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Published in:
Journal of Physical Chemistry C

DOI:
10.1021/acs.jpcc.6b02288

Publication date:
2016

Document Version
Peer reviewed version

Link to publication in Heriot-Watt University Research Portal

Citation for published version (APA):

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Scattering Dynamics of Oxygen Atoms on Imidazolium Tetrafluoroborate Ionic Liquid Surfaces: Dependence on Alkyl Chain Length

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ABSTRACT

The dynamics of oxygen-atom scattering from the surfaces of a series of room-temperature ionic liquids (RTILs) containing the 1-alkyl-3-methylimidazolium cation [Cₙmim] and the tetrafluoroborate anion [BF₄] were studied by reactive-atom scattering with mass spectrometric detection of products (RAS-MS). The length of the alkyl chain was varied \( n = 4, 8, 12 \) in order to investigate the relationship between the scattering dynamics and the density of alkyl chains on the surface and their ordering. RAS-MS uses a beam-surface scattering technique, with a hyperthermal O-atom beam source and a rotatable mass spectrometer detector. Time-of-flight and angular distributions were collected for inelastically scattered O and reactively scattered OH and H₂O, enabling product flux distributions to be obtained as a function of final translational energy and scattering angle, \( P(E_T, \theta) \). A new analysis technique was used to separate these distributions into three distinct components, corresponding to three dynamical pathways for scattered products: fast and slow impulsive scattering and thermal desorption. The results of these experiments support previous findings that surface alkyl coverage increases with increasing alkyl chain length, but these dynamical studies provide the additional insight that the ionic liquids with alkyl chains of \( n = 8, 12 \) have smoother surfaces than the ionic liquid with \( n = 4 \) and the pure alkane liquid, squalane (2,6,10,15,19,23-hexamethyltetracosane).
I. INTRODUCTION

Room temperature ionic liquids (RTILs) are salts that have melting points below 100 °C. The ionic liquid-gas interface is particularly important for many applications of interest such as gas capture and storage, gas chromatography, and supported ionic liquid phase catalysis. Knowledge of how gases react with or enter ionic liquids will hopefully contribute to a set of “design rules” that will ultimately allow ionic liquids to be tailored to maximize efficiency and minimize waste in these processes.

Many experimental and theoretical techniques have been used to study the ionic liquid-gas interface. A large number of studies have focused on a family of ionic liquids that contain the 1-alkyl-3-methylimidazolium ([Cₙmim]) cation. The wide range of experimental techniques employed includes sum frequency generation (SFG), angle-resolved photoelectron spectroscopy (ARXPS), low-energy ion scattering (LEIS), Rutherford backscattering (RBS), neutral impact collision ion scattering spectroscopy (NICISS), direct recoil spectroscopy (DRS), neutron reflectometry, and reactive atom scattering (RAS). Theoretical work has employed molecular dynamics (MD) simulations to study the structure of the interfacial region and a hybrid approach involving quantum mechanics and molecular mechanics (QM/MM) to study reactive collisions at the gas-liquid interface. Both the experimental results and associated simulations indicate that the surfaces of these liquids become increasingly enriched with hydrocarbon moieties as the alkyl chain length on the imidazolium ring increases or as the size of the anion decreases.

An understanding of surface speciation, which many techniques offer, is not sufficient to understand gas-liquid interactions. Impinging gas molecules may follow a multitude of pathways involving direct scattering, thermal accommodation, and reaction. The organization
and structure of interfacial molecules and their ability to absorb energy will dictate the fate of an incident gas atom or molecule. The outermost molecules of a liquid are often organized in a way that is different than the bulk. Several groups have conducted extensive studies of the dynamics of gas-liquid scattering.\textsuperscript{25,29-42} Imidazolium based ionic liquids have been the focus of a number of these studies.\textsuperscript{25,43-46}

We describe here a study which uses the reactive-atom scattering technique with mass spectrometric detection (RAS-MS) to collect translational energy and angular distributions of non-reactive as well as reactive products that scatter from liquid surfaces. In particular, we provide detailed experimental results on the relationship between the reactive O-atom scattering dynamics and the alkyl chain length for the [C\textsubscript{n}mim] cation ($n = 2, 8, 12$) and the tetrafluoroborate, [BF\textsubscript{4}], anion. Such dynamics probe the relative density of alkyl groups at the ionic liquid surface, and they also reflect the relative smoothness of the surface. We also propose a new method to distinguish between two different mechanisms for nonthermal scattering, in which products (either reactive or non-reactive) scatter impulsively from the surface on a time scale too short for thermal equilibrium to be attained. The new dynamical information is complementary to our previous study,\textsuperscript{24} which used LIF and mass spectrometric detection, as well as molecular dynamics (MD) simulations. Our previous work focused on OH product yields as a way to infer the relative number of abstractable hydrogen atoms at the surface, whereas the new work described here uses the dynamical behavior of molecular beam scattering data to gain insight into the surface structure beyond the identity of species that reside at the liquid-gas interface.
II. EXPERIMENTAL METHODS

