

Quantum state-resolved molecular scattering of NO ($^2\Pi_{1/2}$) at the gas-[C_nmim][Tf₂N] room temperature ionic liquid interface: Dependence on alkyl chain length, collision energy, and temperature

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Room temperature ionic liquids (RTILs) represent a promising class of chemically tunable, low vapor pressure solvents with myriad kinetic applications that depend sensitively on the nature of gas-molecule interactions at the liquid surface. This paper reports on rovibronically inelastic dynamics at the gas-RTIL interface, colliding supersonically cooled hyperthermal molecular beams of NO ($^2\Pi_{1/2}$, $N = 0$) from 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (or [C_nmim][Tf₂N]) and probing the scattered NO molecules via laser induced fluorescence (LIF) from the A($^2\Sigma$) state. Specifically, inelastic energy transfer into NO rovibrational and electronic degrees of freedom is explored as a function of RTIL alkyl chain length (n), incident collision energy (E_{inc}) and surface temperature (T_s). At low collision energies ($E_{\text{inc}} = 2.7(9)$ kcal/mol), the scattered NO molecules exhibit a rotational temperature (T_{rot}) systematically *colder* than T_s for all chain lengths, which signals the presence of non-equilibrium dynamics in the desorption channel. At high collision energies ($E_{\text{inc}} = 20(2)$ kcal/mol), microscopic branching into trapping/desorption (TD) and impulsive scattering (IS) pathways is clearly evident, with the TD fraction (α) exhibiting a step-like increase between short ($n = 2, 4$) and long ($n = 8, 12, 16$) alkyl chains consistent with theoretical predictions. For all hydrocarbon chain lengths and RTIL temperature conditions, NO rotational excitation in the IS channel yields hyperthermal albeit Boltzmann-like distributions well described by a “temperature” ($T_{\text{IS}} = 900$ –1200 K) that decreases systematically with increasing n . Non-adiabatic, collision induced hopping between ground and excited spin-orbit states is found to be independent of RTIL alkyl chain length and yet increase with collision energy. The scattering data confirm previous experimental reports of an enhanced presence of the alkyl tail at the gas-RTIL interface with increasing n , as well as provide support for theoretical predictions of an alkyl length dependent shift between chains oriented parallel vs. perpendicular to the surface normal. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4966045>]

I. INTRODUCTION

Room temperature ionic liquids (RTILs) are molten salts with melting temperatures < 100 °C which represent a novel class of green solvents with high electrical/thermal conductivity,¹ low vapor pressures,² and high thermal stability.³ These novel liquids consist purely of ions and have many valuable applications in catalytic reactions,^{4–6} Li-ion batteries,^{7,8} fuel cells,^{9,10} CO₂ capture,^{11–14} and solar cells.^{15,16} Of particular practical importance is that interfacial and bulk properties of RTILs

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can be targeted for specific applications by either changing the anion/cation combination,^{17,18} or even simply varying functional groups within the ions. This results in enormous flexibility in the “design” of such RTILs, with well over 10^6 liquids feasible by combinatorial substitution.¹⁹ These effects are important not only in controlling bulk equilibrium properties (e.g., Henry’s Law solubilities) as well as non-equilibrium dynamical processes, such as molecular solvation kinetics at the gas-liquid interface. An outstanding challenge to the chemical physics community has been to provide a more fundamental and predictive understanding of how cation/anion composition (e.g., cation hydrophobicity) might be used to “tune” the interfacial properties of these novel liquids.

Due to utility in several of the above mentioned applications, many RTIL studies to date have focused on imidazolium based cations with an aliphatic C_n side chain and bis(trifluoromethylsulfonyl)imide anions (denoted $[C_n\text{mim}][\text{Tf}_2\text{N}]$). For such $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs, the charge of the cation is delocalized over the imidazolium ring with a nonpolar alkyl side chain, while the $[\text{Tf}_2\text{N}]$ anion has its charge centered on the central $\text{N}(\text{SO}_2)_2$ group with two outer nonpolar CF_3 groups (Fig. 1). The C_n hydrocarbon chain length plays a crucial role in moderating intermolecular interactions, including hydrogen bonding, dispersion forces, π -stacking, and Coulomb attraction between the cation and anion. For example, dispersion forces between alkyl chains increase for longer hydrocarbons, affecting how the ions arrange and thus overall liquid properties. In particular, theoretical and experimental studies have reported on the formation of bilayers in the bulk for $n > 4$, where the long alkyl chains align, separating charged layers of anions and imidazolium cation

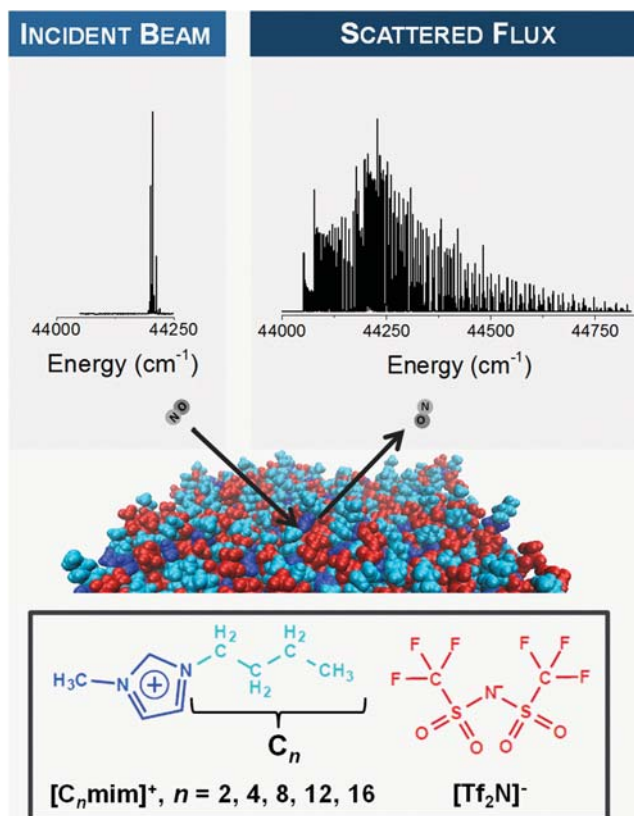


FIG. 1. Experimental cartoon for studies of supersonically cooled NO scattered at $\theta_{\text{inc}} = 45^\circ$ from $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs and detected via laser induced fluorescence (LIF) at near specular angles ($\theta_s = 45^\circ$). Sample LIF spectra are shown in the top panels, with only the $^2\Pi_{1/2}$ state populated and $T_{\text{rot}} \sim 1$ K in the incident beam (top left), whereas the scattered NO flux (top right) shows significant electronic and rotational excitation with both spin-orbit states and rotational states up to $J = 45.5$ observed. The $[C_4\text{mim}][\text{Tf}_2\text{N}]$ surface snapshot was constructed by molecular dynamics simulations by Schatz et. al.,⁴⁸ where the Tf_2N anion is shown in red, the cation imidazolium ring is dark blue and the cation alkyl chain is light blue. The relevant chemical structures of the ions are shown at the bottom of the figure. In the present work, we investigate a series of RTIL cations where the alkyl chain, C_n , is varied over $n = [2, 4, 8, 12, 16]$.

rings.^{3,20–22} Specifically for $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs, an increase in n is accompanied by an increase in bulk viscosity^{23,24} and yet a decrease in both density^{23–25} and ionic conductivity.²³ It is important to stress that bulk composition can in principle differ fundamentally from the gas-liquid interface. For example, the extreme “hydrophobicity” of the vacuum likely plays a dominant role in structure and chemical composition of the interfacial region, which clearly motivates further study of the top most interfacial layer itself.

