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Selectivity in Gas–Liquid Interactions: Molecular Beam Scattering of CD₄ and ND₃ from an Aqueous Flat Liquid Jet

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ABSTRACT

The dynamics of polar and nonpolar molecules colliding with an aqueous surface are characterized by scattering molecular beams of deuterated methane and ammonia, CD₄ and ND₃ ($E_i = 28.9$ and 30.3 kJ mol⁻¹, respectively), from a flat liquid jet of cold salty water (8 m LiBr, 230 K). Translational energy distributions of scattered species collected as a function of collision geometry probe both impulsive scattering (IS) and thermal desorption (TD) mechanisms. We find that CD₄ scattering is dominated by IS and exhibits a super-specular angular distribution. The fraction of TD scattering events is notably smaller for cold salty water than for dodecane, consistent with a higher free energy of solvation for CD₄ in the water jet. In contrast, no scattering signal is seen for ND₃ from the water jet, a result attributed to the high solubility and efficient protonation of ND₃ in liquid water. The IS channel for CD₄ was analyzed using a soft-sphere model, yielding a higher internal energy (E_{int}) and lower effective surface mass (m_{eff}) than was seen for Ne/water; the higher value of E_{int} is attributed to rotational excitation of the scattered CD₄. These findings demonstrate that the outcomes of a gas–liquid collision — scattering trajectory, surface

adherence, and energy transfer — are directed at the molecular level by both the gaseous scatterer and liquid surface.

I. INTRODUCTION

The gas–liquid interface is home to unique chemical and physical processes that are distinct from their bulk phase counterparts and appear in many chemical, biological, and physical contexts. Development of next-generation oral inhalation treatments for respiratory diseases or to provide alternative drug delivery methods for patients that have difficulties with other formats is predicated on understanding the transport of therapeutic molecules across the air–lung interface.^{1, 2} Reactions between trace environmental gases and the liquid surface of aerosols and the ocean control global populations of key atmospheric species such as N_2O_5 , O_3 , NO_x , and H_2SO_4 .^{3–6} Recently, large-scale synthetic methods have been developed that leverage interfacial chemistry to produce materials for electrocatalysis, sensing, and electronic devices.^{7–9}

Several methods have emerged over the last few decades to characterize the properties of liquid interfaces.^{10, 11} There is a large body of literature on microdroplet experiments employing numerous techniques to yield information specific to the interface.¹⁰ A variety of sample conditions have been studied by changing the solution composition,^{12, 13} droplet size,^{13, 14} and reaction environment.¹⁴ Techniques such as mass spectrometry^{12, 15, 16} and Raman,¹⁷ infrared,¹⁴ and fluorescence spectroscopies¹⁸ have been established as powerful methods for probing interfacial processes combined with analysis through kinetic modeling^{16, 19} and comparison to bulk experiments.²⁰ Alternatively, surface-specific spectroscopic techniques have been extensively developed for the purpose of probing the gas–liquid interface. Among them, X-ray photoelectron spectroscopy (XPS) is both element- and surface-specific,²¹ sum frequency generation (SFG) and second harmonic generation (SHG) are surface-sensitive by virtue of being second-order nonlinear processes,^{22, 23} and glancing angle Raman leverages specific angles of incident radiation and detection to essentially skim the sample surface.²³

45 Molecular beam experiments represent an additional avenue for directly sampling the gas–liquid
46 interface. Several groups have developed techniques in which molecular beams are scattered from liquid
47 surfaces and detected post-collision.^{24–28} The wetted wheel was the first major breakthrough, enabling
48 researchers to scatter a molecular beam from a continually refreshed liquid surface in a vacuum
49 environment, provided that the vapor pressure of the liquid is relatively low (typically below ~5 mTorr).
50^{29, 30} Further progress was brought about by the implementation of liquid microjets as the scattering
51 surface, granting access to more volatile liquids.³¹ Our group has developed a molecular beam scattering
52 apparatus based on a flat liquid jet that combines the advantages of the wetted wheel, namely a large
53 surface area to scatter from and a well-defined surface normal, with the capability of the cylindrical jet to
54 introduce volatile liquids into vacuum.³² This setup has been used to investigate the evaporation and
55 scattering of several species (Ne, CD₄, ND₃, and D₂O) from dodecane flat liquid jets, wherein both
56 impulsive scattering (IS) and thermal desorption (TD) mechanisms were observed. IS describes molecules
57 which promptly strike and leave the surface, while TD consists of thermalized molecules desorbing from
58 the surface following adsorption or solvation. We note that the two-step trapping and desorption process
59 may also be abbreviated as “TD” in the literature.³⁰ Herein, TD refers only to the thermal desorption step,
60 both because that is the observable directly measured by our experiments and to maintain consistency with
61 prior work.