The RAS-MS experiments were conducted with the use of a universal crossed-molecular-beams apparatus, configured for beam-surface scattering studies, which employed a rotatable mass spectrometer detector.\textsuperscript{24-25, 38} A laser-detonation source\textsuperscript{47} was used to prepare a pulsed beam containing hyperthermal O atoms from the breakdown of O\textsubscript{2} gas. The production of the hyperthermal beam begins with a pulse of O\textsubscript{2} gas at a stagnation pressure of 550 psig that is injected through a 1 mm orifice into a conical nozzle from a home-built piezoelectric pulsed valve. A 7 J pulse of light from a CO\textsubscript{2} TEA laser is focused into the throat of the nozzle and induces a breakdown and heats the gas to >40000 K, whereupon the associated shockwave dissociates the majority of O\textsubscript{2} in the nozzle and accelerates the gas to a nominal velocity of \~7.8 km s\textsuperscript{-1}. For the experiments described here, the beam pulse that exited the nozzle contained \~96\% atomic oxygen and \~4\% molecular oxygen, both in their ground electronic states, O(\textsuperscript{3}P)\textsuperscript{48} and O\textsubscript{2}(\textsuperscript{3}Σ\textsubscript{g}\textsuperscript{-})\textsuperscript{49} The pumping speed of the source region limited the repetition rate of the laser-detonation source to 2 Hz.

The hyperthermal beam was characterized by aligning the detector and molecular beam axes and collecting time-of-flight (TOF) distributions (number density vs. time, \textit{N}(\textit{t})) of mass-selected products over a known distance from the point near the nozzle orifice where the beam pulse was initiated and the ionizer of the mass spectrometer detector. The hyperthermal beam pulse passed through a 2 mm diameter skimmer that was 77 cm from the nozzle orifice and then through a collimating slit, 1.3 mm wide and 2.8 mm high, which was 3.5 cm downstream from the skimmer. The center of rotation of the rotatable quadrupole mass spectrometer detector was 18.5 cm from the collimating slit, and the distance from this point to the Brink-type electron-impact ionizer\textsuperscript{50} of the detector was 33.7 cm. Thus, the total flight path from the nozzle orifice
to the detector was 132.7 cm. A synchronized chopper wheel, with three 1.5 mm wide slots and a rotation speed of 300 Hz, was placed between the collimating slit and the rotation center of the detector in order to select a narrow range of velocities from the overall beam pulse. Ions, produced in the ionizer, were filtered by mass-to-charge ratio, \( m/z \), using a quadrupole ion filter and then detected by a Daly-type ion counter.\(^{51} \) TOF distributions were registered on a multichannel scaler as ion counts as a function of arrival time. The neutral flight time from the source to the ionizer was found by subtracting the ion flight time (over the distance from the ionizer to the ion counter), given by \( \alpha \sqrt{m/z} \), where the parameter, \( \alpha \), was empirically determined to be \( 3.4 \mu s \sqrt{e/amu} \). From these TOF distributions, the translational energy distributions \( P(E_T) \), proportional to flux) of O and O\(_2\) were derived. Representative translational energy distributions of the O and O\(_2\) components of the chopped beam are shown in Fig. 1. The experiments were performed on several different days, and the beam conditions varied slightly each day. The average translational energy of the oxygen atoms ranged from 504 to 511 kJ mol\(^{-1}\), and the mole fraction of oxygen atoms in the beam varied between 93 percent and 98 percent. These variations have been explicitly corrected for in the analysis as described below.

The hyperthermal O-atom beam was directed at a continually refreshed liquid surface, held at 323 K, that was formed by the pick-up of a film on a stainless steel wheel that rotated at 0.25 Hz through a reservoir of liquid (25 ml volume). The liquid surface was placed at the center of rotation of the mass spectrometer detector such that the surface normal and the molecular beam axis were contained in the detector rotation plane. After the beam pulse struck the surface, the resulting scattered species were detected as TOF distributions using the mass spectrometer, as described above, with a neutral flight path of 33.7 cm. The TOF distributions were collected for a variety of final angles at specific angles of incidence, \( \theta_i \). Thus, for \( \theta_i \), the product flux as a
function of translational energy and final angle, $P(E_T, \theta_f)$, could be derived. Note that $\theta_i$ and all final angles, $\theta_f$, are polar angles with respect to the surface normal and are in the same plane as the incident beam and surface normal, with positive $\theta_f$ being defined as angles on the opposite side of the surface normal from the incident beam.

Three ionic liquids, [C$_4$mim][BF$_4$], [C$_8$mim][BF$_4$], and [C$_{12}$mim][BF$_4$], were used, and these were acquired commercially from IoLiTec Ionic Liquids Technologies Inc. Beam-surface scattering experiments were also performed on a pure liquid alkane (squalane) surface, which is a well-studied liquid that was used as a reference in these experiments. Squalane was purchased from Sigma Aldrich. The purities of the starting liquids are given in Table S1 of Supporting Information. Each liquid sample was degassed under rough vacuum overnight and then transferred to the liquid reservoir inside the scattering chamber. The sample was then degassed for >12 hours at 323 K under high vacuum (<10$^{-6}$ Torr), with the wheel turning in the liquid reservoir, prior to the collection of any data.

