reduction of a loss pathway where incident DCl is transported into the liquid bulk. We have no quantitative information on the fraction of HF or DF molecules that dissolve into the ionic liquid bulk.

**Table 1.** Cartesian integrals of the IS flux angular distributions of F, HF, and DF from *θf* = 20° to *θf* = 80° in arbitrary intensity units.

|  |  |  |  |
| --- | --- | --- | --- |
| **Incident Angle, *θi*** | **IS F** | **IS HF** | **IS DF** |
| 30° | 5.5 | 0.44 | 1.3 |
| 45° | 7.4 | 0.50 | 1.4 |
| 60° | 10.0 | 0.74 | 1.6 |

**Table 2.** Cartesian integrals of the TD flux angular distributions of F, HF, and DF from *θf* = 20° to *θf* = 80° in arbitrary intensity units.

|  |  |  |  |
| --- | --- | --- | --- |
| **Incident Angle, *θi*** | **TD F** | **TD HF** | **TD DF** |
| 30° | 0.44 | 0.44 | 0.99 |
| 45° | 0.34 | 0.41 | 0.78 |
| 60° | 0.24 | 0.49 | 0.43 |

**Table 3.** IS/TD ratios of scattered F, HF, and DF flux, derived from the values in Tables 1 and 2.

|  |  |  |  |
| --- | --- | --- | --- |
| **Incident Angle, *θi*** | **IS/TD Ratio For F** | **IS/TD Ratio for HF** | **IS/TD Ratio for DF** |
| 30° | 13 | 1.0 | 1.3 |
| 45° | 22 | 1.2 | 1.8 |
| 60° | 43 | 1.5 | 3.6 |

IS F, HF, and DF angular distributions for *θi* = 30°, 45°, and 60° are shown in **Figure 3**. As discussed in a previous publication,80 IS angular distributions from soft, atomically rough, and thermally disordered interfaces, such as those of ionic liquids, appear to be dominated by different degrees of damping toward a cos(*θf*) function, which is a signature of angle randomization and one of two defining features of TD. The existing evidence suggests that this phenomenon is a result of changes in the importance of multiple-collision trajectories that contribute to the in-plane scattered products that we observe. For example, lower *θi* increases the number of trajectories that direct the scattered product toward the liquid after the initial collision at the interface, which in turn increases the average number of collisions that the product atom or molecule makes in the interfacial region before it scatters into the vacuum. If the products exit the interface before reaching thermal equilibrium with the liquid, then they have hyperthermal translational energies and are classified as IS products even though their scattering directions have been randomized by the multiple collisions at the interface. The resulting IS angular distributions of IS product flux thus have more cos(*θf*) character when *θi* is lower. Interestingly, the prior work has also demonstrated that IS angular distributions from structurally distinct sites at the liquid-vacuum interface appear to be dominated by differences in cos(*θf*) character.33 Sites leading to higher cos(*θf*) character in angular distributions either promote more secondary collisions, increase the importance of secondary-collision trajectories by reducing the number of in-plane single-collision trajectories, or both. The existing evidence suggests that all three situations should be controlled by the local environment of the scattering site. It appears that products that scatter from reaction sites protruding into vacuum where the local atom density is low have lower cos(*θf*) character on their angular distributions. Similarly, reaction sites that are closer to the instantaneous interface but still accessible to a gas-phase probe tend to lead to angular distributions with higher cos(*θf*) character. As shown in **Figure 3**, the IS DF angular distribution has more cos(*θf*) character than the IS HF angular distribution. By analogy with previous studies on a pure IL, this result suggests that the hydrocarbon groups detected at the liquid-vacuum interface of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] protrude into the vacuum and occupy a low-density region of space above the liquid interface. Note that the average angle of the octyl chains that are exposed to vacuum is currently unknown.

Reactive and nonreactive translational energy transfer dynamics contain information on the nature of the liquid-vacuum interface. TOF distributions can be mathematically inverted to translational energy probability density distributions, from which the average translational energy of a specific product can be determined. Thus, the fraction of the initial average translational energy that is lost during the IS event can be calculated. This quantity is often referred to as the average fractional energy transfer, Δ⟨*Ε*⟩/⟨*Ei*⟩ or (⟨*Εi*⟩ - ⟨*Εf*⟩)/⟨*Ei*⟩. For nonreactive scattering of an atom from the liquid-vacuum interface (with no collision-induced electronic transitions within the incident atom), Δ⟨*Ε*⟩/⟨*Ei*⟩ is equivalent to the average energy delivered to the liquid by the collision. For reactive scattering of an atom from the liquid-vacuum interface, Δ⟨*Ε*⟩/⟨*Ei*⟩ has a more complex meaning because it includes the disposal of the translational energy of the collision and the chemical energy of the reaction into (1) the energy delivered to the liquid, (2) the internal excitation energy of the molecular product, and (3) the average translational energy of the molecular product. With the high incident translational energies used in this experiment, individual collisions should be in the structural scattering regime where the energy transfer trends are qualitatively consistent with the predictions of a hard sphere scattering model.73 The hard sphere scattering model predicts that energy transfer should monotonically increase with the deflection angle *χ* = 180° – *θi* – *θf* = 180° – (*θi* + *θf*). To confirm that Δ⟨*Ε*⟩/⟨*Ei*⟩ is a function of (*θi* + *θf*) and not *θi* or *θf* individually, **Figure 4** shows Δ⟨*Ε*⟩/⟨*Ei*⟩ as a function of *χ* for *θi* = 30°, 45°, and 60°. Although small deviations are visible at *θi* = 30°, it is clear that Δ⟨*Ε*⟩/⟨*Ei*⟩ depends on *χ* and not on *θi* or *θf* individually. The IS F and IS DF data are well-described by an extension of the hard-sphere model that allows for inelastic collisional energy transfer. In this “soft sphere” model,71