The gas-liquid interface is particularly crucial for applications such as CO_2 sequestration and supported ionic liquid phase (SILP) catalysis,⁴ where the adsorption of gas molecules on the liquid surface is a critical first step for dissolving in the liquid. Many experimental techniques have been exploited to investigate the RTIL liquid surface, including surface tension measurements,^{24–26} sum frequency generation (SFG),^{27–31} neutral impact collision ion scattering spectroscopy (NICISS),^{21,32} angle-resolved X-ray photoelectron spectroscopy (ARXPS),^{32–37} X-ray diffraction,^{31,38} neutron reflectivity,³⁹ low-energy ion scattering (LEIS),⁴⁰ metastable atom electron spectroscopy (MAES),⁴¹ and molecular beam scattering,^{42–47} as well as molecular dynamics simulations.^{43,48,49} Each of these studies has varying levels of explicit surface vs. subsurface sensitivity and are therefore capable of extracting different information relevant to the interface, such as density and atomic composition (ARXPS, NICISS, LEIS) or molecular orientation (SFG, MAES). The combination of experimental and theoretical efforts have begun to build up a more complete picture of these liquid surfaces, and specifically have identified for $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs the presence of both anions and cations at the interface.^{32,36,37,40,41,43,48,50} In particular, the studies suggest a preference for nonpolar alkyl chains at the surface pointing into the vacuum with the charged imidazolium rings directly below in the liquid.^{32,41,49} Similarly, the bulky nonpolar CF_3 moieties of the Tf_2N anions point out from the surface,^{36,37,41,48,49} resulting in aggregation of both ionophobic (alkyl chains and CF_3 groups) and ionophilic (anion centers and cation imidazolium rings) groups.

While experiment and theory agree that both anions and cations are present at the gas-liquid interface, the fractional population of anions is found to decrease as n increases.^{25,40–43} LEIS atomic composition studies of the liquid surface report that, as the alkyl chain is lengthened from $n = 2$ to 12, the anion signals diminish by 4x but do not disappear entirely.⁴⁰ Elegant reactive scattering experiments of hyperthermal $\text{O}(^3\text{P})$ with RTILs producing OH radical products have also demonstrated an increased propensity for alkyl chains at the surface for larger n ,^{43,44} as well as sensitivity to fractional methylenic (CH_2) vs. methyl (CH_3) hydrocarbon presence at the interface. Of special interest, a change in the orientation of molecules at the gas-liquid interface has been observed as alkyl chains are lengthened in $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs. For short alkyl chain lengths ($n \leq 4$), both experiment^{29,31} and simulation^{43,48,49} suggest that the alkyl chains point parallel to the surface normal, while for longer hydrocarbons ($n \geq 5$), these appear to “flop over” and lie more or less parallel to the surface plane.^{32,43}

The present study significantly extends our previous efforts^{46,47} to elucidate equilibrium/non-equilibrium collision dynamics of radicals at the gas-RTIL interface, and how these dynamics are affected by conformation changes at the surface. This is done specifically via quantum state-resolved molecular beam scattering as a function of (i) incident collision energy (E_{inc}), (ii) surface temperature (T_s) and (iii) alkyl chain length of the imidazolium cation (n). Full quantum state-to-state resolution of the scattering dynamics is made possible with a supersonically cooled (1K) beam of NO, with the scattered molecules sensitively detected with laser induced fluorescence (LIF). The presence of multiple low-lying electronic states in NO allows *nonadiabatic* surface hopping dynamics to be observed, in addition to inelastic *rovibrational* excitation within the four spin-orbit and Λ -doublet electronic manifolds. In particular, the results provide additional confirmation of fractional population and orientation of alkyl chains at the RTIL surface, as well as insight into how such conformational changes affect state-resolved collision dynamics at the gas-liquid interface.

II. EXPERIMENTAL

The apparatus has been described in detail previously; we present only a brief overview of conditions relevant to the present study.^{46,47} Quantum state-resolved molecular beam experiments at the gas-liquid interface have been carried out for jet cooled $\text{NO}(^2\Pi^{1/2} \text{ (N=0)})$ projectiles^{47,51}

scattering from 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, or $[C_n\text{mim}][\text{Tf}_2\text{N}]$, as a function of i) alkyl chain length ($n = 2, 4, 8, 12$, and 16), ii) collision energy ($E_{\text{inc}} = 2.7$ and 20 kcal/mol) and iii) surface temperature ($T_s = 293 - 373$ K). The center panel in Fig. 1 displays a sample theoretical snap shot at the $[C_4\text{mim}][\text{Tf}_2\text{N}]$ gas-liquid interface, obtained from quantum mechanics/molecular mechanics (QM/MM) simulations by Schatz et. al.⁴⁸ The different molecular components are colored (anions in red, cation imidazolium rings in dark blue and cation alkyl chains in light blue), which highlight the abundance of different functional groups populating the liquid surface. All ionic liquids are purchased from Iolitec with $\geq 98\%$ purity, with samples stirred, heated and degassed for a minimum of 6 hours while pumped on with a liquid nitrogen trap, before being placed in a $4.4 \times 2.4 \times 0.5$ cm³ crucible in a stainless steel vacuum chamber with base pressures of 2×10^{-8} Torr. For each scattering study, the liquid temperatures are varied from 293 K (or 315 K for the highest melting point RTIL $[C_{16}\text{mim}][\text{Tf}_2\text{N}]$ ²⁰) to a maximum of 373 K, where the upper limit to our operating temperature range reflects the increase in vapor pressure with temperature.⁵² Scattering experiments are performed on a stationary liquid surface, with indistinguishable results obtained for sample data skimming of the liquid surface every five minutes. The molecular beam is produced from an Even-Lavie pulsed valve with a 100 μm diameter pinhole and 3000 Torr backing pressure, yielding rotationally cold ($T_{\text{rot}} \approx 1$ K) NO molecules in the ground spin-orbit state ($^2\Pi_{1/2}$). The molecular beam is comprised of 1% NO doped into either H₂ or Ne-70 (70% Ne and 30% He), which yields beam-surface collision energies of $E_{\text{inc}} = 20(2)$ and $2.7(9)$ kcal/mol, respectively. A 3 mm diameter skimmer results in a collimated beam striking the liquid surface at $\theta_{\text{inc}} = 45^\circ$ with a 1.5° half angle divergence.