TOF distributions were collected for scattered species with $m/z = 16$ (O$^+$), 17 (OH$^+$), 18 (H$_2$O$^+$), and 32 (O$_2^+$). The TOF distributions for $m/z = 16$ and 17 were corrected for the known contributions from dissociative ionization of O$_2$ and H$_2$O. For each mass, TOF distributions were collected for three incidence angles, $\theta_i = 30^\circ$, 45$^\circ$, 60$^\circ$. The final angles ranged, in 5$^\circ$ increments, from $\theta_f = -10^\circ$ to 70$^\circ$, $\theta_f = 5^\circ$ to 70$^\circ$, and $\theta_f = 20^\circ$ to 70$^\circ$, for incidence angles of $\theta_i = 60^\circ$, 45$^\circ$, and 30$^\circ$, respectively. The limits to the ranges of final angles were dictated by experimental geometry. In order to reduce the effect of long-term drifts in incident beam intensity and other experimental parameters, the final angle was increased and then decreased systematically until two TOF distributions had been collected for each $m/z$ at each $\theta_f$ for a given $\theta_i$. Then the liquid reservoir was lowered out of the path of the beam, and the incident beam was
interrogated by collecting TOF distributions of the O and O$_2$ components of the beam. This process was then repeated, which resulted in a total of four TOF distributions for each $m/z$ at each $\theta_f$, for a given $\theta_i$. The four TOF distributions were each normalized to the relevant beam intensity and then summed.

III. RESULTS AND ANALYSIS

Representative TOF distributions of O, OH, and H$_2$O scattering from [C$_{12}$mim][BF$_4$] are shown in Fig. 2. These TOF distributions appear to be bimodal, and, as has been widely invoked in previous related work, the two components were first assumed to arise from two limiting dynamical cases for scattering: impulsive, or nonthermal, scattering (IS) and thermal desorption (TD). When a reaction occurs, the analogous cases may also be referred to as Eley-Rideal and Langmuir-Hinshelwood, respectively. The products that arrive at the ionizer after longer flight times (slower component in the TOF distribution) are assumed to be the result of TD, with a Maxwell-Boltzmann (MB) speed distribution characterized by the surface temperature. The TD mechanism implies that the desorbed atoms or nascent reactive products have no memory of the trajectory of the incident O atoms, whereas the IS mechanism involves inelastic or reactive scattering on a time scale so brief that some memory of the incident trajectory is retained. The IS products thus scatter from the surface with a superthermal speed distribution.

From the TOF distributions of scattered species, translational energy distributions, $P(E_T)$, which are flux probability density functions, were determined by using standard analysis methods that convert from number density to flux ($P(E_T) \propto N(t)/t$), on the assumption of a monoenergetic beam. The justification for this assumption is discussed in Supporting Information. The first step in the separation of the IS and TD components of a TOF distribution
is to transform a Maxwell-Boltzmann distribution of translational energies at the surface temperature to a TOF distribution and adjust its amplitude to fit the slow (TD) component (red curves in Fig. 2). Then the IS component of the TOF is determined by subtracting the fitted TD component from the overall TOF distribution (blue curves in Fig. 2). This TOF distribution is then inverted to yield a \( P(E_T) \) distribution for the IS component. The separation of the two components in this way was justified by the clear bimodal appearance of the TOF distributions and the fact that a MB distribution at the surface temperature matches the slower components of the TOF distributions very well. After the smooth TD simulation is subtracted in the TOF domain, there is significant noise in the slow part of the remaining IS TOF distribution, which, when converted to the energy domain results in a high frequency variation in the low-energy region of the \( P(E_T) \) distribution. This apparent noise in the low-energy region is not related to the scattering dynamics, so we have smoothed the \( P(E_T) \) distributions using a spline interpolation (see Supporting Information). Figure 3 shows the smoothed \( P(E_T) \) distributions for impulsively scattered species that correspond to the TOF distributions shown in Fig. 2.

The \( P(E_T) \) distributions were also integrated to give relative flux, allowing angular distributions of scattered flux to be determined. Representative angular distributions for O, OH, and \( \text{H}_2\text{O} \) scattering from the four liquid surfaces for \( \theta_i = 60^\circ \) are shown in Fig. 4. Analogous distributions for \( \theta_i = 45^\circ \) and \( 30^\circ \) are shown in Figs. S1 and S2, respectively. The scattering of O and OH is dominated by nonthermal (IS) mechanisms, whereas both thermal (TD) and nonthermal (IS) mechanisms are significant in the production of \( \text{H}_2\text{O} \) from the surface. The angular distributions of the TD components are described well by the expected \( \cos(\theta_f) \) function for all incidence angles and for every scattered product. The IS components have maxima far
from the surface normal and even beyond the specular direction for the most of the O and OH products.