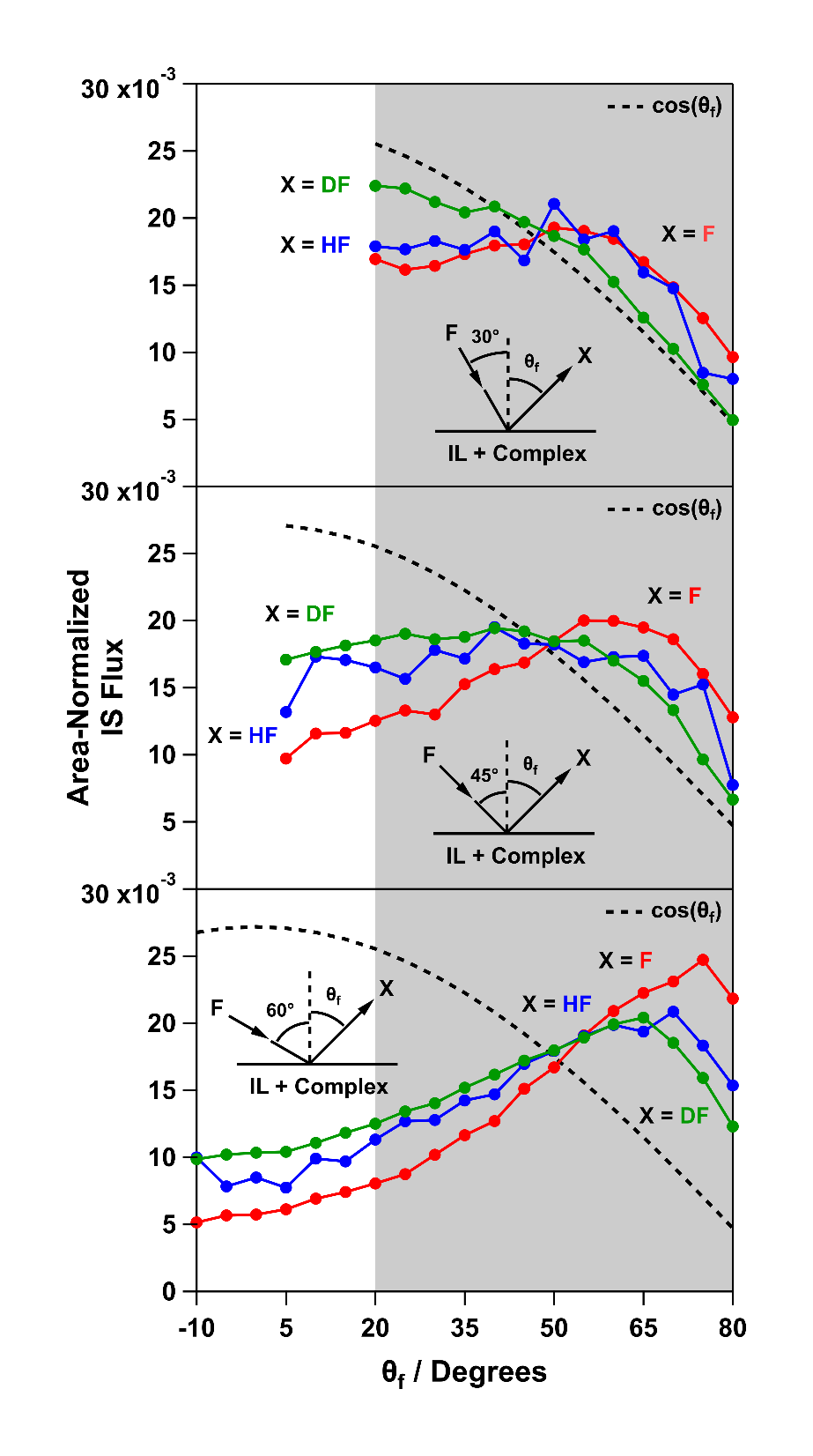
|  |  |
| --- | --- |
|  | (2) |

the average translational energy transfer depends on several factors: the deflection angle *χ*; the mass ratio *μ* = *mgas/msurface* where *mgas* is the mass of the incident F atom and *msurface* is a parameter that may be interpreted as the effective mass of the surface atoms that participate in the scattering event; and the parameter, *Eint*,which is the total internal energy of the surface and scattered product.

As shown in **Figure 4**, Δ⟨*Ε*⟩/⟨*Ei*⟩ and *Eint* are clearly larger for IS HF and DF relative to IS F. There are at least three possible reasons for this observation. First, HF and DF products can have translational-to-rotational and translational-to-vibrational energy transfer, which would increase Δ⟨*Ε*⟩/⟨*Ei*⟩ relative to that for scattered F atoms. Second, IS HF and DF scatter more broadly, reducing single-collision in-plane scattering and/or increasing the relative flux of multiple-collision trajectories that scatter in-plane (see **Figure 3**). Third, IS F preferentially originates from collisions with CF3 groups on the [Tf2N]- anion which may absorb less translational energy, in analogy with other observations that report lower values of Δ⟨*Ε*⟩/⟨*Ei*⟩ for hyperthermal IS from liquid fluorocarbon surfaces relative to liquid hydrocarbon surfaces.71