62 Super-specular scattering indicated anisotropic momentum transfer to the liquid surface.^{33, 34}
63 Recently, we have reported the results of evaporation and/or scattering of Ar and Ne from flat jets of cold
64 salty water.^{35, 36} The latter study showed that Ne undergoes highly super-specular scattering and transfers
65 more energy to the aqueous surface than to dodecane, a result attributed to the extensive hydrogen-bonded
66 network of liquid water.

67 In this work, we report angular and translational energy distributions of CD₄ and ND₃ molecular beams
68 at incidence energies of 28.9 and 30.3 kJ mol^{–1}, respectively, scattered from a flat jet of cold salty water
69 (8 m LiBr, 230 K). Measurements were collected through a range of deflection angles and analyzed with

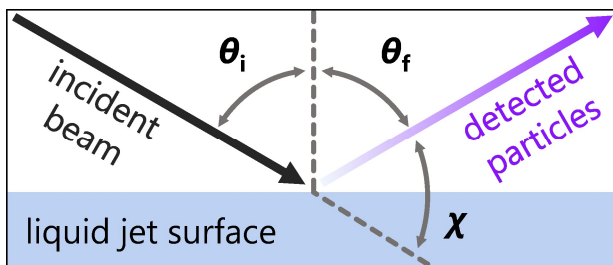
70 kinematic soft-sphere modeling. We find that CD₄ primarily undergoes IS with limited population of the
71 TD pathway. ND₃ exhibits no measurable scattering activity, reflecting its very high solubility in salty
72 water and the efficient protonation of dissolved ND₃. Super-specular scattering is observed for CD₄ at all
73 examined incidence angles, attributable to anisotropic momentum transfer to the liquid surface and a high
74 degree of fractional energy loss, similar to what was seen for Ne.³⁶ However, the energy lost by Ne was
75 insensitive to deflection angle (χ), while the values for CD₄ have a strong dependence on χ . The fraction
76 of scattering events that proceed via TD, the TD fraction defined as TD/(TD + IS), is higher for CD₄
77 scattered from dodecane surface than from cold salty water, in contrast to that of Ne which largely did not
78 differ between the surfaces. Analysis through a soft-sphere model indicates that excitation of internal
79 modes in both the liquid surface and CD₄ results from collisional energy transfer.

80 II. METHODS

81 Experimental

82 A detailed description of the vacuum apparatus used for gas–liquid scattering experiments has been
83 provided previously.^{32, 35, 36} In brief, molecular beams of deuterated methane and ammonia are generated
84 by expanding mixtures of each species seeded in He (CD₄ 5.3%, ND₃ 1.5%) through a pulsed piezoelectric
85 valve (MassSpecpecD BV, Enschede), resulting in incident beam energies of 28.9 and 30.3 kJ mol^{−1} for
86 CD₄ and ND₃, respectively. A microfluidic chip (Micronit) mounted to a rotational stage is used to produce
87 a flat jet of cold salty water with typical dimensions of 0.4 × 1.3 mm² (W × H) and an estimated flow
88 velocity of 7 m s^{−1}. The chip assembly is held at ca. 228±1 K, and the temperature of the liquid jet T_{liq} is
89 assumed equal to this value; at this temperature, the estimated vapor pressure of the solution is 6.3 × 10^{−2}
90 Torr. These conditions give rise to an estimated mean free path of 0.33 cm, which corresponds to an
91 estimated 10% of impinging molecules undergoing collisions with vapor molecules (based on the collision
92 cross section of water, ca. 30 Å²) before entering the detector chamber.³⁰ Aqueous salt solutions were
93 prepared at 8 m concentration (approximately 7 M) by dissolving LiBr (anhydrous, Thermo Scientific) in
94 ultrapure H₂O (Milli-Q, MilliporeSigma) and degassing with He prior to each experiment. Molecules

95 scattered from the jet are detected by a rotatable mass spectrometer that consists of a 1.5 mm circular
 96 entrance aperture, an electron impact ionizer (80 eV electron kinetic energy), a quadrupole mass filter,
 97 and a Daly-type ion detector. Time-of-flight (TOF) spectra are collected by recording the arrival times of
 98 species scattered from the liquid jet; the time at which the peak intensity of the molecular beam pulse
 99 reaches the jet defines the start of the flight time, and the detector viewing time is $\sim 150 \mu\text{s}$.