The $P(E_T)$ distributions and flux angular distributions have been combined into flux distributions that are a function of both translational energy and final angle, $P(E_T, \theta_f)$. Because the scattered products must have lower translational energies than the incident beam, these distributions were created by truncating all of the smoothed flux-weighted $P(E_T)$ distributions at the incident beam energy (discussed in Supporting Information in the context of the monoenergetic beam assumption in the analysis). The reactions of hydrocarbons with O($^3P$) to form OH and hydrocarbon radicals are only modestly exothermic. The enthalpies of hydrogen abstraction are -4.5 and -18.5 kJ mol$^{-1}$ for primary and secondary H atoms, respectively.$^{56}$ These reaction exothermicities are less than 4% of the energy of the incident beam. Because the OH products may come from abstraction of primary or secondary H atoms and these processes are nearly thermoneutral, the contributions of these reaction exothermicities to the available energy have been neglected in the analysis. The $P(E_T, \theta_f)$ distributions shown in Fig. 5 are interpolated between measured $P(E_T)$ distributions, collected at 5° increments in $\theta_f$, to create a smooth image of the flux as a function of translational energy and final angle for an incidence angle of $\theta_i = 60^\circ$. The red color in Fig. 5 indicates maximum flux and the dark blue color indicates zero flux. The scale is different for each column, but it is consistent within each column (corresponding to a given scattered product).

IV. DISCUSSION

The relationship between surface structure and scattering dynamics is manifested in the translational energy and angular distributions of the scattered products. We previously proposed
a soft-sphere kinematic model,\textsuperscript{52} similar to the hard-sphere or Baule model,\textsuperscript{53} that allows the observed laboratory scattering dynamics to be related to collisions in the center-of-mass (c.m.) reference frame, by analogy with gas-phase scattering experiments using crossed molecular beams.\textsuperscript{57} This kinematic model implies that an impulsive (nonthermal) atom-surface collision is localized on the surface, with a relatively small number of surface atoms being involved. Such localized gas-surface collisions have been linked to scattering in the “structural regime” for atom scattering on metal surfaces.\textsuperscript{58} If the collisions are localized, then the IS dynamics should contain information about the nature of the surface on a molecular level. Accordingly, we focus on the IS, or nonthermal, components of the TOF distributions from which IS translational energy and angular distributions are derived. Implicit in this discussion is the assumption that the IS collisions that lead to scattered O and OH involve single collisions on a stationary surface. Earlier theoretical work has shown that the majority of the collisions of O atoms on a liquid hydrocarbon surface have one inner turning point and lead to superthermal (IS) products, whereas a minority of collision trajectories that lead to superthermal products may have multiple inner turning points. These multiple-bounce collisions tend to yield products with lower translational energies and broader angular distributions than are observed for single-bounce collisions.\textsuperscript{59} We have taken steps to minimize the influence of multiple-bounce collisions in the analysis (see below). In addition, we note that the velocities of the surface atoms due to thermal motion are much smaller than the hyperthermal incident velocities used in our experiments and can effectively be ignored.

The IS translational energy distributions seen in Figs. 3 and 5 appear to be bimodal, with a broad distribution at higher energies ($E_T \approx 100$-500 kJ mol$^{-1}$) and a narrower distribution at lower energies ($<E_T> \sim 50$ kJ mol$^{-1}$) that are still roughly an order of magnitude higher than the
energies of thermally desorbed species in a MB distribution at the surface temperature ($<E_t>$ ~ 5 kJ mol$^{-1}$). Such bimodal translational energy distributions have been observed in several studies of hyperthermal atom-surface scattering.$^{25, 52, 54-55}$ The kinematic analysis in the earlier study of hyperthermal O-atom scattering on squalane$^{54}$ suggests that the high energy component in the translational energy distributions corresponds to scattering in the sideways direction in the c.m. frame, whereas the low energy component corresponds to backward scattering in the c.m. frame. The backward-scattered products presumably come from more head-on collisions with surface moieties that transfer large amounts of energy into the surface collision partner in a single (nonthermal) collision. Thus, the kinematic factors that lead to backward scattering in the c.m. frame following single collisions with large energy transfers are largely responsible for the low-translational-energy products that are observed in the lab frame. It has been shown in gas-phase scattering of hyperthermal O atoms with ethane that collisions that lead to backward-scattered products, which presumably come from low-impact-parameter (“head-on”) collisions, correspond to more energy transfer into internal modes of ethane, on average, than those that lead to forward- and sideways-scattered products.$^{60}$ In that study, the coupling between the translational energy release and the scattering angle in the c.m. frame motivated an analysis procedure in which different c.m. translational energy and angular distributions were used to describe the forward/sideways-scattered products and the backward-scattered products. Given the likelihood that the low and high energy components in the IS translational energy distributions shown in Fig. 3 represent qualitatively different dynamics for single-bounce scattering and the possibility that multiple-bounce collisions play a larger role in trajectories that lead to low energy products than high energy products, we have considered only the high energy
products when attempting to find relationships between scattering dynamics and surface structure.