Also, **Figure 4** clearly shows that *msurf* associated with IS F is consistently smaller than *msurf* associated with IS DF and, likely, IS HF (given that Δ⟨*Ε*⟩/⟨*Ei*⟩ for IS HF is equivalent to that for IS DF within the noise of the data). This observation is consistent with previous (unpublished) data on hyperthermal F-atom scattering from deuterium-labeled variants of pure [C4mim][Tf2N] where the data unambiguously confirm that IS F consistently has a lower Δ⟨*Ε*⟩/⟨*Ei*⟩ relative to IS HF or IS DF. However, the precise origin of this effect is currently unknown. It is possible that the *msurf* differences derived from IS F as compared to IS HF or DF are the result of differences in the nature of the liquid-vacuum interfacial sites that yield each product. IS HF and DF must be produced from a C-H or C-D group that is accessible to an F-atom probe at the liquid-vacuum interface. Thus, IS HF and DF must involve a collision with [C2mim]+ or the hydrocarbon components of the Ru complex at the liquid-vacuum interface. Although the precise nature of the liquid-vacuum interfacial sites that yield IS F is unknown, it is reasonable to assume that this pathway would be more probable when an F-atom collides with a CF3 group from [Tf2N]–, as this ion cannot yield HF or DF. The similarity between the best-fit soft-sphere parameters for IS F at *θi* = 60° (*msurf* = 38 amu, *Eint* = 0 kJ mol-1) and IS O(3P) from a fluorinated liquid with *Ei* = 504 kJ mol-1 (*msurf* = 34 amu and *Eint* = 5 kJ mol-1)71 may be indirect evidence supporting this assumption. Note that *msurf* associated with IS from hydrocarbons is typically larger than *msurf* associated with IS from fluorocarbons because the total mass of atoms that are displaced during the gas-surface collision is larger for the hydrocarbon system.71 If F-atom collisions with [Tf2N]– have a small displaced mass relative to F-atom collisions with d11-[C2mim]+ or the hydrocarbon components of the Ru complex, then IS F would be expected to have a smaller *msurf* relative to IS HF or DF.

As discussed below, several observations suggest that the IL-Ru complex solution is contaminated by trace amounts of PDMS that were probably introduced during the custom synthesis of the Ru complex: unambiguous identification of PDMS in the Ru complex solution with TOF-SIMS, detection of Si in the XPS spectrum of the Ru complex mixture, and detection of Si and O in XPS investigations of the solid Ru complex). Although we have evidence that suggests that the continually refreshed liquid-vacuum interface produced by the rotating wheel of the liquid reservoir is effective in reducing interference from the adsorption of background gases in the vacuum chamber at the liquid vacuum interface (**Figure S2**), it is unclear if the rotating wheel assembly will prevent the diffusion of a trace PDMS contaminant to the liquid-vacuum interface. However, RAS from the contaminant is unlikely to dominate the HF signals we observe. Experimental results detailed below demonstrate the Si and Ru have a similar relative number density in the volume probed by XPS at a photoelectron emission angle of 45° with respect to the interfacial normal. However, the H:Si ratio in PDMS is approximately 6:1 while the H:Ru ratio in the Ru complex is 65:1. Even in the situation where both species expose all of their hydrogen atoms to the vacuum at the extreme liquid-vacuum interface, RAS from the Ru complex should dominate the HF signals observed in this experiment.



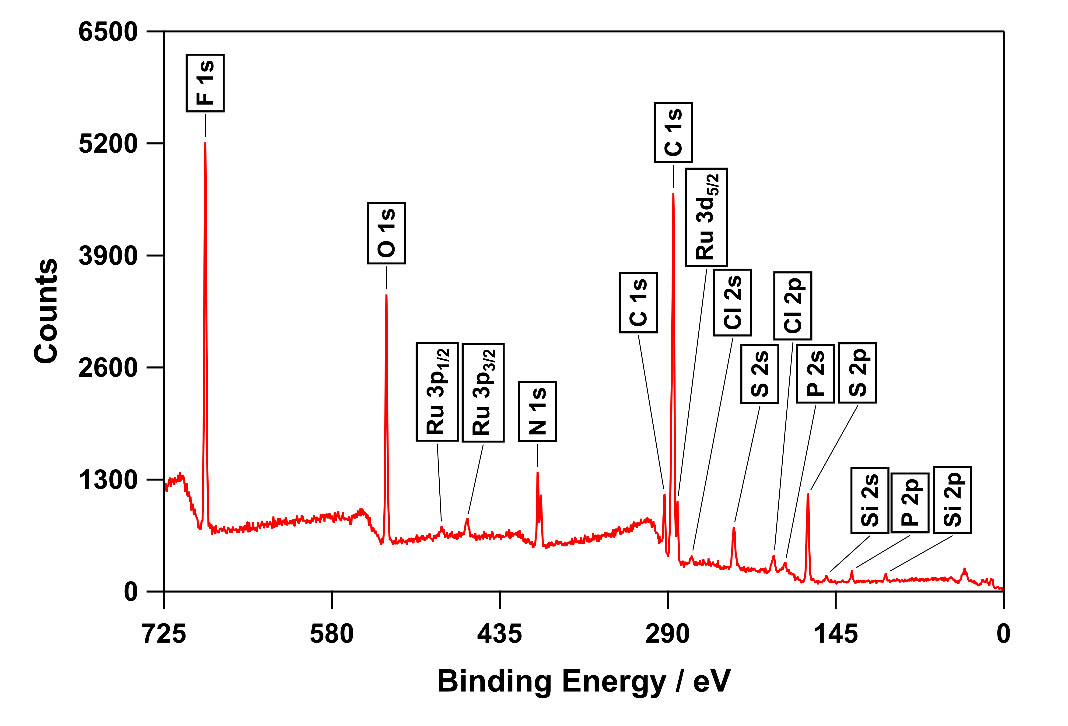
**Figure 3.** Area-normalized fluxangular distributions of IS F, HF, and DF flux from the liquid-vacuum interface of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. Each trace has been scaled so the Cartesian area between *θf* = 20° and *θf* = 80° (range shown in gray) has a value of 1.

