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Reactive Scattering as a Chemically Specific Analytical Probe of Liquid Surfaces

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ABSTRACT In this Perspective, we highlight some recent progress in the reactive scattering of "chemical probe" species such as atoms or small radicals from liquid surfaces. We emphasize in particular the evolution of this area from purely dynamical studies of the scattering mechanism. The mechanistic understanding that has now been gained is sufficiently mature to allow the same methods to be used as an effective analytical tool. The use of this approach to measure liquid-surface composition and structure is illustrated through the scattering of $O(^3P)$ atoms from a common, imidazolium-based family of ionic liquids.
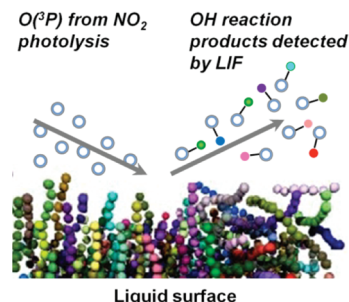
The surfaces of liquids are complicated places. They lack the long-range order characteristic of many solids. The breaking of isotropic symmetry at the interface means that the surface may have a composition and local structure quite different from that of the bulk. The changes in composition and density are not necessarily sharp and can extend over a significant depth range that may be several times the effective diameters of the individual molecular components. The surface may appear quite rough at a molecular scale. Furthermore, it is typically highly fluxional, with sub-ns time scales for transport of molecules to and from the bulk or for reorientation of molecules in the surface layer.

The characterization of liquid surfaces therefore presents a considerable challenge to both experiment and theory. Nevertheless, the gas—liquid interface lies at the center of many real-world processes. A greater understanding would be of considerable benefit in the enhanced design or prediction of behavior in interfacial systems ranging from heterogeneous atmospheric chemistry, through multiphase catalysis, to biological respiration. In this Perspective, we briefly review some of the principal existing methods used to probe the composition and structure of liquid surfaces to set the context for some recent progress[1-3] in the scattering of gas-phase projectiles from liquids that reveals its potential to add to the armory of available techniques. Although the focus here is primarily on experimental methods, we also emphasize that the interpretation of the experimental results is greatly aided by parallel theoretical effort, particularly through realistic molecular dynamics simulations.

A key issue in any experimental method designed to probe surface composition or structure is its surface specificity. It is an elementary fact that in almost all realistic liquid samples, the surface layer represents a very small proportion of the total volume. Some physical restriction that confines the origin of an observed signal to the vicinity of the surface is therefore required. There are, of course, classical properties such as surface tension[4] or contact angle[5] that are inherently surface-specific, but they are rather generic and

only very indirectly interpretable in isolation. The main current methods include various forms of nonlinear optical spectroscopy,[4,6] evanescent wave spectroscopy,[7] the scattering of neutrons,[8] electrons,[9] or X-rays,[10] the ejection of photoelectrons,[11] or "direct recoil" of fragments from ballistic, relatively high-energy probe particles.[12,13] We have chosen to cite here representative examples of their application to ionic liquids related to those to which we return below, but these methods are general and have been applied much more widely.

The nonlinear spectroscopies gain their surface specificity from the symmetry breaking at the interface that makes allowed a second-order process such as sum frequency generation, which is forbidden in the bulk.[4] They also contain information on molecular orientation at the interface due to the restriction on direction of the transition dipole for transitions to be allowed.[4] The other methods all essentially rely in one form or another on a restricted mean-free path for penetration into or escape out of the liquid medium of electromagnetic radiation or particles. A principal example that has been used with considerable success is angle-resolved X-ray photoelectron spectroscopy (ARXPS), where the depth resolution is determined by the mean-free path for escape of the photoelectrons.[11,14-16] This turns out to be on the order of $1-10$ nm,[11] which is comparable to the length scale over which interesting compositional changes often take place.

The distinct approach that we wish to highlight here is based on scattering of potentially reactive gas-phase atoms from liquid surfaces. This also relies for its surface specificity on restricted penetration of the projectiles and/or escape of the products. Importantly, we will show that satisfaction of this condition is not merely an assertion; the measurements

themselves confirm that the observed products must have been generated in the extreme outer layers of the liquid.