Molecular scattering in the specular direction ($\theta_s \approx 45^\circ$) is detected with quantum state resolution via LIF, yielding density measurements of rovibrational and electronic state populations. A pulsed UV light source (225 nm) is generated by tripling the output of a YAG-pumped dye laser operating with LDS-698 dye at 10 Hz. Final state distributions of NO 1.6 cm above the liquid surface are probed on the ($A^2\Sigma^+ \leftarrow X^2\Pi$) γ band, with the laser scanned over 800 cm^{-1} to access $J \leq 45.5$ for each electronic manifold, spin-orbit and Λ -doublet state ($^2\Pi^e_{1/2}$, $^2\Pi^f_{1/2}$, $^2\Pi^e_{3/2}$, $^2\Pi^f_{3/2}$). The fluorescence signals (normalized to laser pulse energy and $< 5\text{ }\mu\text{J/pulse}$ to ensure operation in the linear regime) are imaged on a photo-multiplier tube (PMT) with spatial filtering to limit the probe volume to 15 mm^3 . Data are primarily taken near $\theta_s = 45(6)^\circ$, with additional tests of angle resolved scattering at $\theta_s = -60(3)^\circ$, $0(12)^\circ$, and $60(3)^\circ$. The PMT is electronically gated at the peak of the arrival time distribution, which, for an 80 μs gas pulse duration, reflects both thermally desorbing (TD) and hyperthermally scattering (IS) pathways. LIF spectral scans are analyzed with homemade software and STARPAC least squares subroutines^{51,53} to fit overlapping peaks and extract populations for each quantum state. The quantitative accuracy of the procedure is confirmed by Boltzmann analysis of room temperature NO thermally equilibrated (298 K) with the vacuum chamber.

III. RESULTS

Sample LIF spectra ($E_{\text{inc}} = 20(2)$ kcal/mol) for both i) incident and ii) scattered NO molecules are found in the top panel of Fig. 1, which highlight the extreme differences between incident (1K) and outgoing (collisionally excited) quantum state distributions. Scattered NO ($v=0$) molecules are detected with up to $J = 45.5$ for both e/f parities within each spin-orbit manifold, $^2\Pi_{1/2}^{(e,f)}$ and $^2\Pi_{3/2}^{(e,f)}$. Since all incident NO molecules have been cooled into the ground $^2\Pi_{1/2}$ state, electronic spin-orbit excitation at the gas-liquid interface represents a significant pathway, with clear differences between *spin-orbit conserving* collisions than *spin-orbit changing* collisions. By way of contrast, no statistically significant differences are observed between the two Λ -doublet states within each spin-orbit manifold, for which we report only populations averaged over e/f parity channels for the remainder of this paper.

The rotational populations within each spin-orbit manifold can be further analyzed in logarithmic Boltzmann plots of population scaled by rotational degeneracy vs. total internal energy, as displayed in Fig. 2. At low incident collision energies ($E_{\text{inc}} = 2.7(9)$ kcal/mol), where all molecules accommodate with the liquid surface, the data are well fit to a single straight line reflecting a single temperature Boltzmann distribution. Note that this rotational temperature is close to but distinctly cooler

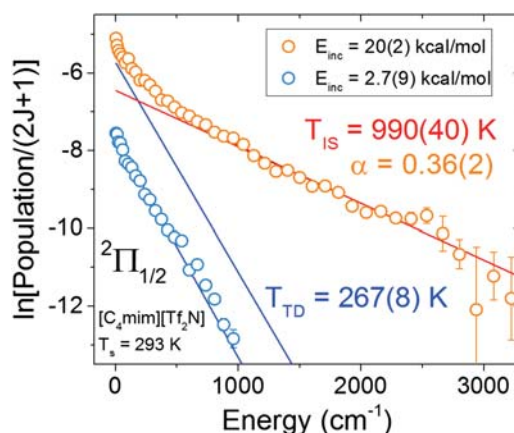


FIG. 2. Boltzmann plots of scattered NO rotational populations for $E_{\text{inc}} = 2.7(9)$ and $20(2)$ kcal/mol. At low E_{inc} , rotational populations fit well to a line, describing molecules thermally desorbing from the surface that are characterized by a single rotational Boltzmann temperature. At higher E_{inc} , significant curvature is observed, which can be well fit to a simple two-temperature model physically representing the TD and IS scattering pathways. The colder component is fixed at T_{rot} from the data at low E_{inc} , while the hotter component, T_{IS} , and the branching ratio into the TD channel, α , are floated.

(≈ 30 K) than the surface temperature ($T_S = 293$ K). This *non-equilibrium* behavior is consistent with our previous NO gas-liquid studies,⁴⁷ but in clear contrast to closed shell gas molecules such as CO_2 and HCl , which at similarly low E_{inc} desorb with rotational/translational distributions in *equilibrium* with the surface temperature.^{54,55} From detailed balance considerations, the CO_2 and HCl data imply unity sticking coefficients in the reverse (i.e., incident) direction, independent of quantum state, translational energy, and angle impinging on the surface. The dynamics for NO colliding with RTILs at low incident energies is clearly more complicated, as indeed confirmed by observation of similarly sub-thermal distributions in scattering experiments on other single crystal, liquid and molten metal surfaces.^{47,51,56–58} At the very least, detailed balance arguments imply a rotational state dependence to the sticking coefficients for NO in the reverse direction, with the *higher* NO rotational states being less likely to trap, accommodate and eventually desorb.

It is worth considering whether all NO molecules at these low collision energies trap on the surface, or whether there might still be some residual energy dependence to the sticking coefficient.