**3.2. X-Ray Photoelectron Spectroscopy (XPS).** As expected from prior results reported in the literature,23 the pure ionic liquid [C2mim][Tf2N] and the mixture of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] are both stable under the UHV conditions of the XPS instrument (base pressure <10-9 Torr). All 9 elements expected in the ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] are observed in the survey spectrum shown in **Figure 5**, demonstrating that there is no solute or contaminant film thicker than the XPS probe depth present at the liquid-vacuum interface of the ionic liquid mixture. In addition, a small concentration of Si was observed (<1%), likely from the presence of a small polydimethylsiloxane (PDMS) contaminant that was unambiguously identified by comparison of the TOF-SIMS spectra discussed below with reference data on pure PDMS (see **Figure S3**). Note that PDMS is frequently detected in samples that are analyzed with the TOF-SIMS and XPS instruments used in this study. PDMS was not detected during characterization of the liquid bulk but this compound is highly surface active on static surfaces that are not continually refreshed. The relative number density percentages of all elements detected are shown in **Table 4**. The atomic sensitivity factors (ASFs; also known as relative sensitivity factors or RSFs) were obtained from a standard source74 and were not optimized for the specific instrument used or the specific samples studied in this experiment. This is acceptable for the elements that are unique to the ionic liquid, because no quantitative conclusions are drawn from the relative number densities of N, S, O, C, and F. We validated the sensitivity factors for Ru, Cl, and P by verifying that the relative number density derived from XPS of solid RuCl2(*p*-cymene)P(C8H17)3 was in good agreement with the expected stoichiometric ratio of 1:2:1 for Ru:Cl:P . Specifically, Ru:Cl:P was measured to be 1.0:1.9:0.97 at a photoelectron emission angle of 45° degrees with respect to interfacial normal.

A close up of a map

Description automatically generated

**Figure 4.** Average fraction of incident translational energy lost during IS from the liquid-vacuum interface of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. Soft-sphere fits are shown as solid lines and the associated fitting parameters are shown in the same color alongside the fit.



**Figure 5.** Survey X-ray photoelectron spectrum of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N].

The Ru, Cl, and P atoms are unique to the catalyst. The observation of photoelectron signal from these atoms is unambiguous evidence that the Ru atom, Cl– ligand, and P(C8H17)3 ligands are present in the ~6.1-7.8 nm deep layer probed by the XPS instrument. The detected Ru, Cl, and P atoms are present at a concentration that is much higher than expected from the bulk concentration of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] (approximately 0.04% of the total number density of the Ru complex, d11-[C2mim]+, and [Tf2N]–). The relative number density of the Ru complex can be quantified with photoelectron signals from the Ru, P, and Cl atoms. Note that our calculation of the relative number densities at the interface used a Ru complex molecular weight of 676.83 amu, a d11-[C2mim]+ molecular weight of 122.165 amu, a [Tf2N]– molecular weight of 280.15 amu, and a d11-[C2mim][Tf2N] density of ~1.56 g cm–3. Depending on which atom is selected to quantify the complex, (Ru complex)/(Ru complex + d11-[C2mim]+ + [Tf2N]–) is ~11-14%. It is encouraging that the XPS estimate of (Ru complex)/(Ru complex + d11-[C2mim]+ + [Tf2N]–) is within an order of magnitude of the RAS estimate of the same percentage given the crude and very preliminary assumptions made about the relative number density of D atoms from d11-[C2mim]+ and H atoms from the Ru complex that are accessible to vacuum. Other dynamical effects like IS/TD partitioning may also impact the RAS estimate.

**Table 4.** Composition of the near-interface volume of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] probed by XPS, as determined by the relative intensities of the indicated photoelectron peaks. The photoelectron emission angle is 45° with respect to interfacial normal. Note that the integrated and corrected areas are in arbitrary units. The expected percentage is based on the relative number density in the liquid bulk as calculated from the stoichiometry of the solution.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Atom** | **Orbital** | **Integrated Area** | **Atomic Sensitivity Factor** | **Corrected Area** | **Percentage Observed** | **Percentage Expected** |
| N | 1s | 3330 | 0.477 | 6980 | 8.3 | 8.8 |
| F | 1s | 12700 | 1.00 | 12700 | 15. | 18 |
| O | 1s | 7150 | 0.711 | 10100 | 12 | 12 |
| C | 1s | 13600 | 0.296 | 46000 | 55 | 23 |
| Cl | 2p | 616 | 0.770 | 799 | 0.95 | 0.0022 |
| S | 2p | 3170 | 0.570 | 5570 | 6.6 | 5.9 |
| P | 2p | 263 | 0.412 | 638 | 0.76 | 0.0011 |
| Si | 2p | 194 | 0.283 | 685 | 0.81 | 0 |
| Ru | 3d | 2630 | 3.70 | 713 | 0.85 | 0.0011 |