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The particular demonstration of this approach that we feature is the scattering of ground-state $O(^3P)$ atoms from liquid surfaces containing abstractable hydrogen atoms. This emerges from recent broader efforts[17−25] to gain a mechanistic understanding of $O(^3P)$ reactions at hydrocarbon liquid surfaces, particularly of the "benchmark" branched chain molecule squalane ($C_{30}H_{62}$, 2,6,10,15,19,23-hexamethyltetracosane). This work was originally built[17] on the foundation of pioneering studies by Nathanson and co-workers[26,27] of the inelastic scattering of rare gas atoms and closed-shell molecules from a range of liquid surfaces using a method based on incident molecular beams coupled with mass spectrometric detection. There have been complementary developments in the inelastic scattering of similar projectiles from self-assembled monolayer (SAM) surfaces.[28,29] Reactive studies have been more restricted, being confined essentially to the $O(^3P)$ systems above, for which we first introduced laser-induced fluorescence (LIF) as an alternative, spectroscopically based method for the detection of the OH products,[21] some early related work on $Cl(^2P)$ atoms,[18] and more extensive independent studies of $F(^2P)$ atoms with squalane by Nesbitt and co-workers.[30,31] The Nesbitt group also used a spectroscopic method (IR absorption) to detect the product HF, having first developed this successfully for inelastic scattering of CO_2 from liquid surfaces.[32]

In these previous studies, the surface was largely considered as a "known" quantity, and the focus was on deriving dynamical information on the scattering mechanism. What sets apart the very recent work[1−3] that we wish to emphasize here is the idea that the same techniques can be used effectively as an analytical method on "chemically interesting"

surfaces. This proposition was first successfully demonstrated for a common family of ionic liquids where the surface composition itself was the "unknown" quantity of interest.[1−3] These liquids were based on the 1-alkyl-3-methylimidazolium ([$C_n$mim]) cation, in this case with a commonly used bis-(trifluoromethylsulfonyl)imide ([NTf_2]) counterion. The object of the experiments was to establish the degree to which the aliphatic H atoms on the cation were exposed at the liquid surfaces for a series of [$C_n$mim] cations containing 1-alkyl chains of varying length ($n = 2−12$) and a fixed 3-methyl group.

In both of the complementary sets of experiments carried out in our own laboratory[1,2] and in that of Minton,[3] the liquid surface is prepared in essentially the same way. A wheel partly immersed in the liquid rotates in vacuum. This ensures that a continually refreshed surface is presented. The method of $O(^3P)$ generation is distinctly different, as are the methods of detection. In the Minton experiments, a unique high-energy detonation source[19] is used to generate a beam of $O(^3P)$ atoms with mean laboratory-frame kinetic energies at around 500 kJ mol^{-1}. The scattered products are detected by time-of-flight mass spectrometry. In contrast, we generate the $O(^3P)$ atoms with significantly lower but still superthermal kinetic energies (in this case, mean = 16 kJ mol^{-1}, fwhm = 26 kJ mol^{-1}) by pulsed laser photolysis of a low pressure of a precursor gas (specifically here, NO_2 at 355 nm) typically 5−10 mm above the liquid surface. An independent, pulsed, tunable probe laser beam intercepts the scattered products at a similar distance above the surface, in this case exciting a LIF signal from the OH radical. This combined photolytic−spectroscopic method is illustrated schematically in Figure 1.

For the purpose of the current application, both experimental approaches allow chemically identified products to be detected. Their complementary nature can be used to advantage, particularly for the mechanistic studies that are an essential prerequisite to any reliable analytical interpretation. The molecular beam experiments provide superior speed resolution and unique angular scattering information, whereas the photolytic−spectroscopic measurements are uniquely quantum-state-specific and therefore provide additional information on internal state distributions. The beam experiments, through their use of "universal" mass spectrometric detection, can also, in principle, see any scattered reaction products and also the inelastically scattered incoming projectiles. More subtly, the different collision energy
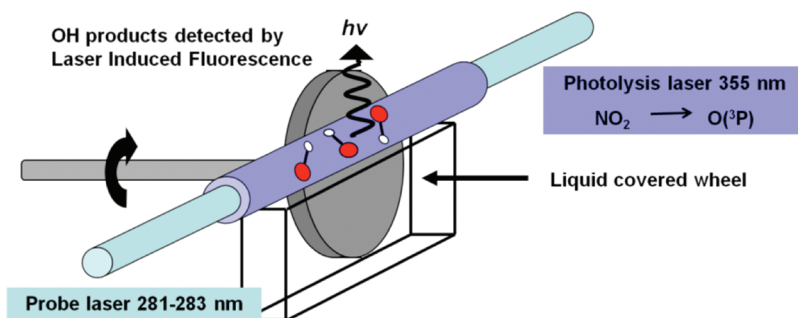