The distributions shown in Fig. 3 and Fig. 5 show two distinct components in impulsive scattering, one with a relatively low energy and broad angular distribution and another with a much higher energy and super-specular angular distribution. The high and low energy components were separated algorithmically. Figure 6 shows a graphical representation of this separation for at \( \theta_i = 60^\circ \). At this incidence angle, TOF data were collected from -10° to 70° in 5° increments. As shown in Figs. 3 and 5, the \( P(E_T, \theta_f) \) surface contains a high-energy peak and a low-energy peak. In general, these peaks are maximally separated at high final angles. Relative to the high-energy peak, the low-energy peak is radially narrow with relatively small changes in the extent of energy with angle. Also, as \( \theta_f \) is reduced from 70° to -10°, spectral weight is ultimately transferred from the high-energy-peak to the low-energy peak. Because the separation of these two distributions is most obvious at final angles far from surface normal, the first step in the algorithm is to separate the two components at the maximum final angle, \( \theta_f = 70^\circ \). A region of the high energy portion of the \( P(E_T, \theta_f = 70^\circ) \) distribution (blue curve in Fig. 6A) that contains the peak is fit with a log-normal distribution:

\[
P_{\text{high}}(E_T) = A \exp \left( -\frac{\ln\left(\frac{E_T}{E_0}\right)^2}{w} \right)
\]

which provides a good empirical fit to asymmetric shape of the high energy portion of the translational energy distribution, \( P_{\text{high}}(E_T) \). In this analysis, \( A, x_0, \) and \( w \) are fitting parameters. The log-normal fit (green curve in Fig. 6A) defines \( P_{\text{high}}(E_T, \theta_f = 70^\circ) \), and its residual (orange curve in Fig 6A) defines \( P_{\text{low}}(E_T, \theta_f = 70^\circ) \). For all angles below \( \theta_f = 70^\circ \), \( P_{\text{high}}(E_T, \theta_f) \) is defined by a log-normal fit to \( P(E_T, \theta_f) - P_{\text{low}}(E_T, \theta_f + 5^\circ) \) (red curve in Fig. 6B), and \( P_{\text{low}}(E_T, \theta_f) = \)
This iterative approach is justified by the fact that \( P_{\text{low}}(E_T, \theta_f) \) changes only slightly between final angle increments and in this way the high energy portion is somewhat isolated before it is fit. This method was tested for robustness by adjusting the initial log-normal distribution fitting parameters and observing the changes in the resulting separated components of \( P(E_T, \theta_f) \).

\( P_{\text{low}}(E_T, \theta_f) \) and \( P_{\text{high}}(E_T, \theta_f) \) have very different flux angular distributions. Figure 7 shows the flux angular distributions for both the low and high translational energy components of IS O and OH, for a representative incidence angle of \( \theta_i = 60^\circ \). The distributions in Fig. 7 have been normalized to their peaks, in order to compare their shapes. The low-energy scattering components have angular distributions that are roughly \( \cos \theta_f \), while the angular distributions of the high-energy components are lobular in shape with maxima beyond the specular angle. The angular distributions in Figs. 7A and 7B look similar to those for the total IS flux in Fig. 4, because the majority of the flux is contained in the high-energy component.

The energy transfers to the surface associated with the \( P_{\text{low}}(E_T, \theta_f) \) and \( P_{\text{high}}(E_T, \theta_f) \) product distributions are also remarkably different. Figure 8 shows the fractional energy transfers as a function of deflection angle, \( \chi = 180^\circ - (\theta_i + \theta_f) \), for the high- and low-energy components of IS O and OH. The energy transfers for the low-energy components are high, close to 90%, and vary little with deflection angle. On the other hand, the energy transfers for the high-energy components are strongly dependent on deflection angle and cover a broad range from about 35-75%. The fractional energy transfers for the high-energy components are all fit well by the soft-sphere kinematic model that was presented in a previous publication.52

The near-cosine distributions and the large energy transfers that are characteristic of \( P_{\text{low}}(E_T, \theta_f) \) are superficially reminiscent of thermal desorption. However, these products are
clearly nonthermal (compared with average thermal desorption energies of ~ 5 kJ mol\(^{-1}\)), with an average translational energy of ~50 kJ mol\(^{-1}\) and a high-energy tail extending above 100 kJ mol\(^{-1}\) and are likely the result of atom-surface collisions that involve a single bounce or, perhaps, only a few bounces, but in any case an interaction that occurs on a timescale too short for thermal equilibrium to be attained. The reason for the thermal-desorption-like appearance is that backward scattering in the c.m. frame accompanied by a relatively large transfer of energy to internal modes of the liquid is reflected by relatively slow product velocities in the laboratory frame. This interpretation might apply also to Ne scattering on a self-assembled monolayer film, where it was observed theoretically that single-bounce collisions could lead to a population of scattered Ne atoms that appeared to be Maxwellian.\(^{61}\)

