Supporting Information: Reactive-Atom Scattering from Liquid Crystals at the Liquid-Vacuum Interface: [C₁₂mim][BF₄] and 4-Cyano-4'-Octylbiphenyl (8CB)

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[C₁₂mim][Tf₂N] Synthesis and Characterization

1.1. General considerations

All air-sensitive experimental procedures were performed under an inert atmosphere of nitrogen using standard Schlenk line and glovebox techniques. Toluene was purified with the aid of an Innovative Technologies anhydrous solvent engineering system. 1-methylimidazole was dried over calcium hydride and distilled under reduced pressure. 1-bromododecane was distilled immediately prior to use in the presence of activated 4 Å molecular sieves under reduced pressure. ¹H NMR spectra were acquired at 298 K on a JEOL ECX-400 using an operating frequency of 399.78 MHz. The ionic liquids synthesized are highly hygroscopic and should be stored under an inert atmosphere.

1.2. Preparation of 1-dodecyl-3-methylimidazolium bromide, [C₁₂mim][Br]

A slight excess of freshly distilled 1-bromododecane (170.5 g, 177 mL, 0.73 mol), distilled 1methylimidazole (56.6 g, 55 mL, 0.69 mol) and dry toluene (150 mL) were heated at 60 °C under nitrogen overnight. The homogeneous solution obtained was concentrated under vacuum at 60 °C to give a white solid, which was ground in the glovebox and further dried under vacuum (~ 10⁻² mbar) at 60 °C for 7 days (219.0 g, 96% yield). ¹H NMR (400 MHz, D₂O, 298 K), δ (ppm): 7.42 (*s*, 1 H), 7.37 (*s*, 1 H), 4.13 (*t*, ³*J* = 6.7 Hz, 2 H), 3.83 (*s*, 3 H), 1.85-1.80 (*m*, 2 H), 1.22 (*br s*, 18 H), 0.81 (*t*, ³*J* = 5.6 Hz, 3 H).

1.3. Preparation of 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,

[C₁₂mim][Tf₂N]

[C₁₂mim]Br (124.2 g, 0.38 mol) was dissolved in deionized water (300 mL) and treated with a solution of Li[Tf₂N] (109.0 g, 0.38 mol) in deionized water (300 mL). The biphasic system was stirred overnight at room temperature. The IL phase was separated and thoroughly washed with deionized water (16 × 100 mL). Efficient removal of halides was tested by addition of a solution of AgNO₃ in deionized water to an aliquot of the aqueous phase from the previous wash. The pale yellow oil was then dried under vacuum (~ 10⁻² mbar) at 60 °C for 7 days (165.7 g, 83% yield). ¹H NMR (400 MHz, acetone- d_6 , 298 K), δ (ppm): 8.78 (*s*, 1 H), 7.56 (*m*, 1 H), 7.50 (*s*, 1 H), 4.28 (*t*, ³*J* = 7.0 Hz, 2 H), 3.99 (*s*, 3 H), 2.00-1.93 (*m*, 2 H), 1.30 (*br s*, 18 H), 0.92 (*t*, ³*J* = 6.6 Hz, 3 H).





Figure S1: RAS-LIF setup showing vacuum chamber, carousel, photolysis and probe laser beams.

Figure S1 shows the RAS-LIF apparatus. The vacuum chamber had a 10" cylindrical design and had a base pressure of $\sim 3 \times 10^{-7}$ mbar. The chamber had a CF100 port to which a rotatable flange (M-RP-100CF, LewVac, U.K.) was mounted. The carousel was attached to the rotation flange and could be rotated through 360°. The center of the carousel consisted of a copper block which had four bearing blocks attached. Each bearing block had an 8 mm axle attached to a stainless steel wheel of diameter 5 cm. The four wheels were rotated simultaneously by a single intersecting bevel gear at the center of the carousel. This was driven by a 10 mm diameter axle which was connected *via* a feedthrough to a motor outside the vacuum chamber, which rotated at 20 rpm due to gearing on the carousel. The liquid baths were made of stainless steel (304) and were detachable for cleaning. Photolysis of NO₂ was induced by a laser (Continuum Surelite II, 355 nm, ~60 mJ per pulse, ~5 ns FWHM). This photolysis beam was elliptical with major and minor axis lengths of 6 mm and 4 mm, respectively. The major axis was parallel to the wheel surface. The beam passed parallel to the wheel surface at a distance of 6.7 mm and at a height of 15 mm above the wheel axis. The probe beam was provided by a Sirah Cobra Stretch, (281-283 nm, 250 μ J, ~5 ns FWHM, Rhodamine 6G, 2400 line/mm, KDP doubler) pumped by a frequency-doubled Nd:YAG laser (Continuum Surelite II). The probe beam was approximately circular with an irised diameter of 4 mm and had an energy of 250 μ J. Both photolysis and probe lasers were operated at 10 Hz.