Figure 1. Schematic representation of the photolytic−spectroscopic method used to probe liquid surfaces by reactive scattering of atoms and small radicals.
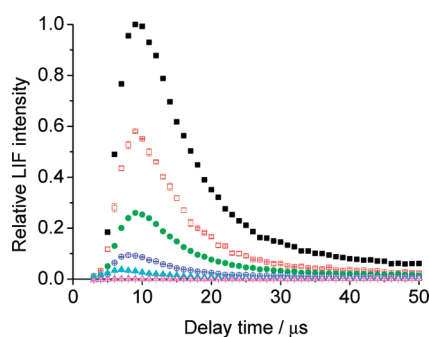
Figure 2. Measured appearance of the OH A−X (1,0) $Q_1(1)$ LIF signal as a function of photolysis−probe laser delay time from a series of $[C_n mim][NTf_2]$ ionic liquids with alkyl chain lengths of n = 12 (red open squares), 8 (green closed circles), 5 (blue open circles), 4 (cyan closed triangles), and 2 (magenta open triangles). Signals are normalized to those from the benchmark pure hydrocarbon, squalane (black closed squares). Reproduced from ref 2.
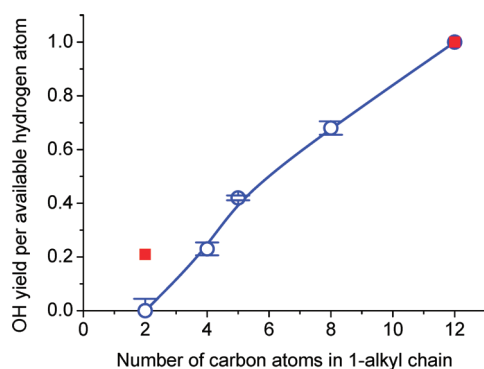

Figure 3. Relative OH yield per available hydrogen atom as a function of alkyl chain length for a series of $[C_n mim][NTf_2]$ ionic liquids, as measured by photolytic−spectroscopic experiments (blue open circles, with 2σ error bars) and the complementary molecular beam approach (red squares). Yields per atom are normalized for n = 12 for both experiments. The available hydrogen atoms are assumed to be restricted to CH_2 groups in the photolytic experiments but include CH_3 and CH_2 groups in the molecular beam experiments. This reflects the relationship between collision energies and barrier heights for the different C−H bond types. Constructed from data in refs 2 and 3.

regimes allow a further distinction in the site specificity of the reactivity, which we indeed find in the case of $O(^3P)$ + $[C_n mim][NTf_2]$ ionic liquids, as we explain shortly below.

The key "analytical" outcomes of these studies are illustrated in Figures 2 and 3. A more complete selection of chain lengths across the full range n = 2−12 was investigated by the spectroscopic approach.[2] The appearance profiles (OH LIF signal as a function of the delay between the photolysis and probe laser pulses; setting aside experimental broadening effects, this time is essentially inversely proportional to the speed at which the OH leaves the liquid surface) are shown in Figure 2. The primary analytical information that they convey is the relative yields of OH from the different $[C_n mim][NTf_2]$ liquids. This has been represented in Figure 3, where we have plotted the OH yield per reactive H-atom group present in the cation as a function of the 1-alkyl chain length. Only the CH_2 groups are considered to be significantly reactive in the photolytic experiments, as is explained in detail

elsewhere.[1,2] This assumption is derived from the well-known[33] relative strengths, and hence activation barriers, for abstraction from different H−C bond types. A purely stoichiometric dependence, reflecting only the changes in bulk composition of the liquids, would correspond to a horizontal line in this plot. This is clearly not observed, with a strong relative increase in the yield as the chain length increases. A distinct but still nonstoichiometric variation in yield was observed for the more restricted measurements on the first and last members of the series using the molecular beam approach.[3] In that case, the two terminal CH_3 groups are expected to be reactive due to the much higher kinetic energies of the incident $O(^3P)$ atoms. Nevertheless, even taking this stoichiometric factor into account, the less extreme suppression at shorter chain lengths implies that the more energetic atoms may sample a different range of depths than that in the photolytic experiments. We return to this point below.

The clear qualitative conclusion from all of these results is that the availability of the aliphatic chains at the surface increases dramatically with chain length. There are many reasons that we can be confident that the measurements really are surface-specific. It is beyond the scope of this Perspective to reproduce all of the detailed mechanistic evidence here, but one example is the shapes of the appearance profiles in Figure 2. As we have shown,[2] if these are compared with a prediction of the profile that would have resulted if the OH radicals had been thermally accommodated at the surface before escaping, then they are found to be much too fast; the peak in the observed profile corresponds to a speed of order twice that of the thermal average. The majority of the OH must have been formed in a relatively direct process involving only one, or at most a few, elementary encounters. This necessarily confines the site of reaction to the extreme outer layers of the liquid. There are consistent signatures of nonthermal rotational excitation of the OH in the spectroscopic experiments[1,2] and a wealth of information on strongly directed, near-specular angular distributions and highly nonthermal translational energy distributions for the majority of the OH products in the molecular beam experiments.[3]