Although the stoichiometry of the solid catalyst leads to the expectation that the Ru:Cl:P ratio should be 1:2:1, the associated XPS signals are in the proportion 1.0:1.1:0.89. If the speciation of the complex is dominated by a single structure, we can draw two conclusions from the XPS data alone. First, the complex is not completely intact within around 6.1-7.8 nm of the gas-liquid interface, and the Ru atom must at least be ligated by the P(C8H17)3 ligand and one Cl– ligand. The 198.4 eV binding energy of the Cl 2p peak supports the conclusion that the Cl is bound to Ru because it is closer to the value observed in solid [(RuCl2(*p*-cymene))2] (198.1 eV)81 and much larger than the value observed in [C2mim][Cl] (197.1 eV).25 Although the solvation structure of Cl– in [C2mim][Tf2N] is expected to differ from the solvation structure of Cl– in [C2mim][Cl], much of the shift should be the result of short range interactions between the Cl– anion and the cation of the ionic liquid solvent, which is identical in [C2mim][Cl] and [C2mim][Tf2N].20 Second, the enrichment of the partly dissociated Ru complex must be much larger than any enrichment of the dissociated Cl– anion in the ~6.1-7.8 nm depth probed by the XPS measurement.

The stoichiometry of [Tf2N]– suggests that the relative number densities of NAnion:S:O:CAnion:F should be 1:2:4:2:6. However, the relative number densities derived from the observed photoelectron peaks are 1.0:1.9:3.4:2.6:4.3. Although these numbers are in rough agreement, significant deviations from stoichiometry are clearly observed for the ~6.1-7.8 nm depth probed by the XPS measurement. As mentioned above, the ASFs are taken from a standard source74 and are not specifically calibrated for the XPS data collected in this study. Therefore, small ASF inaccuracies are expected to contribute to the observed discrepancies between anion stoichiometry and the relative number densities derived from XPS data. With the exception of sulfur, the sign of the deviations from stoichiometry roughly correlate with the photoelectron kinetic energy. Because higher kinetic energy photoelectrons can escape from deeper regions of the liquid,23 photoelectrons from atoms with significantly different binding energies reflect different thicknesses of the liquid-vacuum interface, resulting in discrepancies between anion stoichiometry and the relative number densities derived from XPS data. In principle, one could test this effect by comparing the relative number densities derived from different photoelectron peaks (or set of peaks) that originate from the same atom. Unfortunately, the set of AFSs used in this study only provide correction factors for the highest intensity photoelectron peaks of common elements. Interestingly, the *impact* of this peak-dependent escape depth on the relative number densities derived from photoelectron peak intensity may be highly dependent on the number density distribution along the macroscopic interfacial normal. If an atom number density is relatively large at or near the maximum depth in the distribution of photoelectron escape depths, then variation in the depth may induce large deviations in the derived number density of this atom. This situation is expected for the atoms in [Tf2N]– because the concentration of the solvent in the liquid bulk must be very large. However, if an atom number density is at a maximum at the extreme liquid-vacuum interface and is relatively small at or near the maximum in the photoelectron escape depth distribution, then variation in the escape depth may have a small or negligible impact on the derived number density of this atom. In particular, this situation may apply to the Ru complex solute if it is preferentially enriched at or near the extreme liquid-vacuum interface.

For pure [C2mim][Tf2N], two N 1s peaks are observed at 402.1 eV and 399.5 eV (green curve in **Figure 6**) The lower binding energy peak23 corresponds to the nitrogen atom in [Tf2N]– and the higher binding energy peak23 is associated with the two nitrogen atoms in [C2mim]+. However, the integrated intensity of the cation peak divided by the integrated intensity of the anion peak is ~1.94 at a photoelectron emission angle of 45° with respect to interfacial normal because ~6% of the cation N 1s signal is lost to shake-up/shake-off phenomena.23, 25 As shown by the red curve in **Figure 6**, this ratio decreases to ~1.48 for the ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] at a photoelectron emission angle of 45° with respect to the interfacial normal. Additionally, the blue curve in **Figure 6** demonstrates that this ratio decreases further to 1.12 for the same Ru complex solution at a photoelectron emission angle of 75° with respect to the interfacial normal. This decreased ratio can be interpreted as evidence that the number of d11-[C2mim]+ cations has decreased relative to the number of [Tf2N]– anions. If we continue to assume that the d11-[C2mim]+ N 1s signal is 6% lower than expected, then the d11-[C2mim]+ to [Tf2N]– number density ratio in the mixture is 1.48/1.94 = 0.763 at a photoelectron emission angle of 45° with respect to the interfacial normal and 1.12/1.94 = 0.577 at a photoelectron emission angle of 75° with respect to the interfacial normal. Thus, the cation percentage of the number density ratio (d11-[C2mim]+)/(d11-[C2mim]+ + [Tf2N]–) is 43.3% and 36.6% at photoelectron emission angles of 45° and 75°, respectively. Thus, there are ~13.4% and 26.8% more anions than cations in the volume probed by our XPS measurement at photoelectron emission angles of 45° and 75°, respectively.

XPS experiments that are not optimized to probe the extreme outermost regions of pure ionic liquid interfaces generally yield relative compositions that are consistent with the stoichiometry of the bulk liquid.23 This common observation highlights the importance of charge neutrality in dictating the average structure of the liquid volume probed. Our XPS experiment on the composition at and near the liquid-vacuum interface of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] shows that the number density of the [C2mim]+ + Ru complex is nearly equal to the number density of [Tf2N]–. Depending on the atom used to quantify the complex, the number density fraction ([C2mim]+ + Ru complex)/([Tf2N]–) is between 0.93 and 0.98 at a photoelectron emission angle of 45° with respect to the interfacial normal. Similarly, the number density fraction ([C2mim]+ + Ru complex)/([Tf2N]–) is between 0.97 and 1.2 at a photoelectron emission angle of 75° with respect to the interfacial normal. It is likely that this observation is also a consequence of charge neutrality.