To collect the fluorescence from the OH molecules, a liquid light guide (Ultrafine 300) was placed perpendicular to the laser beam axis 20 mm above the probe beam. Two dichroic filters (308 nm center, 8 nm FHWM, peak transmission 60%) were placed between the light guide and a photomultiplier tube (Thorn EMI 9813QB) to spectrally isolate the fluorescence signal. The fluorescence signal was recorded using an oscilloscope (LeCroy Wavesurfer 3024, 200 MHz) and was sent to a data acquisition computer. The oscilloscope was triggered from the Q-switched signal from the probe laser. The fluorescence signal was gated with a window (2 μ s wide) positioned just after the probe pulse, to exclude signal generated by scattered light from the probe beam. A background window (250 ns wide) positioned before the probe pulse was used to correct for DC fluctuations. Timing between the probe and the photolysis lasers was controlled by a delay generator (Quantum Composers 9520).

The measured OH fluorescence intensity depends strongly on the distance between the probe beam and wheel surface.¹ Therefore, the relative distance between each of the wheels in the carousel was adjustable and set to be within $\pm 125 \ \mu$ m, which is sufficiently small to contribute negligibly to variations in the OH LIF signal magnitude from each wheel.

Temperature control of the carousel was *via* a circulator (Cole Parmer 6.5 L, Sil-180 fluid). Oil from the circulator was flowed through channels in the copper block of the carousel which in turn heated the liquid baths. The bulk temperature of the liquid under study was inferred by submersing a K-type thermocouple into the squalane liquid to measure its bulk temperature. A thermometer (RS 1314) was connected *via* a vacuum feed through to measure the bulk squalane temperature. Any systematic temperature difference between the squalane liquid and the liquid under study was estimated to be <1 °C. The precision of the bulk squalane temperature measurement during the experiment was calculated to be ± 0.5 °C (95%)

CL). The absolute temperature calibration of the thermocouple was stated to be ± 1.5 °C. Therefore the precision of the temperature measurement is expected to be ± 0.5 °C while the overall systematic uncertainty could be as large as ± 2.0 °C.

To record appearance profiles, an average of five individual profiles of 20 laser shots per 1 μ s time step were recorded. Additionally, scattered light contributions from the photolysis laser were subtracted prior to normalizing the profiles. These were recorded by scanning the delay between the photolysis and probe lasers with the probe laser blocked in order to measure the effect of the photolysis signal as it was stepped through the signal window on the oscilloscope.

RAS-MS Experimental Detail

The liquid reservoir contained a 5 cm diameter stainless steel wheel that was rotated by a motor mounted onto the reservoir in vacuum. The reservoir was made from aluminum. The bulk liquid in the reservoir was heated using a 1/8" OD coil of stainless steel tubing that was immersed into the liquid. Water was flowed through the coil from a circulator and the bulk liquid temperature was monitored using a thermocouple attached to the outside of the liquid reservoir. The estimated uncertainty was ± 1 °C. The reservoir was mounted on a manipulator and aligned such that the wheel surface normal was in the plane defined by the incident beam and the detection axis. Care was taken to ensure that the wheel surface coincided with the center of rotation of the mass spectrometer. The angular error was estimated to be $<2^{\circ}$. The manipulator also allowed the reservoir to be lowered out of the path of the beam so that the incident O-atom beam could be interrogated.

The O-atom beam was created using a CO₂ TEA laser (7 J pulse⁻¹) whose output was focused into a conical nozzle as an O₂ gas pulse from a stagnation pressure of 550 psig entered through a 1 mm hole in the apex of the nozzle cone. The rapidly heated, laser induced plasma in the throat of the nozzle created a detonation wave which dissociated and accelerated the oxygen gas, creating a largely dissociated neutral pulse that exited the nozzle with a nominal velocity of 8 km s⁻¹. The source chamber, where the O-atom beam was formed, had a base pressure of $\sim 3 \times 10^{-7}$ mbar and was pumped by a turbo pump (Osaka TG2400MBWC), which allowed the source to operate at 3 Hz. After formation in the source chamber, the hyperthermal beam passed through a skimmer into the main chamber ($\sim 3 \times 10^{-7}$ mbar) and then through a 1.3 mm collimating aperture. The total distance from the pulsed valve to the liquid surface was 0.99 m. The beam was velocity selected using a chopper wheel which provided a synchronous source from which the pulsed valve and laser were triggered.

To record a time-of-flight distribution, the signal was accumulated as a function of arrival time (including neutral flight time to the electron-bombardment ionizer and ion flight time to the Daly-type ion counter) over a period of 10 ms with a bin size of 1 μ s using a multichannel scaler. For each temperature studied, the total number of beam pulses collected was 1000 for O and OH, 2000 for H₂O, and 4000 for O₂.