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The absolute surface coverage by the target alkyl groups can also be estimated, at least empirically, by comparison with a calibrant liquid for which the surface coverage is reliably known. In the case of the $[C_n mim][NTf_2]$ ionic liquids, the OH yields can be compared with those from the
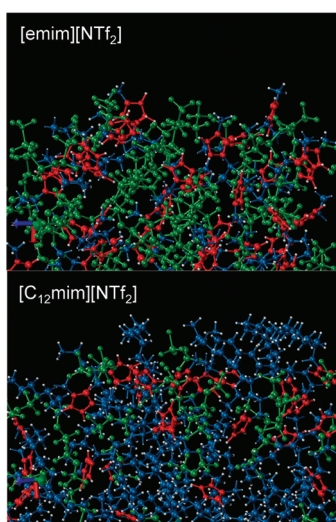
Figure 4. Representative snapshots from molecular dynamics simulations of the surfaces (at 323 K) of [emim][NTf$_2$] (top) and [C$_{12}$mim][NTf$_2$] (bottom) ionic liquids, showing the anion (green), imidazolium ring (red), alkyl chains (blue), and hydrogen atoms (white). Reproduced from ref 3.

benchmark pure hydrocarbon, squalane. In the photolytic experiments, the reactivity of the most reactive, longest-chain ionic liquid [C$_{12}$mim][NTf$_2$] is found to be around 60 % of that of squalane.[1,2] Taking account of the fraction of the squalane surface predicted to be occupied by the more reactive secondary and tertiary groups,[34−36] but neglecting any considerations such as different degrees of roughness of the two surfaces, the absolute fraction of the ionic liquid covered by alkyl chains is estimated to be correspondingly around 35 %.[1] The inferred alkyl exposure for the other liquids can be scaled to their OH yields accordingly.

As is a general feature of this field, any more quantitative interpretation requires comparison with parallel theory. Molecular dynamics simulations of the structures of the [emim] and [C$_{12}$mim][NTf$_2$] surfaces have indeed been carried out,[3] predicting a very satisfying increase in the extent to which the alkyl groups are present at the surface of the [C$_{12}$mim] surface, as illustrated in Figure 4. Recognizing that Figure 4b is only a single representative snapshot of a small area of the surface, it nevertheless agrees qualitatively with the conclusion above that the alkyl chains and the nonalkyl components are both significantly exposed at the [C$_{12}$mim] surface. The simulations provide a level of detail not yet easily accessible experimentally, including a prediction that the last ∼6 units of the C$_{12}$ chain tend to lie flat on the surface. Related information has been inferred on these and similar ionic liquid systems from a number of the distinct experimental methods discussed above, including nonlinear spectroscopies[4] and ARXPS.[11,14−16] The majority of the previous methods, and indeed earlier molecular dynamics simulations,[10,37,38] predict some form of preference for alkyl chains to project out of the liquid surface. Perhaps the major disagreement is with direct recoil spectroscopy.[12] We speculate that this may be related to the fact that the current photolytic and even the molecular beam methods are much "gentler" than direct recoil spectroscopy as previously implemented with

higher-energy particles such as Ar$^+$ and Ne$^+$ ions.[12] The current methods are also much more chemically specific, relying on the particular reactivity of the incoming atoms toward a selected functional group or groups.

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Turning to future prospects for these techniques, the abstraction of H atoms by O(^{3}P) could obviously be applied to other ionic liquids. It would provide an independent test of the influences on surface composition of variables such as chain length and the nature of the anion that have been inferred using other techniques.[14,15] The method could be extended to the site as well as the overall group or atom-type specificity by the simple (at least in principle, although it may involve nontrivial synthetic chemical effort) expedient of site-specific isotopic labeling. We have used this approach in related work as a way to establish unambiguously the depth of penetration of O(^{3}P) into alkylthiolate SAMs.[39] Interestingly, perhaps reminiscent of the situation with direct recoil spectroscopy on ionic liquids above, we again found distinct contrasts with the previous conceptually similar experiments of Jacobs[40] using much higher energy ionic projectiles. We have considered the possible reasons for the differences,[39,41] which perhaps most probably relate to the escape probability of the OH$^-$ anions detected in the Jacobs experiments.