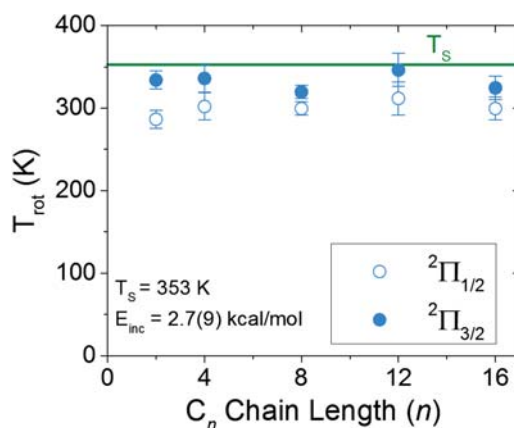


FIG. 3. Rotational temperatures for NO scattered from $[\text{C}_n \text{mim}][\text{Tf}_2\text{N}]$ at low $E_{\text{inc}} = 2.7(9)$ kcal/mol. These temperatures have been extracted from linear Boltzmann fits (e.g., see Fig. 3) for each spin-orbit state. Note that T_{rot} is systematically *lower* than T_S , while $T_{\text{rot}}(^2\Pi_{3/2})$ is consistently *hotter* (by ~ 30 K) than $T_{\text{rot}}(^2\Pi_{1/2})$. This signals the influence of non-equilibrium dynamics in the desorbing channel and, by detailed balance considerations, a rotational and spin-orbit dependence to the sticking coefficients in the adsorption event. Furthermore, increasing the cation chain length (n) for the RTIL does not appear to affect rotational temperatures at low E_{inc} .

Towards this end, we have initiated *angle-resolved* studies and obtained preliminary data on final angular dependent scattering at these low collision energies, probing at $\theta_s = -60^\circ, 0^\circ, 45^\circ$ and 60° . The results consistently support that rotational temperatures for the desorbing NO flux are i) independent of the final scattering angle and yet ii) weakly *sub-thermal* (≈ 30 K) with respect to the RTIL temperature. Thus, although a sub-thermal nature of the desorbing population signals a clear rotational state dependence to the adsorption event, the observed independence with respect to outgoing scattering angle implies an efficiency of trapping-desorption events independent of incident angle (as discussed in greater detail in previous work⁴⁷). Specifically, if accommodation of NO on RTILs has no dependence on incident beam angle, then, via detailed balance considerations, there can be no difference in the quantum state distributions probed as a function of scattering angle, as observed experimentally.

At high E_{inc} , distinct curvature is observed in these Boltzmann plots (Fig. 2), with significant contributions from molecules impulsively scattering (IS) from the surface and yielding excess population in high J states. These distributions can be fit to a two-temperature model^{46,47} where the total distribution reflects a sum of hot and cold components representing the IS and TD scattering pathways, and α reflects the microscopic branching between the TD and IS channel, summed over all final J states. To be consistent with this model, the (cooler) TD temperatures are fixed from the corresponding quantity observed at low E_{inc} , while the (hotter) component, T_{IS} , and branching fraction, α , are determined by least squares fit to the data. As seen in Fig. 3, the rotational temperatures obtained under such low $E_{\text{inc}} = 2.7(9)$ kcal/mol scattering conditions appear to be independent of RTIL chain length, within 1σ error bars based on repeated measurements. However, the rotational temperatures for both spin-orbit states are again systematically *below* the actual liquid temperature (solid line) for all RTILs probed, with a weak but clear additional sensitivity to the outgoing spin-orbit state. By detailed balance, these observations imply the presence of dynamical barriers

TABLE I. Summary of least squares analysis fit parameters for NO scattered from $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ at $E_{\text{inc}} = 20(2)$ kcal/mol as a function of T_s and C_n , for both ground ($^2\Pi_{1/2}$) and excited ($^2\Pi_{3/2}$) spin-orbit states.

α at $E_{\text{inc}} = 20(2)$ kcal/mol						
	Ts	$n = 2$	4	8	12	16
${}^2\Pi_{1/2}$	293	0.34(3)	0.22(2)	0.38(2)	0.32(2)	
	313	0.33(2)	0.26(3)	0.39(3)	0.29(3)	
	333	0.32(3)	0.29(3)	0.42(3)	0.37(3)	0.42(2)
	353	0.37(3)	0.31(3)	0.40(3)	0.40(3)	0.42(3)
	373	0.39(3)	0.33(3)	0.43(3)	0.41(3)	0.41(2)
${}^2\Pi_{3/2}$	293	0.22(3)	0.16(1)	0.28(2)	0.28(2)	
	313	0.23(2)	0.21(3)	0.32(3)	0.28(3)	
	333	0.26(3)	0.25(3)	0.34(3)	0.33(3)	0.38(2)
	353	0.29(3)	0.26(3)	0.36(3)	0.37(3)	0.44(3)
	373	0.29(3)	0.25(3)	0.36(3)	0.40(3)	0.37(3)
T_{IS} (K) at $E_{\text{inc}} = 20(2)$ kcal/mol						
	Ts	$n = 2$	4	8	12	16
${}^2\Pi_{1/2}$	293	1060(70)	1030(40)	920(40)	980(50)	
	313	1030(40)	1070(90)	930(70)	940(80)	
	333	1070(70)	1160(90)	970(70)	990(80)	880(30)
	353	1120(70)	1210(90)	930(70)	1030(80)	900(30)
	373	1140(70)	1070(90)	1050(70)	1180(80)	890(50)
${}^2\Pi_{3/2}$	293	1160(70)	1190(40)	1010(40)	1090(50)	
	313	1190(40)	1260(90)	1050(70)	1110(80)	
	333	1190(70)	1210(90)	1020(70)	1070(80)	1050(30)
	353	1140(70)	1280(90)	1050(70)	1080(80)	1100(30)
	373	1140(70)	1180(90)	1130(70)	1140(80)	1000(50)

to adsorption that depend on both rotational and spin-orbit state, but insensitive to length of the alkyl chain.

It is worth stressing that a simple description of the quantum state resolved scattering populations microscopically bifurcating into thermal (TD) and hyperthermal (IS) components *must fail* at sufficient level of scrutiny. Indeed, a quite plausible anticipation would be to observe a *continuum* of possible IS scattering pathways, as suggested in trajectory simulations^{59–63} with different molecular interaction potentials. In spite of such expectations, it is therefore remarkable that such a simple, dual-temperature model empirically fits the data over two orders of magnitude in dynamic range and, in particular, up to internal rotational energies more than 10-fold higher than kT_S (see Fig. 2). Although it is reasonable to exploit such behavior for a simplest empirical characterization of the data, our intention is for such quantum state resolved data to provide the requisite stimulus for development and testing of more sophisticated theoretical models that go beyond the canonical assumption of a microscopic bifurcation into TD/IS components.