RAS-MS: Analysis of Time-of-Flight Distributions from [C₁₂mim][BF₄]

Figure S2 shows representative time-of-flight distributions for O, OH, and H₂O from $[C_{12}mim][BF_4]$ at temperatures of 33 °C, 40 °C, and 60 °C. The angle of incidence, θ_i , was 60° and the final angle, θ_f , was 15°. Each TOF distribution was normalized to the peak number of counts and has the *x*-axis corrected such that it corresponds to the neutral flight time of scattered species from the liquid surface to the ionizer of the detector, 33.7 cm away. The overall shape of each distribution is bimodal and characteristic of the empirical impulsive scattering (IS) / thermal desorption (TD) separation widely observed in previous work on ILs and other liquids.² In liquid-surface scattered products that retain much of their incident momentum; the fastest-moving IS species arrive at the detector first and are interpreted unambiguously as being predominantly from single or few-collision impulsive scattering other products, that on average arrive later and can be described by a Maxwell-Boltzmann velocity distribution characterized by the surface temperature.



Figure S2: Representative time-of-flight spectra for O, OH, and H₂O from $[C_{12}mim][BF_4]$ at 33 °C, 40 °C and 60 °C. The total signal (yellow circles) at longer flight times is fitted with a Maxwell-Boltzmann velocity distribution determined by the liquid temperature (red lines). The IS TOF distributions (blue lines) are generated by subtracting the fitted Maxwell-Boltzmann distributions from the total signals.

To analyze the data in Figure S2, a Maxwell-Boltzmann distribution was fitted to the slower moving species and then subtracted from the total TOF to leave the IS component of the TOF. The apparent bimodality in the IS component has been discussed previously.⁵ To quantify the number of molecules or atoms in the IS and TD components, each respective TOF was converted to flux and integrated using the relation — , where I(t) is the flux, N(t) is the number of counts at the detector as a function of flight time, t, and is the width of the bin in the distribution. For the IS component, the upper and lower limits of the integration were set to be the average energy of the incident O beam energy and $2kT_l$, respectively, where k is Boltzmann's constant and T_l is the liquid temperature. $2kT_l$ is the average energy of a particle that desorbs in thermal equilibrium with the surface.⁶ The TD flux component was calculated by integrating the Maxwell-Boltzmann function that was fitted to the TOF. To calculate the average energy, , of the IS component, the O, OH, and H₂O TOFs were converted to an energy distribution *via* the transformation $P(E_f) \propto t^2 N(t)$ and an average was computed, for which the limits of the integration were the same as used to calculate the flux. The translational energy distribution of the incident O beam was approximated to a single translational energy equal to the average translational energy. Under this approximation, the effects of the shape of the O beam velocity distribution can be ignored. This monoenergetic beam approximation has been shown to be valid when considering the average final energies of the scattered species.^{5,7}

RAS-LIF: Rotational Populations from [C₁₂mim][BF₄] and 8CB

The excitation spectra recorded from $[C_{12}mim][BF_4]$ used a step size of 0.0025 nm, and data were collected for 30 laser shots at each step. The photolysis-probe delay was fixed at 15 µs. This process was repeated five times at liquid temperatures of 30.5 °C and 65.0 °C. Spectra were recorded on the $Q_1(N)$ branch.

The excitation spectra recorded from 8CB used a step size of 0.001 nm, and data were collected for 30 laser shots at each step. The photolysis-probe delay was fixed at 15 μ s. This process was repeated ten to twelve times at liquid temperatures of 20.0 °C, 26.5 °C, 36.5 °C, and 42.5 °C. Spectra were recorded on the R₁(*N*) branch only.

The rotational populations for 8CB and $[C_{12}mim][BF_4]$ were extracted using LIFBASE.⁸ The populations were normalized over the number of respective rotational levels sampled. Figure S3 shows normalized populations up to N = 5 from $[C_{12}mim][BF_4]$, and Figure S4 shows normalized populations from 8CB up to N = 6 at 20.0 °C, 26.5 °C, 36.5 °C, and 42.5 °C.



Figure S3: $[C_{12}mim][BF_4]$ rotational populations for 30.5 °C and 65.0 °C. Error bars are 95% confidence limits.



Figure S4: 8CB normalized rotational populations at various bulk temperatures. Error bars are 95% confidence limits.

RAS-LIF: 8CB HONO Contribution Estimation

The procedure for correcting for the HONO contribution to the surface reactivity in RAS-LIF is described in detail in previous work.⁹ The inelastically scattered OH was generated by photolysis of a HONO precursor gas at 355 nm, at a pressure of 1 mTorr. Figure S5 shows the inelastically scattered OH signal from the 8CB surface at 26.5 °C, corresponding to the smectic A phase. An averaged HONO appearance profile was typically comprised of 20 individual photolysis-probe delay scans. Also shown in Figure S5 is the averaged 8CB appearance profile over the temperature range 20.0 °C to 31.5 °C. The early peak in the 8CB appearance profile close to t = 0 corresponds to OH that is still in the probe volume after the photolysis of the background HONO. It also provides a measure of the background HONO concentration.