Assuming that the speciation of the Ru complex at and near the liquid-vacuum interface is dominated by one structure, the three most likely compounds would be: [RuCl(*p*-cymene)P(C8H17)3]+, [RuCl(*p*-cymene)P(C8H17)3(Tf2N)], and [(RuCl(*p*-cymene)P(C8H17)3)2]2+. If the first Ru complex is associated with one [Tf2N]– counterion and the third Ru complex is associated with two [Tf2N]– counterions, all three of the proposed compounds are consistent with the XPS observations suggesting that the Ru:Cl ratio is ~1 and each Ru complex adds a [Tf2N]– anion or displaces a d11-[C2mim]+ cation from the near-surface volume probed by the measurement. Our hypothesized compounds are also consistent with the observed binding energy of the Ru 3d5/2 photoelectron peak at 281.64 eV, which is closer to the value observed for Ru(II) and Ru(III) compounds and farther from Ru0 (279.01 to 280.20 eV).82 Note that the Ru 3d5/2 photoelectron peak is at 281.3 eV81 for [RuCl(*p*-cymene)((R)-BINAP)][Cl], 281.5 eV81 for [(RuCl2(*p*-cymene))2], 281.2 eV83 for [RuCl2(*p*-cymene)PR3], and [RuCl(*p*-cymene)(κ2-N-sulfonyl-1,2-ethylenediamine)] at 282.0 eV.84

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**Figure 6.** Relative intensities of the N 1s photoelectron peaks from [C2mim]+ (or d11-[C2mim]+) and [Tf2N]‒. The spectrum from pure [C2mim][Tf2N] at a photoelectron emission angle of 45° with respect to interfacial normal is shown in green. The spectrum from a solution of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] at a photoelectron emission angle of 45° with respect to interfacial normal is shown in red. The spectrum from a solution of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] at a photoelectron emission angle of 75° with respect to interfacial normal is shown in blue.

Unfortunately, X-ray radiation from XPS measurements can induce chemical changes in sensitive samples. From the initial exposure of all samples to Al Kα X-ray radiation, no dramatic changes were observed in the survey and high-resolution XPS peaks associated with [Tf2N]– or [RuCl2(*p*-cymene)P(C8H17)3]. As shown in **Figure 6**, we observed a correlated increase in the N 1s counts near 400 eV with a decrease in the undamaged N 1s peak from [C2mim]+ at 402.1 eV at both photoelectron emission angles. This observation is consistent with some degree of X-ray induced damage to the cation imidazolium ring. However, at both photoelectron detection angles, the relative number density of the Ru complex very nearly matches the relative number density deficit of the IL cation suggesting that displacement of [C2mim]+ by the Ru complex is the dominant effect modulating the intensity of the undamaged N 1s signal at 402.1 eV relative to the anion N 1s peak at 399.5 eV.

**3.3. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS).** TOF-SIMS spectra were collected from a solution of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. In both the positive- and negative-ion TOF-SIMS spectra, fragmentation patterns that are characteristic of the pervasive contaminant polydimethylsiloxane (PDMS) were identified (see **Figure S3**). In the negative-ion spectrum, the peak with the highest *m*/*z* ratio was observed at *m/z* = 280 and clearly corresponds to the intact [Tf2N]– anion. Other notable and easily identifiable peaks in the negative-ion spectrum are [CF3SO2]– at *m*/*z* = 133 and [CF3SO2N]– at *m*/*z* = 147. Peaks corresponding to 35Cl– and 37Cl– were also observed in the TOF-SIMS negative-ion spectrum, with peak intensity percentages of 77% and 23%, respectively. Note that the relative intensities of these TOF-SIMS peaks are in good agreement with the expected isotopic abundances of the chlorine atom (76% for 35Cl and 24% for 37Cl). The TOF-SIMS positive-ion spectrum clearly shows a peak at the mass of the intact d11-[C2mim]+ ion at *m/z* = 122.

In **Figure 7**, three peaks in the positive-ion spectrum at *m*/*z* = 459.0, 603.4, and 641.4 are shown. All three peaks have a base width Δ(*m*/*z*) of ~10, which is in good agreement with the expected isotopic distribution of the Ru complex which should be dominated by the isotopic distribution of the Ru atom itself (note that Ru has 7 stable isotopes at *m*/*z* = 96, 98, 99, 100, 101, 102, and 104). The peak at *m/z* = 641.4 is the peak with the highest *m*/*z* ratio observed in the positive-ion spectrum and clearly corresponds to the complex, [RuCl(*p*-cymene)P(C8H17)3]+. As shown in **Figure S1**, the isotopic fine structure of the *m*/*z* = 641.4 peak is in excellent agreement with the isotope distribution that is expected for [RuCl(*p*-cymene)P(C8H17)3]+. Thus, the TOF-SIMS spectrum provides no *direct* evidence for the presence of the doubly charged dimer [(RuCl(*p*-cymene)P(C8H17)3)2]2+. If the dimer is present at the extreme liquid-vacuum interface, it must be ejected as a larger neutral complex or it must fragment to other species like [RuCl(*p*-cymene)P(C8H17)3]+ with high efficiency. If the Ru complex is present as [RuCl(*p*-cymene)P(C8H17)3(Tf2N)] at the extreme liquid-vacuum interface, unfragmented ejection into vacuum would not be detected by TOF-SIMS because it is a neutral. However, it is possible that [RuCl(*p*-cymene)P(C8H17)3(Tf2N)] fragments to yield charged species that are detected in the positive- and negative-ion TOF-SIMS spectra. For example, [RuCl(*p*-cymene)P(C8H17)3(Tf2N)] may fragment to [RuCl(*p*-cymene)P(C8H17)3]+ and [Tf2N]– with high efficiency.