With open shell species such as NO, we also probe collisional energy transfer at the gas-RTIL interface into low lying electronic degrees of freedom, with information on nonadiabatic scattering dynamics obtained from relative populations of the final spin-orbit states. As the incident NO molecules are cooled into the ground $^2\Pi_{1/2}$ state, the presence of NO($^2\Pi_{3/2}$) in the scattered flux necessarily represents nonadiabatic, surface hopping collisional events.⁶⁴ As the range of J states sampled is quite large ($J \approx 45.5$) one should confirm that NO is adequately described as a Hund's case (a) molecule, i.e., with spin and orbital angular momenta strongly coupled to the internuclear axis. This requires differences in NO end-over-end tumbling energies ($\Delta E \approx 2B_{\text{NO}}N$) to be comparable to or less than the spin-orbit energy splitting (E_{SO}), a condition satisfied up to all but the highest few NO rotational states detected. The spin-orbit distributions obtained as a function of surface temperature and alkyl chain length are summarized in Table I and will be discussed below in Sec IV.

IV. DISCUSSION

A. Alkyl chain length dependence

We first begin by considering the effects of alkyl chain length on the low E_{inc} scattering dynamics. Sample results are shown in Fig. 3 for a single liquid temperature ($T_S = 353$ K), with all error bars representing standard deviations of the mean obtained from multiple measurements. Although at these energies essentially all NO molecules trap and thermally desorb from the surface, this does not necessarily mean that the desorbing flux remains in equilibrium with the liquid temperature. Indeed, both ground and spin-orbit excited states are distinctly *cooler* rotationally than the surface temperature for all RTILs probed, which signals the presence of angular anisotropy and/or dynamical barriers for the desorption event as well as, from detailed balance considerations, rotational quantum state dependence in sticking coefficients for the incoming flux.⁴⁷ Furthermore, the spin-orbit excited ($^2\Pi_{3/2}$) state NO rotational distributions are consistently ~ 30 K hotter than the ground ($^2\Pi_{1/2}$) state, indicating sensitivity in these dynamical barriers and sticking probabilities at the gas-liquid interface to spin-orbit electronic excitation. As mentioned earlier, this behavior is reminiscent of NO dynamics scattering/desorption from single crystal metals (e.g. Ag(111) and Ru(001)), for which a similar propensity toward colder rotational distributions was reported.^{56,58}

Although the results in Fig. 3 reflect a single surface temperature ($T_S = 353$ K), the same qualitative trends are observed over a wide range of T_S , with desorbing NO rotational temperatures from low incidence energy scattering systematically *lower* than the liquid reservoir. Interestingly, Fig. 3 indicates both i) T_{rot} and ii) sub- T_S cooling trend in T_{rot} to be relatively *insensitive* to alkyl chain length. Based on a nearly unity trapping probability for jet cooled low J states of NO, such an independence on chain length is not surprising. The persistent cooling trend in T_{rot} implies that as RTILs are varied by lengthening the hydrocarbon chain, any dynamical barriers to adsorption/desorption do not change significantly.

While sticking probabilities governing the trapping-desorption channel at low energies appear to be independent of n , significant differences as a function of chain length are indeed observed in scattering dynamics at higher collision energies. At $E_{\text{inc}} = 20(2)$ kcal/mol, the TD/IS two-temperature

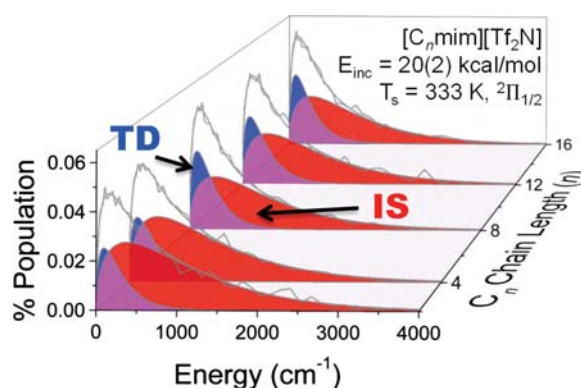


FIG. 4. Two-temperature fits to rotational populations for NO scattered at $E_{\text{inc}} = 20(2)$ kcal/mol from $[C_n\text{mim}][\text{Tf}_2\text{N}]$. As the alkyl chain is lengthened, the relative magnitude of the TD component *increases*, consistent with a larger fraction of the incident NO molecules thermally trapping on the liquid surface. The above data represent surface temperatures of $T_s = 333$ K and only the ground $^2\Pi_{1/2}$ spin-orbit state, though similar trends are observed for the $^2\Pi_{3/2}$ spin-orbit excited state and over multiple liquid temperatures (see text for details).

fits to rotational populations are summarized in Fig. 4, with normalized populations for the $^2\Pi_{1/2}$ state plotted vs. rotational energy and alkyl chain length (n). For each rotational distribution, the IS component (red) represents the majority species, while the TD component (blue) comprises the remainder of the scattered flux. As the alkyl chain is lengthened, the relative intensity of the TD component systematically *increases* from low $n = [2, 4]$ to high $n = [8, 12, 16]$, representing a comparable *increase* in the fraction of NO molecules trapping at the surface. Two-temperature fit parameters to these data, in addition to those for the $^2\Pi_{3/2}$ state, as a function of alkyl chain length are plotted in Fig. 6 at $T_s = 333$ K, with the complete data set at all liquid temperatures summarized in Table I.

As immediately evident in Fig. 4 and 5a, the TD branching fraction α for these RTILs is strikingly low ($\alpha = 0.25 - 0.40$) for all chain lengths, with nearly 60 - 75% of the molecules experiencing impulsive scattering (IS) events at the gas-RTIL interface. This contrasts with the nearly 200% *larger* values ($\alpha \approx 0.70$) observed in previous scattering studies of CO_2 from $[C_n\text{mim}][\text{Tf}_2\text{N}]$ at $E_{\text{inc}} = 15$ kcal/mol.⁴⁵ This significant difference in accommodation is not explained solely by slight discrepancies in the incident energies and, in the limit of thermal accommodation as the rate limiting step, implies proportionately *slower kinetics for NO vs CO₂ solvation* into the bulk RTIL liquid. The fundamental reasons must reflect differences in chemical/physical interactions at the interface. As a simple physical picture, this could be rationalized to arise from the 4-5 fold larger NO vs. CO_2 rotational constants, and thus the 4-5 fold larger gap between final rotational levels impeding energy transfer from incident translation into rotation at the gas-liquid interface. This would be interesting to explore systematically by probing gas-liquid collisional energy transfer into rotation for different isotopomeric molecular rotors with larger rotational constants such as DCl ($B \approx 5.39$ cm^{-1}) and HCl ($B \approx 10.4$ cm^{-1}).