100

101 **Figure 1.** Definition of the incidence angle θ_i , scattering angle θ_f , and deflection angle $\chi = 180^\circ - (\theta_i +$
 102 $\theta_f)$.

103 Rotation of both the liquid jet and detector allows for precise control of the collision geometry (Figure
 104 1) through setting θ_i , the incidence angle of the molecular beam relative to the liquid surface normal, as
 105 well as the outgoing scattering angle θ_f . In this work, incidence angles of 45° , 60° , and 75° were chosen,
 106 and the scattering angle was swept from 90° to $90^\circ - \theta_i$. The deflection angle, defined as $\chi = 180^\circ - (\theta_i +$
 107 $\theta_f)$, is varied through control of these parameters. TOF spectra are background-corrected by subtracting
 108 “beam-off” from “beam-on” data, and systematic error is reduced by alternating the order in which
 109 different scattering angles are sampled. For each θ_i , TOF profiles are intensity-calibrated through
 110 normalization to the integrated intensity of the $\theta_f = 90^\circ$ spectrum. Spectra are collected over multiple days
 111 and averaged to improve signal-to-noise ratios and ensure reproducibility.

112 Data Analysis

113 Each TOF profile is fitted by the sum of two curves that correspond to contributions from IS and TD
 114 trajectories. The faster IS component is represented by a supersonic flux velocity distribution

$$115 \quad f_{SS}(v) \propto v^3 \exp\left(-\frac{m(v - v_{SS})^2}{2RT_{SS}}\right) \quad (1)$$

116 in which v and m are the velocity and mass of an individual particle in the scattered molecular beam, while
 117 v_{ss} and T_{ss} denote the average flow velocity and temperature.^{37,38} A Maxwell-Boltzmann flux distribution
 118 at T_{liq} is used to describe the slower TD channel:

$$119 \quad f_{MB}(v) \propto S_0(v, \theta) v^3 \exp\left(-\frac{mv^2}{2RT_{liq}}\right) \quad (2)$$

120 $S_0(v, \theta)$ corresponds to the velocity- and angle-dependent sticking coefficient, which is assumed to be
 121 unity.³⁹

122 The fitted IS component reports on the translational energy of scattered molecules, thereby providing
 123 information about the collisional energy transfer that occurs during gas-liquid scattering events. A soft-
 124 sphere kinematic model is used to describe the average fractional energy loss of impulsively scattered
 125 molecules as a function of deflection angle as given in eq. 3.⁴⁰

$$126 \quad \left(\frac{\Delta E}{E_i}\right) \approx \frac{2\mu}{(1+\mu)^2} \left[1 + \mu(\sin \chi)^2 - \cos \chi \sqrt{1 - \mu^2(\sin \chi)^2 - \frac{E_{int}}{E_i}(\mu+1) + \frac{E_{int}}{E_i} \left(\frac{\mu+1}{2\mu}\right)} \right] \left[1 + \frac{V - 2RT_{liq}}{E_i} \right] \quad (3).$$

127 Here, ΔE is the absolute change in translational energy equal to $E_i - \langle E_{IS} \rangle$, where E_i and E_{IS} are the
 128 incident translational energy and the average translational energy in the IS channel, and χ is the deflection
 129 angle. A constant representing the gas-surface interaction potential V is included and assumed to be
 130 equivalent to the Lennard-Jones well depth between CH_4 and water, 2.2 kJ mol^{-1} .⁴¹ The free parameters
 131 consist of the total internal excitation E_{int} and the mass ratio $\mu = m_{gas}/m_{eff}$ between the gas particle and the
 132 effective surface mass. This approach models the scatterer and the liquid as two spheres with internal
 133 degrees of freedom that can be excited during an inelastic collision, in contrast to the hard-sphere model
 134 that considers two rigid spheres and imposes the restriction that $E_{int} = 0$.