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**Figure 7.** Selected peaks from the positive-ion TOF-SIMS spectrum of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. The *m*/*z* values reported in the figure identify our best estimate of the most probable isotopologue. The peak at *m*/*z* = 641.4 is the highest mass-to-charge peak observed in the positive-ion TOF-SIMS spectrum.

For the d11-[C2mim]+ and [Tf2N]– ions, the TOF-SIMS signal is expected to be higher than the TOF-SIMS signal from uncharged surface molecules that require both fragmentation/ionization *and* sputtering. Similarly, if the Ru complex is present as [RuCl(*p*-cymene)P(C8H17)3]+ at the extreme liquid-vacuum interface, the signal from this charged complex is also expected to be enhanced relative to the presence of any analogous neutral Ru complex which would require fragmentation/ionization *and* sputtering. If the Ru complex is present as [RuCl(*p*-cymene)P(C8H17)3]+ at the extreme liquid-vacuum interface, it may be stabilized by counterions from the ionic liquid solvent or the liquid-vacuum surface structure. The peaks at *m*/*z* = 459.0 and 603.4 are probably smaller fragments of the Ru complex or of larger clusters of the Ru complex and solvent. The three positive-ion peaks observed in **Figure 7** are the only peaks that can be clearly assigned to the Ru complex in both the positive- and negative-ion TOF-SIMS spectra. The presence of only three well-defined peaks that correspond to Ru-containing fragments suggests that speciation of the complex at the liquid-vacuum interface is fairly simple and the incident Ga+ ions do not induce excessive fragmentation of the complex. However, future experiments may find it informative to explore fragmentation patterns of the Ru complex obtained with different ion beams. For example, cluster ion beams (beyond the capability of the current instrument) may reduce the fragmentation of the Ru complex that is ejected from the liquid-vacuum interface. Note that simple speciation of the Ru complex at the liquid-vacuum interface is consistent with MAS NMR data (see above), which suggest that only one phosphorus-containing species is present in the bulk IL.

**4. DISCUSSION**

Assuming that the speciation at or near the liquid-vacuum interface is simple, the Ru complex appears to have lost a Cl– ligand and is probably present as [RuCl(*p*-cymene)P(C8H17)3]+, [RuCl(*p*-cymene)P(C8H17)3(Tf2N)], or [(RuCl(*p*-cymene)P(C8H17)3)2]2+. This conclusion is based on the combined observations of the XPS and TOF-SIMS data. The TOF-SIMS positive-ion peak at *m*/*z* = ~641.3 most likely corresponds to [RuCl(*p*-cymene)P(C8H17)3]+, suggesting that the *p*-cymene ligand is still associated with the Ru atom at the liquid-vacuum interface. The XPS data clearly show that the Ru, Cl, and P atoms from the catalyst are present in equal amounts and that the Ru and Cl binding energies are consistent with an Ru-Cl bond. Loss of a Cl– ligand could imply that the remaining complex has a charge of +1. In this case, a TOF-SIMS peak at *m*/*z* = ~641.3 could be produced by direct sputtering of the [RuCl(*p*-cymene)P(C8H17)3]+ ion from the liquid-vacuum interface without any need for collision-induced fragmentation/ionization. This peak could also be the result of efficient fragmentation/ionization of [RuCl(*p*-cymene)P(C8H17)3(Tf2N)] or [(RuCl(*p*-cymene)P(C8H17)3)2]2+. All three of the hypothesized Ru complexes are consistent with the observed changes in the relative intensities of the N 1s photoelectron peaks from d11-[C2mim]+ or [C2mim]+ and [Tf2N]– if we assume that this population shift is driven by charge neutrality in the near-surface volume probed by XPS. Specifically, the addition of [RuCl2(*p*-cymene)P(C8H17)3] to an isotopologue of [C2mim][Tf2N] results in a decrease in the number density of [C2mim]+ relative to [Tf2N]– in the interfacial liquid volume probed by XPS. The deficit of [C2mim]+ is roughly equal to the Ru-complex concentration, as determined by photoelectron peaks that are associated with elements that are unique to the Ru complex. A similar enrichment/depletion effect has been observed previously in 50 mg/mL [Pt(NH3)4]Cl2 in 1-ethyl-3-methylimidazolium ethyl sulfate ([C2mim][EtOSO3]), where the N 1s photoelectron peak from [Pt(NH3)4]2+ increased in intensity at the expense of the N 1s photoelectron peak from [C2mim]+ as the electron emission angle was increased from 0° to 70° with respect to interfacial normal.26

While multimeric structures that are consistent with the XPS relative atom number densities are possible, the TOF-SIMS data provide no evidence for the formation of ions with a mass-to-charge ratio larger than [RuCl(*p*-cymene)P(C8H17)3]+. Note that the relative atomic number densities derived from XPS are only able to resolve the loss of the Cl– ligand because this ion is not simultaneously enriched at the liquid-vacuum interface. This failure of the Cl– ion to compete with the [Tf2N]– anion at or near the liquid vacuum interface is expected, as large polarizable ions tend to be enriched at the liquid-vacuum interface at the expense of smaller non-polarizable ions.32