The angular distributions corresponding to the \(P_{\text{high}}(E_T, \theta_f)\) components in Figs. 7A and 7B suggest a qualitatively different surface structure on the \([\text{C}_8\text{mim}][\text{BF}_4]\) and \([\text{C}_{12}\text{mim}][\text{BF}_4]\) surfaces than on the \([\text{C}_4\text{mim}][\text{BF}_4]\) and squalane surfaces. Both the O and OH angular distributions corresponding to \([\text{C}_8\text{mim}][\text{BF}_4]\) and \([\text{C}_{12}\text{mim}][\text{BF}_4]\) are narrower and more superspecular than the corresponding distributions for \([\text{C}_4\text{mim}][\text{BF}_4]\) and squalane. The same trends are observed in Figs. 4 and S1, which show plots of total IS flux as a function of angle. Note that the angular distributions for O and OH in Figs. 4 and S1 are dominated by the high-energy scattering component, but they may be slightly distorted by the low energy component, which was removed before creating the plots in Fig. 7. The angular distributions may be linked to relative surface roughness. Rougher surfaces would be expected to correspond to localized groups that protrude from the surface and promote more “head-on” and multiple-bounce collisions with an incident O atom or a nascent OH radical, thus deflecting the scattered products over a broad angular range. In contrast, the higher probability of glancing collisions on a smooth
surface would be expected to result in products that scatter into a relatively narrow range of super-specular ("forward") angles. Thus, the angular distributions for \([C_8\text{mim}][BF_4]\) and \([C_{12}\text{mim}][BF_4]\), with their narrower and more super-specular shapes, suggest that the surfaces of these liquids are slightly smoother than the surfaces of the other two liquids. A relatively smooth surface could result if the \(C_8\) and \(C_{12}\) alkyl chains of the imidazolium cations tended to occupy the surface in an orientation that is parallel to the liquid-vacuum interface or if these chains packed tightly, either lying parallel to the interface or standing up vertically. Our recent experimental study\textsuperscript{24} clearly shows that the hydrocarbon density at the surfaces of \([C_n\text{mim}]\)-based ionic liquids grows with \(n\) but is not saturated even with \(n = 12\); therefore, the surfaces cannot have a structure of tightly packed chains. Earlier MD simulations\textsuperscript{25} of the surfaces of \([C_2\text{mim}][\text{NTf}_2]\) and \([C_{12}\text{mim}][\text{NTf}_2]\) and our more recent simulations\textsuperscript{24} of \([C_n\text{mim}][\text{NTf}_2]\) and \([C_n\text{mim}][BF_4]\) surfaces indicate that the \(C_n\) alkyl chains of these liquids are concentrated at the interface and do indeed tend to lie more parallel to the interface as the alkyl chain length grows, but without forming tightly packed layers. Squalane, which is a branched alkane, appears to project both methyl and methylene groups toward the interface\textsuperscript{24,41,59} and therefore may have a more molecularly rough surface than the \([C_8\text{mim}]\) or \([C_{12}\text{mim}]\) ionic liquids. Thus, the conclusion from the angular distributions that the surfaces of \([C_8\text{mim}][BF_4]\) and \([C_{12}\text{mim}][BF_4]\) are smoother than those of \([C_4\text{mim}][BF_4]\) and squalane is direct experimental evidence of what has been inferred from prior experimental data and MD simulations.

Turning to the fractional energy transfer data, the high-energy components of the IS O and OH (Fig. 8) should, in principle, reflect the molecular nature of the four surfaces studied. As the H-atom abstraction reaction to produce OH is almost thermoneutral\textsuperscript{62} and the mass change on going from O to OH is small, the observed differences in the scattering behavior of O and OH
should reflect the fact that O atoms can scatter from any site on the surface, while OH can only come from an incident O-atom collision with a hydrocarbon moiety. In the case of non-reactive scattering of O atoms (Fig. 8A), the energy transfers on [C₈mim][BF₄], [C₁₂mim][BF₄], and squalane are essentially the same, within the error of the experiment, whereas the energy transfer on [C₄mim][BF₄] is significantly less. The earlier experimental/molecular dynamics study of alkyl surface coverage as probed by relative yields of OH indicates that the alkyl coverage increases monotonically with alkyl chain length, with squalane by necessity being entirely covered with alkyl groups. The relatively low O-atom energy transfer on [C₄mim][BF₄] may thus be explained by the small fraction of alkyl groups at the surface and the concomitantly large fraction of anions. However, the energy transfers for O atoms on the other three liquids do not follow the expected trend, where one would expect the energy transfer to increase with alkyl chain length at the surface. We considered the possibility that the grazing incidence angle of 60° might result in the incident O atoms being obscured by protruding alkyl groups that would block access to stiffer, anion regions of the [C₈mim][BF₄] and [C₁₂mim][BF₄] surfaces, but we found that these surfaces and squalane also exhibited the same trends in O-atom energy transfer when the incidence angle was 45° (see Fig. S3). Apparently, the energy transfer of inelastically scattered O atoms is not sensitive to the surface hydrocarbon density of RTILs with alkyl chain lengths of at least C₈ and higher. A similar observation was reported for the inelastic scattering of CO₂ on RTILs, where the insensitivity of the inelastic energy transfer data to alkyl chain length on the imidazolium cation beyond 8 carbons led to the conclusion that the surface was saturated with alkyl chains.⁴⁴ Although reasonable, this was conclusion was demonstrated not to be correct through the more-incisive monitoring of the yield of the reactive-product OH yield from O atom scattering.[ref 24]
The fractional energy transfer data for reactively scattered OH (Fig. 8B) are apparently more sensitive to the surface structure and show slight differences between all four liquids. As might be expected, the energy transfer is lowest for reactive scattering on [C₄mim][BF₄]. Surprisingly, however, energy transfer is greatest on [C₈mim][BF₄] and it decreases somewhat on going from [C₁₂mim][BF₄] to squalane. The reactive scattering dynamics are thus sensitive to the nature of the liquid surface, but the origin of this sensitivity is unclear. A possible explanation might be the number of primary hydrogen atoms at the surface relative to secondary or tertiary hydrogen atoms. Our previous molecular dynamics simulations do indeed reveal relative surface methyl group coverage that decreases in the order, [C₈mim][BF₄] > [C₁₂mim][BF₄] > squalane > [C₄mim][BF₄]. If methyl groups present a stiffer collision partner to the incident O atoms than methylene groups, then the observed trend in fractional energy transfer should be observed. Other explanations are possible and are under investigation through a detailed analysis of the molecular dynamics results.