Secondly, Fig. 5a indicates a systematic spin-orbit state dependence for the trapping-desorption fraction, i.e., $\alpha(^2\Pi_{1/2}) > \alpha(^2\Pi_{3/2})$, which based on the incident beam population in $^2\Pi_{1/2}$ implies that electronically adiabatic *spin-orbit conserving* collisions ($^2\Pi_{1/2} \rightarrow ^2\Pi_{1/2}$) undergo trapping-desorption more readily than non-adiabatic *spin-orbit changing* collisions ($^2\Pi_{1/2} \rightarrow ^2\Pi_{3/2}$). This has been noted in earlier studies with NO scattering from RTILs, and provides additional evidence for the presence of *non-adiabatic surface hopping* dynamics taking place at the gas-liquid interface.^{46,47} An intriguing parallel observation is the fact that fully accommodated TD collisions desorb from the surface *with colder ground* ($^2\Pi_{1/2}$) vs. *excited* ($^2\Pi_{3/2}$) spin-orbit state rotational temperatures, which by detailed balance considerations would suggest i) decreased trapping efficiency for higher J states and ii) lower trapping efficiency for ground vs. excited spin-orbit states for a given high J state. This latter prediction would at first seem to contradict the *larger* sticking coefficients for the *lower* spin-orbit state noted above. There is no paradox, however, as these scattering experiments sample very *low* J states in the incident beam, whereas the detailed balance arguments are

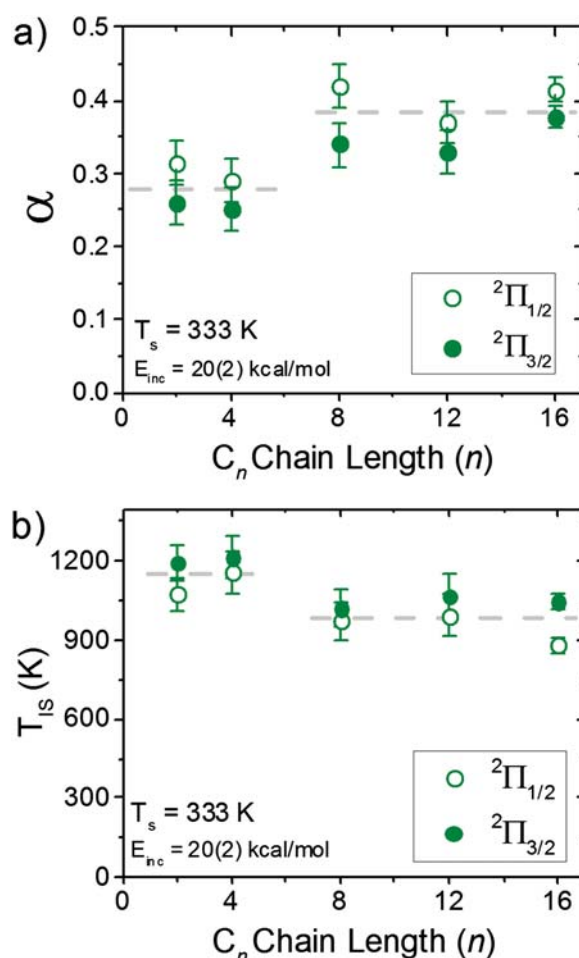


FIG. 5. Two-temperature Boltzmann fit parameters for $E_{inc} = 20(2)$ kcal/mol as a function of alkyl chain length. As n increases, α , the branching ratio into the TD channel, also increases and then plateaus at longer alkyl chain lengths. Spin-orbit changing collisions ($^2\Pi_{1/2} \rightarrow ^2\Pi_{3/2}$) have a higher propensity to impulsively scatter (i.e., lower α) than spin-orbit conserving collisions. Additionally, the degree of rotational excitation into the IS channel decreases with alkyl chain length. As indicated by the dashed lines, both accommodation and IS rotational temperature plots suggest a discontinuous shift between short ($n \leq 4$) and long ($n \geq 8$) chain lengths, which would be consistent with molecular dynamics predictions of surface reorganization of the alkyl groups over a similar range in n (see text for details).

based on depletion of *high J* state populations in the outgoing NO flux. In any event, the data clearly indicate an unusually rich coupling between i) rotational and ii) spin-orbit state collision dynamics of NO at the gas-RTIL interface, which offer many challenges for non-adiabatic theoretical study.

Thirdly, the TD branching fraction α shows a clear sensitivity to alkyl chain length (n), with systematically more trapping/desorption with increasing hydrocarbon tail. These trends are in agreement with molecular beam experiments of both CO_2 and $\text{O}(^3\text{P})$ inelastically scattering from $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs, which have also shown an increase in the TD fraction for longer alkyl chains.^{43,45} Such behavior is certainly consistent with a propensity for buildup of the soft and longer hydrophobic hydrocarbon chains at the interface, as also supported by theoretical molecular dynamics simulations.^{43,49} Of particular interest, however, is that Fig. 5a and 5b suggest that these shifts do not appear to occur uniformly, but rather with a more nearly *discontinuous* upward shift between *short* ($n = 2 - 4$) and *long* ($n = 8 - 16$) alkyl chains. We will return to this below, but simply note again that this is the same region of hydrocarbon length over which a *discontinuous* shift in gas-RTIL interfacial alkyl chain orientation (extended outward vs. folded over) is also predicted from MD simulations.^{32,43}

Fig. 5(b) displays the measured IS rotational temperatures as a function of n and spin-orbit state. It is worth noting that these rotational temperatures range from 900 to 1200 K, i.e., considerably hotter than the 333 K surface and indicating significant energy transfer from hyperthermal translational energy of the beam into the rotational degree of freedom. Secondly, these IS rotational temperatures cool slightly as n increases and again suggest a break from short ($n = 2 - 4$) to long ($n = 8 - 16$) alkyl chains, as similarly noted in Fig. 5a for the sticking coefficient α . On closer inspection, the excited spin-orbit state is rotationally hotter than the ground electronic state, which was also previously observed at low E_{inc} . These results are in good qualitative agreement with both experimental and theoretical work, which suggest that the interfacial landscape changes significantly for alkyl chain lengths between $n = 4$ and 8. Specifically, for larger n , theoretical studies suggest i) alkyl chains preferentially populating the surface more at the expense of anion representation, ii) alkyl chains reorienting and lying flat on the surface, as opposed to pointing perpendicular to the surface (as seen for small n) and iii) a more loosely packed, less dense interfacial region with lower surface tension.

Such compositional changes at the surface have been confirmed with LEIS⁴⁰ and XPS^{25,32} experiments, which are able to extract atomic densities at the gas-liquid interface. These studies have found more hydrocarbons and fewer anions present at the surface for larger n , with a distinct change in the orientation of alkyl chains at the surface observed around $n = 4$. Based on combinations of various photoelectron spectroscopy and atom scattering techniques, the hydrocarbon tails for $n \leq 4$ [C_{*n*}mim][Tf₂N] RTILs are found to stick outward into the vacuum, while the longer hydrocarbons ($n \geq 8$) tend to flop over on top of the surface.^{32,41} Moreover, as a function of hydrocarbon length, Kolbeck and coworkers²⁵ found the surface tension to decrease from $n = 1$ to 4, with the surface tension then remaining constant out to larger n . These results support significant topological changes in hydrocarbon/anion surface structure up to $n \leq 4$, beyond which the alkyl chains have established a dominant compositional presence at the [C_{*n*}mim][Tf₂N] surface.