The observation of IS HF is unambiguous evidence that C-H bonds are available at the continually-refreshed liquid-vacuum interface of a solution of ~2 mg/mL [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N]. The only source of C-H bonds is the Ru complex, so [RuCl(*p*-cymene)P(C8H17)3]+ is presumably oriented to expose the P(C8H17)3 ligand (and perhaps the *p*-cymene ligand) to the vacuum. PDMS contamination in the solid Ru complex sample is an issue in the RAS and TOF-SIMS experiments. However, if the large and nonpolar Ru complex and the PDMS contaminant have a roughly equal affinity for the extreme liquid-vacuum interface, the relative number density of Si and Ru detected in our XPS experiments suggest that it shouldn’t dominate our IS HF yields. Although the dynamical RAS observables are complex, we can tentatively conclude that our observations are consistent with a Ru complex orientation that exposes the hydrocarbon ligands toward the vacuum by drawing parallels with other results in the literature. Specific examples include a smaller IS/TD ratio for HF relative to DF (consistent with the scattering behavior DCl from a THABr-glycerol)79 and the smaller cos(*θf*) character from IS HF relative to IS DF (consistent with the smaller cos(*θf*) character in the angular distribution of IS HF from the butyl group in [C4mim][Tf2N]).33 Also, a Ru complex orientation that directs the hydrocarbon ligands toward the vacuum is consistent with our inability to observe RAS-MS signal that can be confidently assigned to reactively scattered FCl. However, it is important to note that there is currently no evidence to support the assumption that F-atoms can form FCl by reacting with the Ru-Cl bond.

If the Ru complex is present as [RuCl(*p*-cymene)P(C8H17)3]+ at the extreme liquid-vacuum interface, the positive charge is almost certainly localized at or near the metal center. Thus, the Ru complex resembles a surfactant with a charged head group and a long hydrocarbon tail. In this case, the behavior of surfactants in ionic liquids may provide insight into the behavior of the Ru complex at the liquid-vacuum interface. In a recent study combining RAS with MD simulations,31 it was found that [C12mim]+ was enriched at the liquid-vacuum interface of [C2mim](1‑x)[C12mim]x[Tf2N] for a variety of mole fractions, *x*. Visual inspection of snapshots of the simulated interface suggested that ions in pure [C2mim][Tf2N] that expose atoms to the vacuum tend to pack in a sheet with a disordered alternating charge pattern. Qualitatively, as the mole fraction of [C12mim]+ increases, [C2mim]+ ions are displaced from this sheet by the [C12mim]+ headgroup. For these interfacially-active [C12mim]+ ions, there is a clear preference for the dodecyl chain to adopt configurations where C-H bonds along the chain are accessible to the vacuum. Interestingly, these simulations report a decrease in the average angle of the dodecyl chain (with respect to interfacial normal) as the number density of [C12mim]+ is increased at the liquid-vacuum interface. If the Ru complex is present as [RuCl(*p*-cymene)P(C8H17)3]+ at the extreme liquid-vacuum interface, it may behave similarly.

Orientation and speciation could be investigated with explicit simulations of the Ru complex in [C2mim][Tf2N]. Purely quantum mechanical (QM) methods have the potential to provide the most physically accurate description of this condensed phase system but are currently too difficult to be practical for a large transition metal complex in a molecular solvent. Hybrid quantum-mechanics/molecular-mechanics (QM/MM) methods are more promising. For studies of orientation only, it should be possible to use gas-phase QM calculations to guide the construction of a purely classical molecular mechanics (MM) model for the Ru complex that captures its behavior as a solute in [C2mim][Tf2N]. A preliminary study to select the most appropriate QM method for the description of mononuclear Ru-Cl-H-PR3 isomers has been recently reported.85 It would be straightforward to extend this study to [RuCl(*p*-cymene)P(C8H17)3]+, [RuCl(*p*-cymene)P(C8H17)3(Tf2N)], and [(RuCl(*p*-cymene)P(C8H17)3)2]2+ to confirm that the conclusions drawn for the Ru-Cl-H-PR3 isomers still apply. If so, a validated QM method could be used to run QM/MM simulations that would allow speciation to be investigated as well as the derivation of the intra- and intermolecular potential functions necessary to construct an MM forcefield for the simulation of a possible Ru complex at the liquid-vacuum interface of [C2mim][Tf2N].

**CONCLUSION**

We have studied the liquid-vacuum interface of a ~2 mg/mL solution of [RuCl2(*p*-cymene)P(C8H17)3] in d11-[C2mim][Tf2N] by reactive-atom scattering (RAS), X-ray photoelectron spectroscopy, and time-of flight secondary ion mass spectrometry. This transition metal complex is related to organometallic complexes that catalyze a range of transformations and so is a good model for homogeneous catalyst systems dissolved in ILs, in particular those where the gas-liquid interface is important. All three vacuum surface science methods detect signatures of the atoms associated with the Ru complex at or near the liquid-vacuum interface in a concentration that is much higher than expected from pure stoichiometry (~2-3% from RAS vs. ~0.04% when the number density of the Ru complex is expressed as a percentage of the total number density of the Ru complex, d11-[C2mim]+, and [Tf2N]–). Although we are unable to identify unambiguously the speciation of the Ru complex, our data provide constraints on the nature of the Ru complex and the ionic liquid environment at or near the liquid-vacuum interface. We suggest that the Ru complex may be present as [RuCl(*p*-cymene)P(C8H17)3]+, [RuCl(*p*-cymene)P(C8H17)3(Tf2N)], or, possibly, [(RuCl(*p*-cymene)P(C8H17)3)2]2+ at the extreme liquid-vacuum interface. These observations are an important prerequisite for potential future RAS experiments that can probe the catalytic activity of transition metal complexes supported at the ionic liquid-vacuum interface.

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**Notes**

The authors declare no competing financial interest.

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