The dynamics of the reactively scattered H₂O product are much different than the scattering dynamics of O and OH. These differences are clearly shown in the $P(E_T)$ distributions in Fig. 3, as well as the total flux angular distributions in Fig. 4. This is not surprising because water molecules must be formed by a more complex interaction of O atoms with the interface.¹⁵ It is reasonable that these interactions require more energy transfer from the incident atom as two hydrogen atoms must be abstracted. It is also important to note that the relative yield of H₂O is not the same for each of these liquids, which is to be expected because the evidence suggests that the surfaces have differing fractions of hydrogen atoms present. Previous work also hypothesizes that the nearly monotonic increase in TD H₂O products with increasing chain length is a good representation of the amount of hydrogen present at the interface.¹⁴
V. CONCLUSION

The dynamics of inelastic and reactive collisions of hyperthermal \( \text{O}^3P \) on \([\text{C}_n\text{mim}][\text{BF}_4]\) \((n = 4, 8, 12)\) ionic liquids and their comparison with the analogous scattering dynamics on the pure hydrocarbon liquid, squalane, offer a direct experimental window into the surface structure at the vacuum-liquid interface. The extent to which the scattering dynamics can serve as a useful probe of the details of the surface structure depends on the localized nature of the atom-surface collision. The picture of localized atom-surface collisions is justified in this work and in several previous studies by the success in describing the impulsive-scattering dynamics with a simple kinematic model. However, trajectories that involve multiple bounces on the surface or that lead to very large energy transfers during a single bounce may reduce the quality of the information on surface structure that is contained in the scattering dynamics. Therefore, we have focused on the relatively simple inelastic collisions of \( \text{O} \) and the reactive collisions that produce \( \text{OH} \), as opposed to the more complex reactive collisions that produce \( \text{H}_2\text{O} \). Furthermore, in an effort to minimize the influence of trajectories with multiple bounces and large energy transfers on our analysis, we developed a technique to remove the \( \text{O} \) and \( \text{OH} \) products that scattered backward in the c.m. frame, manifested by their low (but still superthermal) translational energies, and keep only those with high translational energies that scattered sideways in the c.m. frame. The high-energy products are most likely to arise from single-bounce collisions and retain the information about the localized region of the surface where the collision occurred. The energy transfers associated with these collisions (for both \( \text{O} \) and \( \text{OH} \) products) were described well by a two-parameter (effective surface mass and internal excitation) kinematic model, but the differences in the parameters were too small to gain physical insight from their relative values. The key insight
derived from this work has thus come from the assumptions behind the novel separation the impulsive scattering dynamics into two components, the angular distributions of scattered O and OH and, to some extent, the differences in energy transfer associated with these inelastic and reactive collisions.

The scattering dynamics presented here go beyond our earlier studies that focused on surface reactivity. The earlier studies showed clearly that as the alkyl chain on the imidazolium ring became longer, or if the anion were smaller, then the surface became more hydrocarbon-rich. The angular distributions of inelastically scattered O and reactively scattered OH indicate that the ionic liquid surfaces with \( n = 8 \) and 12 are smoother than the ionic liquid surface with \( n = 4 \) and the squalane surface. This increased smoothness is interpreted as a propensity for the longer alkyl chains on the imidazolium cation to congregate at the surface and lie down more or less parallel to the interface, and not as a tight packing of the chains at the surface with any particular order. The information revealed through the energy transfer dynamics is more subtle than what was evident from the angular distributions. The inelastic energy transfers for squalane and the ionic liquids with \( n = 8 \) and 12 were indistinguishable, indicating (in light of our earlier work) that inelastic scattering alone is an insensitive probe of the hydrocarbon density at the surface. However, the energy transfer associated with reactive scattering to form OH, which can only originate from collisions with a hydrogen-containing moiety at the surface, was sensitive to the liquid – albeit in an as yet unexplained way. The energy transfers in these collisions followed the trend, \([C_4\text{mim}][BF_4] < \text{squalane} < [C_{12}\text{mim}][BF_4] < [C_8\text{mim}][BF_4]\), which cannot be related simply to the hydrocarbon density at the surface. The energy transfers in reactive collisions to form OH must therefore probe more detailed aspects of the surface structure, a
relationship we expect to be revealed with future theoretical studies of the liquid surfaces themselves or of gas-liquid collision dynamics.