Elegant molecular beam scattering studies from RTILs have been performed by Minton, McKendrick and coworkers, who scattered hyperthermal O(³P) from [C₂mim][Tf₂N] and [C₁₂mim][Tf₂N] and detected inelastically scattered O atoms as well as reactively scattered OH and H₂O from hydrogen abstraction at the liquid surface, which provide a probe of fractional hydrocarbon presence at the surface.⁴³ Given the stoichiometric difference in the number of CH₂ groups in each RTILs, (where H-abstraction reactions are expected to occur), they found a higher than stoichiometric reactivity for $n = 12$ compared to $n = 2$, thus inferring an increase in alkyl chain presence at the surface for [C₁₂mim][Tf₂N] RTIL.⁴³ Further efforts by McKendrick et al. reactively scattered O(³P) from [C_{*n*}mim][Tf₂N] RTILs, with $n = 2, 4, 5, 8$, and 12, and detected OH, the yield of which was found to increase with n .^{42,44} These results again support increasing alkyl coverage at the surface with hydrocarbon length, in good agreement with the current results, but where the OH yield increases continuously and does not saturate, thus suggesting alkyl chain coverage may still be evolving at $n = 12$. This may suggest a differential sensitivity to RTIL surface features between O(³P) and NO(²Π), for which lengthening of alkyl chains between $n = 8$ to 16 does not appear to affect the scattering dynamics. However, given the quite different reactive vs. inelastic scattering methods of probing the surface, the qualitative trends between these molecular beam studies are clearly in excellent agreement.

A greater propensity for alkyl groups present at the surface coupled with a more flexible interface with increasing n is also in very good agreement with inelastic scattering results presented in Figs. 4 and 5. As a simple physical picture, smaller chain lengths result in a rougher surface, where incident translational energy is more efficiently transferred into the rotational degree of freedom. For small n , this would predict hotter IS rotational temperatures, with slightly cooler temperatures for larger n where the alkyl chains are lying flat on the surface. The branching ratio, α , increases even more dramatically ($\approx 40\%$) over this same range of chain lengths, consistent with a softer, more flexible surface at higher n that can more readily absorb molecular incident energy. Simply stated, larger n leads to a looser arrangement of alkyl chains with a lower effective surface mass, whereby molecules can more readily rearrange and become trapped transiently on the surface. Our data reveal that such a longer, looser arrangement of alkyl chains on the surface leads to increased trapping of NO gas molecules on the surface, which is a necessary prerequisite for solvation into the bulk.

B. Spin-orbit distribution: Dependence on C_n

We next explore the nonadiabatic interactions occurring at the surface by considering the electronic spin-orbit ratios of the scattered NO, $[^2\Pi_{3/2}]/[^2\Pi_{1/2}]$, as a function of alkyl chain length (n) and collision energy (see Fig. 6). At low $E_{\text{inc}} = 2.7(9)$ kcal/mol and $T_S = 353$ K, spin-orbit ratios of $[^2\Pi_{3/2}]/[^2\Pi_{1/2}] \approx 0.5$ are observed (Fig. 6), which implies only roughly one-third of the incident NO molecules are electronically excited ($^2\Pi_{1/2} \rightarrow ^2\Pi_{3/2}$) in the collisional process. A simple estimate of an “electronic temperature” can be extracted from the Boltzmann expression $[^2\Pi_{3/2}]/[^2\Pi_{1/2}] = \exp(-E_{\text{SO}}/kT)$, with the energy difference between the two spin-orbit states (E_{SO}) equal to 123 cm^{-1} .⁶⁵ At low E_{inc} , these spin-orbit ratios correspond to ~ 250 K, i.e., significantly hotter than the ~ 1 K rotational/electronic temperatures in the incident beam and yet still significantly colder than the 353 K liquid interface itself. Interestingly, the magnitude of this spin-orbit excitation appears to be *insensitive* to the alkyl chain length, recapitulating the trends observed for T_{rot} . This is not surprising, as both rotational and electronic populations resulting from fully accommodated species could be additionally sensitive to dynamical barriers along the desorption pathway. At high collision energies ($E_{\text{inc}} = 20$ kcal/mol) which facilitate both TD and IS scattering pathways, a greater spin-orbit ratio of $[^2\Pi_{3/2}]/[^2\Pi_{1/2}] \approx 0.66$ is observed (see Fig. 6), corresponding to electronic temperatures now in excess of T_S . Since spin-orbit excitation out of the incident $^2\Pi_{1/2}$ ground state reflects a non-adiabatic event, a surface hopping sensitivity to incident translational energy would be at least qualitatively consistent with simple 1D Landau-Zener models for curve-crossing dynamics.^{66,67}

C. Dependence on surface temperature

Scattering dynamics of NO from this series of $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs have also been investigated as a function of surface temperature, with the resulting two-temperature fit parameters at high E_{inc} plotted vs. T_S in Fig. 7. For visual clarity, only data for NO scattering from $[C_2\text{mim}][\text{Tf}_2\text{N}]$ and $[C_{12}\text{mim}][\text{Tf}_2\text{N}]$ into the excited spin-orbit states are plotted, with the complete set of data for all RTILs and both spin-orbit states summarized in Table I as a function of surface temperature. Trends in alkyl chain length discussed earlier are apparent here as well, with longer alkyl chains resulting in a larger fraction of molecules trapping on the surface (i.e., higher α) and lower rotational excitation in the impulsively scattered channel (i.e., colder T_{IS}). As seen in Fig. 7a, the trapping-desorption fraction increases very nearly linearly with T_S , as observed in other gas-liquid scattering experiments^{54,68,69} and can be ascribed to an increase in microscopic surface roughness with surface temperature. The slope is approximately $0.0015(19)/\text{K}$ for $[C_{12}\text{mim}][\text{Tf}_2\text{N}]$, i.e., $15(2)\%$ more NO trap and desorb from the surface per 100 K increase in T_S , and $0.0010(12)/\text{K}$ for $[C_2\text{mim}][\text{Tf}_2\text{N}]$. As evident from Table I, similar slopes (e.g., $6(4) - 16(3)\%$ per 100 K) are observed for all RTILs studied and for both spin-orbit states. By way of comparison, CO_2 scattering (at $E_{\text{inc}} = 15$ kcal/mol) from perfluoropolyether