However, there is a potentially much wider range of other suitable projectiles that could, in principle, be used as probes of the availability of specific atoms or groups at liquid surfaces. Interfacial reaction of Cl has already been demonstrated with squalane[18] but not pursued beyond that in an analytical sense, as is similarly the case with F atoms.[30,31] Electronically excited species such as O(^{1}D) provide an interesting alternative, being known to be much more reactive, but via very distinct mechanisms, than O(^{3}P). The use of different probes cannot only provide sensitivity, in principle, to different elements or groups but also may offer the interesting possibility of variable depth resolution. Recent scattering calculations on F atoms with hydrocarbon surfaces[42] predict that they react very efficiently with essentially the first group that they encounter at sites consequently confined to the extreme outer layers. In contrast, less reactive O(^{3}P) atoms subject to higher activation barriers are predicted to penetrate somewhat deeper into hydrocarbons,[43] indeed consistent with our experiments on the labeled SAMs above.[39] Theory also predicts[44,45] a significant collision energy dependence to the depth of penetration. As we have remarked above, there is evidence for this in Figure 3, where, even allowing for the different numbers of potentially reactive atoms, there is a

difference in relative OH yields from the shortest- and longest-chain $[C_n\text{mim}][NTf_2]$ ionic liquids with high- and low-energy $O(^3P)$ atoms. The higher-energy atoms appear more able to reach the ethyl and methyl groups in $[\text{emim}][NTf_2]$, consistent with the prediction in the MD simulations[3] that they are more deeply buried than the alkyl chains in $[C_{12}\text{mim}][NTf_2]$. The projectile kinetic energy may therefore provide another experimental handle that could be used for depth profiling.

The probes need not also be restricted to atoms; the same methods could easily be extended to small reactive molecular radicals. Although we have emphasized above the particularly direct type of experiment in which the projectile abstracts an atom and therefore reports on its availability at the liquid surface, there is also the alternative of monitoring the loss of the projectile and inferring from this the presence of selectively reactive groups. We have, for example, already demonstrated the reactive loss of OH at the squalane surface[46] by comparison with an inert reference liquid (PFPE). This could, in principle, be extended to liquids containing other functional groups, which would be of direct atmospheric relevance given the known role of OH in the heterogeneous aging of aerosol particles.[47−49] Although again less apparently conclusive than abstraction reactions, the inelastic scattering of projectiles can also contain chemically specific information on the surface. In the molecular beam experiments of Minton and co-workers, the differences in the translational energy distributions between $O(^3P)$ atoms inelastically scattered from the $[C_n\text{mim}][NTf_2]$ ionic liquids[3] and those from squalane[17,19] indicate the presence of $[NTf_2]$ anions at the surface, corroborating the OH reactive product observations. Similarly, very recent work by the Nesbitt group[50] on ionic liquids in the same family as those described above has shown that inelastically scattered CO_2 contains a signature of the presence of the anion groups at the liquid surface.

The applications highlighted above have been confined to low-vapor-pressure liquids due to the method of surface preparation. However, there are many extensions that become possible for liquids with higher vapor pressures if the scattering can be carried out at the surfaces of the liquid jets. These have been used successfully in conjunction with a number of other surface probe techniques, including nonlinear spectroscopy.[51] This opens up particularly the possibility of studies of aqueous systems.

Although some technical challenges clearly remain to be overcome for these methods to be implemented more widely, we see the prospect for rapid future development in this area and anticipate that the scattering of gas-phase probe species will increasingly be used to interrogate the surfaces of chemically interesting liquids.

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Carla Waring was an undergraduate student at Heriot-Watt University and is currently completing her graduate studies there in gas−liquid interfacial dynamics, leading to a Ph.D.

Paul Bagot did his graduate research studies in Materials Science at The University of Oxford, after which he held a position as a Higher Research Scientist at the National Physical Laboratory. He joined Heriot-Watt University as a postdoctoral researcher and served a period as a temporary lecturer in Physical Chemistry. He has very recently returned to the University of Oxford.

Matthew Costen also began his research career in Oxford with Gus Hancock. He went on to complete a postdoctoral fellowship with Greg Hall at Brookhaven National Laboratory. He won a BP-Royal Society of Edinburgh Fellowship, held at Heriot-Watt University, where he was subsequently an RCUK Academic Fellow and is now a Lecturer in Physical Chemistry.

Kenneth McKendrick is Professor of Physical Chemistry at Heriot-Watt University, leading a group (see http://www.che.hw.ac.uk/laser/index.htm) with broad interests in reactive and inelastic collision dynamics in the gas phase and at gas−condensed-phase interfaces. He did his graduate work under Gus Hancock at the University of Oxford, followed by an EPSRC-NATO Fellowship with Dick Zare at Stanford University. He held a lectureship at The University of Edinburgh before taking up his current position.

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