Figure S5: 8CB LIF signal overlaid with a scaled HONO LIF signal. The ripple noise on the HONO signal is due to background 8CB fluorescence. Errors are 95% confidence limits.

Only a single HONO appearance profile, recorded from 8CB at 26.5 °C, was used to fit all of the data. Nominally, a HONO appearance profile would be recorded at the same temperature for each reactive appearance profile. Given the overall the magnitude of the HONO contribution as seen in Figure S5, and the error in its scaling, this was deemed unnecessary. In general, HONO appearance profiles have such small inelastic OH signals that any variation between surface conditions cannot be resolved. This was confirmed by recording HONO profiles from squalane and 8CB at 26.5 °C and 44.0 °C. No significant difference could be seen between the liquids or temperatures. Therefore, the best quality HONO appearance profile was selected in order to proceed with the analysis. In Figure S5, the error in scaling the HONO profile is mainly due to noise in the HONO and 8CB appearance profiles in the 2-4 μ s region, which was caused by background fluorescence from 8CB.

To estimate the average inelastic OH contribution to the 8CB reactivity, the 8CB profiles were averaged from 20.0 °C to 31.5 °C to form a "cold" temperature 8CB appearance profile

and from 33.5 °C to 46.0 °C to form a "hot" temperature 8CB appearance profile. A HONO appearance profile was then scaled to the decay of the early peak in each of these averaged profiles. A squalane appearance profile, generated from an average of all temperatures was also fitted with a HONO appearance profile. The three resultant scaled HONO profiles were then integrated over the range, 9 μ s to 30 μ s, which was used for all integrals in this analysis. The hot and cold 8CB appearance profiles were then integrated and divided by the squalane appearance profile integral.

	Average reactivity relative to	Estimated average HONO correction,
	squalane (%)	relative to squalane (%)
8CB Hot	0.324	~ -0.012
8CB Cold	0.518	~ -0.013

Table S1. Estimated average HONO contribution to averaged 8CB profiles.

Each respective HONO integral was subtracted from the squalane, and hot and cold 8CB profile integrals. The difference between these corrected and uncorrected integrals was used to estimate the size of the HONO contribution to the reactivity. The results are shown in Table S1. The reactivity relative to squalane represents the uncorrected integrals from hot and cold 8CB, while the HONO correction is expressed as a percentage of the squalane reactivity. The correction for both 8CB averaged profiles is \sim 1%.

RAS-MS: OH and H₂O Product Ratios



Figure S6: Product flux ratio for a) OH/O and b) H₂O/O as a function of bulk temperature.

Figure S6 shows the product ratios for OH and H_2O , respectively, relative to O at 33 °C, 40 °C, and 60 °C. The product ratio was calculated from the sum of the IS and TD fluxes of O and the respective product, OH, or H_2O . Both product ratios show there was little change with temperature over the angular range studied.

RAS-MS: IS/TD Ratio

Figures S7 (a) to (c) show the IS/TD flux ratios for O, OH, and H₂O at 33 °C, 40 °C, and 60 °C. For the O-atom ratios, there is little difference between temperatures at low final angles. At higher final angles $\theta_f > 50^\circ$, the 60 °C data diverges slightly from the 33 °C and 40 °C data, showing a decrease in the IS/TD ratio at large final angles. This is consistent with thermal roughening for inelastically scattered atoms and has been reported previously for $[C_{12}mim][Tf_2N]$.²



Figure S7: IS/TD ratio for each detected species as function of bulk temperature.

MD Simulation Detail

Molecular dynamics simulations were used to model directly the vacuum-liquid interface of $[C_{12}mim][BF_4]$ following a procedure similar to that reported previously.⁹ Briefly, all calculations where performed with GROMACS¹⁰ using the CL&P¹¹ additions to the OPLS-AA^{12,13} force field. A vacuum-liquid-vacuum slab structure was generated using 640 ion pairs in a 8.6 nm x 7.9 nm x 15.6 nm unit cell. 3D periodic boundary conditions, CH bond constraints, and a 2 fs time step were used throughout. Long-range electrostatic interactions were computed with the smooth-particle mesh Ewald method. Following 500 ps of simulated annealing at 500 K, the liquid slab system was propagated toward equilibrium for a total of 4 ns under NVT ensemble conditions at 323 K. The final frame of this trajectory was used as a representative snapshot of the vacuum-liquid surface structure. Atom number density profiles for selected atoms were computed by averaging information in the final 1 ns of this trajectory.

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