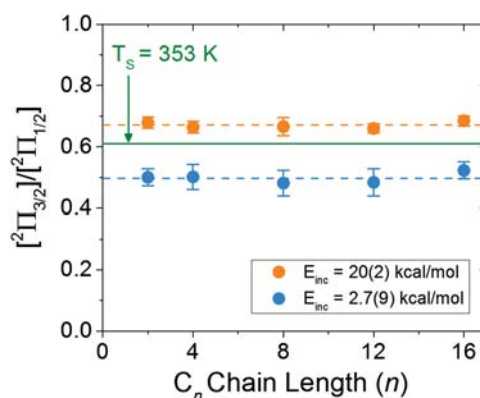


FIG. 6. Spin-orbit ratio of scattered NO at both low/high E_{inc} and as a function of alkyl chain length. The horizontal green line represents the “spin-orbit temperature” corresponding to the surface temperature where $[^2\Pi_{3/2}]/[^2\Pi_{1/2}] = e^{-E_{\text{SO}}/kT}$ and $E_{\text{SO}} = 123 \text{ cm}^{-1}$. Error bars represent 2σ standard deviations.

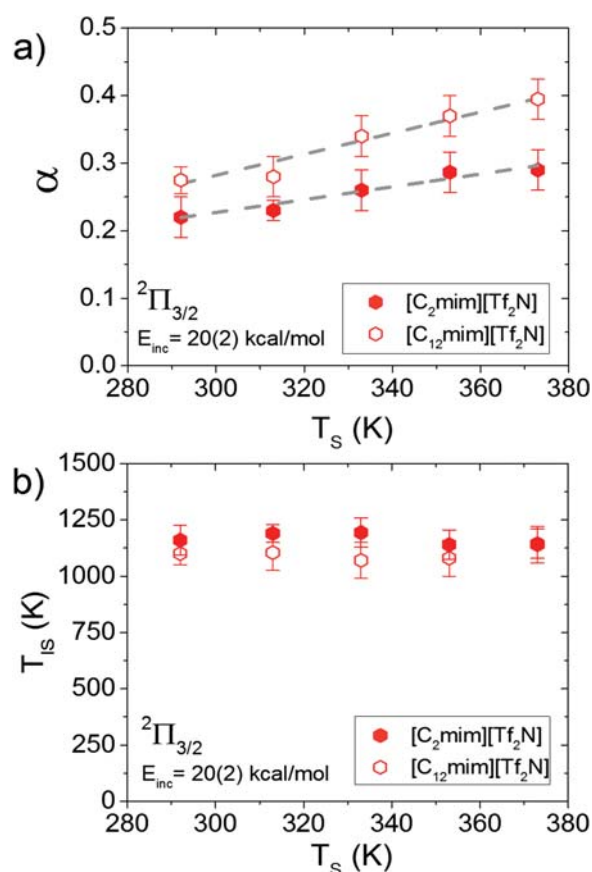


FIG. 7. Two-temperature fit parameters to rotational distributions at $E_{inc} = 20(2)$ kcal/mol as the surface temperature is varied for two alkyl chain length RTILs, $n = 2$ and 12. As the liquid temperature increases and the surface roughens, the branching into the TD channel increases linearly whereas the IS rotational temperatures remain essentially flat.

(PFPE) and fluorinated self-assembled monolayer surfaces (F-SAMs) has also been studied over $T_s = 232 - 323$ K.⁵⁴ An equivalent analysis of the temperature dependence of α yields slopes of 17(3)% and 11(6)% per 100 K for the PFPE and F-SAM surfaces, respectively, i.e., reflecting a comparable range of NO + RTILs values as reported herein.

The impulsively scattered rotational temperatures are plotted in Fig. 7b, again focusing on the $2\Pi_{3/2}$ state of $n = 2$ and 12 $[C_nmim][Tf_2N]$ RTILs. As noted earlier, the $T_{IS}(n = 2)$ values are slightly hotter than the $T_{IS}(n = 12)$ values. Furthermore, each of these T_{IS} rotational temperatures is significantly hotter than T_s , though with remarkably little sensitivity to the actual surface temperature. Thus, while the branching ratio α into the TD channel is clearly strongly influenced by T_s , the temperature of the liquid surface appears to have little influence over the impulsively scattered IS temperatures observed experimentally. One simple physical picture for such behavior would be that interaction times with the surface for IS events are too short to be significantly influenced by liquid temperature, though the fraction of trajectories that proceed via IS vs. TD channels remains sensitive to thermally induced surface roughness.⁶⁸

V. CONCLUSIONS

We report molecular beam scattering results of supersonically cooled NO from $[C_nmim][Tf_2N]$ RTILs with state-to-state resolution. The energy transfer between the surface and incident NO molecules is explored as a function of the incident collision energy, surface temperature and the cation alkyl chain length, which is varied over $n = [2, 4, 8, 12, 16]$. At low collision energies, all molecules accommodate and thermally desorb from the surface in a single Boltzmann temperature.

However, even in this simplest of dynamical scenarios, we observe rotational and spin-orbit temperatures that are systematically *cooler* than the surface temperature. Furthermore, the rotational and spin-orbit temperatures are unaffected by the alkyl chain length. Thus, while physiochemical changes are occurring on the surface as n is varied in these $[C_n\text{mim}][\text{Tf}_2\text{N}]$ RTILs, the sticking probabilities that govern the TD channel for both the rotational and electronic degree of freedom are not influenced.

At high incident collision energies ($E_{\text{inc}} = 20$ kcal/mol), rotational populations of scattered molecules are well described by a two temperature TD/IS model. As these alkyl chains are lengthened, the landscape of the RTIL surface is changed such that more incident gas molecules trap on the surface and those that do impulsively scatter leave the surface with less rotational energy. These results are in agreement with a simple physical picture building on other theoretical and experimental work,^{32,43–47} whereby longer hydrocarbon RTILs have an enhanced presence of alkyl chains at the surface that result in a more flexible, loosely packed surface more able to promote energy transfer into the liquid. Additionally, the surface temperature dependence of these RTILs on scattering dynamics has been explored, revealing for all RTILs studied that, as T_S increases, more molecules trap on the surface and yet the rotational component of the IS channel remains unaffected. In summary, these studies provide quantitative data into the rich quantum-state resolved dynamics for both inelastic and non-adiabatic scattering of open-shell species with the surfaces of room temperature ionic liquids, and how qualitative conformational changes occurring at the gas-liquid interface affect these dynamics. Detailed theoretical modeling will clearly be invaluable in interpreting the T_S and alkyl chain length dependence of these interfacial collision dynamics with more molecular level of detail, and toward which we hope these studies help provide the requisite stimulus.

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