ACKNOWLEDGMENTS

This work has been supported by the U.S. National Science Foundation (NSF-CHE-1266032) and by the U.K. Engineering and Physical Sciences Research Council (EP/K032062/1). We are grateful to Maria A. Tesa-Serrate for many valuable discussions and to Philip J. Woodburn for assistance in the collection of the data.
SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6022886. Angular distributions of scattered flux for \( \theta_i = 45^\circ, 30^\circ \). Average fractional energy transfers for \( \theta_i = 45^\circ \). Comparison between directly inverted and smoothed translational energy distributions for impulsive scattering. Justification for the use of the monoenergetic beam approximation. Details of the purities of the four liquids used for the experiments.

NOTES

The authors declare no competing financial interest.
REFERENCES


Figure 1. Representative translational energy distributions of the velocity-selected atomic and molecular components of the hyperthermal beam (used for the experiment with [C\textsubscript{12}mim][BF\textsubscript{4}]). The O-atom curve has been normalized to 1, and the area under each curve reflects the relative flux of the respective species.
Figure 2. Representative TOF distributions for products scattered from [C_{12}mim][BF_{4}] with $\theta = 60^\circ$. The yellow circles are the total distribution which is then partitioned empirically into two components. The red (TD) curves correspond to the TOFs of atoms or molecules that desorb from the surface with speeds described by a Maxwell-Boltzmann distribution at the surface temperature of 323K. The blue (IS) curves are the differences between the total signal and the TD curves; as such they correspond to the TOF of molecules that have not reached thermal equilibrium with the surface. Time zero is the nominal time at which the atomic beam pulse struck the surface. All offsets, including ion flight time, have been subtracted.
Figure 3. Representative flux-weighted translational energy distributions for IS O, OH, and H$_2$O scattered from a [C$_{12}$mim][BF$_4$] surface. The complete IS distribution without the TD component is shown. These curves have been smoothed because the $P(E_T)$ distribution that is derived from the direct inversion of the TOF data has a significant amount of noise in the low energy region of the distribution (see text). The area under each curve is proportional to the flux of the scattered species.
Figure 4. Flux angular distributions of O, OH, and H$_2$O, corresponding to $\theta_i = 60^\circ$. The yellow circles represent the total signal; the blue circles represent the IS component; and the red circles represent the TD component. The angular distributions of the thermal components are well described by a cosine distribution about the surface normal, shown here as black lines.
**Figure 5.** Flux as a function of translational energy and final angle, $P(E_T, \theta_f)$, for $\theta_i = 60^\circ$. Every panel is derived from 17 individual translational energy distributions, each collected at a given final angle. The overall distribution is then interpolated between the individual translational energy distributions. Red indicates maximum flux and dark blue indicates zero flux. The color scale is different between columns, but it is the same within each column. The left, center, and right columns show the IS behavior of O, OH, and H$_2$O, respectively. Each H$_2$O distribution has a sharp maximum at low energies and relatively low amounts of signal at high energies. Because most of the scattered H$_2$O flux has relatively low translational energies, the $E_{\text{trans}}$ scale for H$_2$O has a maximum of 100 kJ mol$^{-1}$ to facilitate viewing of its $P(E_T, \theta_f)$ distributions.
Figure 6. Representative decompositions of impulsive scattering $P(E_T, \theta)$ distributions into low-energy $P_{low}(E_T, \theta)$ and high-energy $P_{high}(E_T, \theta)$ components, for an incidence angle of 60°. (A) The high-energy peak in $P(E_T, \theta_f = 70°)$ (blue) is well-fit with a log-normal distribution (green) over the majority of its width (gray box). The residual (orange) defines $P_{low}(E_T, \theta_f = 70°)$. (B) Analogous decomposition of $P(E_T, \theta_f = 50°)$ distribution (blue). $P(E_T, \theta_f) - P_{low}(E_T, \theta_f + 5°)$ is shown in red. $P_{high}(E_T, \theta_f)$ is shown in green. $P_{low}(E_T, \theta_f)$ is shown in orange.
Figure 7. Flux angular distributions of scattered products from squalane (yellow) and [Cₙmim][BF₄] ionic liquids, where θᵢ = 60° and n = 4 (blue), 8 (red), and 12 (green). Panels A and B show the flux angular distributions of inelastically scattered O atoms and reactively scattered OH radicals, respectively, that correspond to $P_{\text{high}}(E_f, \theta_f)$. Panels C and D show the flux-angular distributions of O and OH, respectively, that correspond to $P_{\text{low}}(E_f, \theta_f)$. All distributions have been normalized to their maxima in order to facilitate a comparison of their shapes.
Figure 8. Average fractional energy transfer as a function of deflection angle, $\chi$, for (A) inelastically scattered O and (B) reactively scattered OH from four different liquids: [C$_4$ mim][BF$_4$] (blue), [C$_8$ mim][BF$_4$] (red), [C$_{12}$ mim][BF$_4$] (green), and squalane (black). These data were collected with $\theta_i = 60^\circ$. The circles correspond to the $P_{\text{high}}(E_T, \theta_f)$ component and the squares correspond to the $P_{\text{low}}(E_T, \theta_f)$ component. The colored lines represent the best fit according to the soft sphere kinematic model. The values of the two parameters from the model (effective surface mass, $m_s$, and the ratio of internal excitation to incidence energy, $E_{\text{int}}/E_i$) are shown. The two parameters are coupled, so subtle differences in energy transfer, as observed here, cannot be interpreted in terms of these parameters.