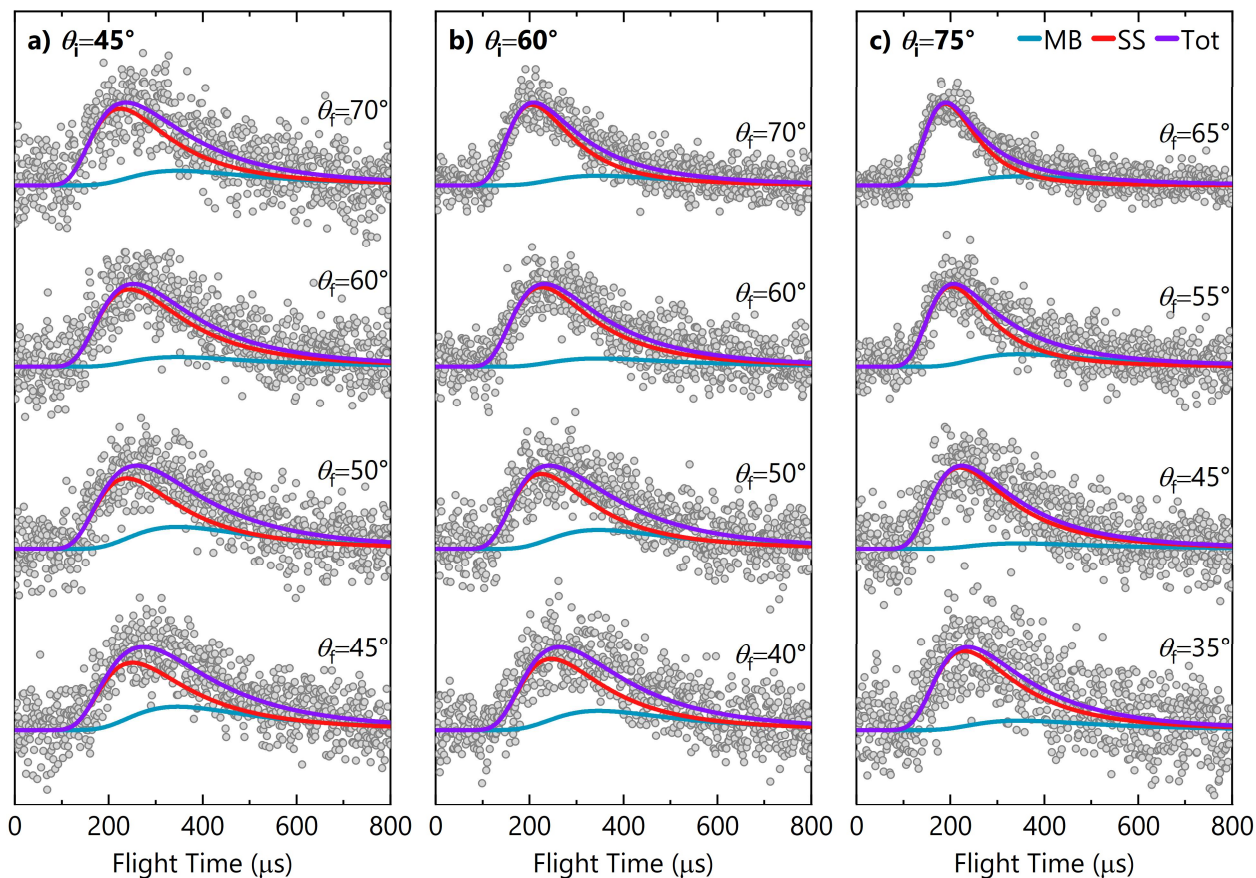
135 Error bars are reported for TD fraction and $\Delta E/E_i$ vales by performing jackknife resampling, a cross-
 136 validation method wherein one scan at a time is systematically removed from the averaged spectrum, the
 137 parameters of interest are calculated for the resultant spectra, and the standard error of the extracted values
 138 is determined.⁴² This approach is preferred over other statistical analyses, such as a Student's t -test or Z -

139 test, because TD fraction and $\Delta E/E_i$ are derived from an averaged spectrum rather than calculated for
 140 individual scans in replicate and aggregated into one value.

141 III. RESULTS

142 A. Scattering Data

143 Time of flight spectra of CD_4 scattered from a cold salty water jet are presented in Figures 2a–c.
 144 Measurements were performed at incidence angles of $\theta_i = 45^\circ$, 60° , and 75° , and select outgoing angles θ_f
 145 are shown. The spectra are fitted as a sum of supersonic (SS) and Maxwell–Boltzmann (MB) distributions,
 146 representing the IS and TD contributions to the signal, respectively, and producing fitted curves unique to
 147 each spectrum.



148

149 **Figure 2.** Time-of-flight (TOF) spectra (grey circles) of CD_4 scattered from a flat jet of cold salty water
 150 at incidence angles (a) $\theta_i = 45^\circ$, (b) $\theta_i = 60^\circ$, and (c) $\theta_i = 75^\circ$. The spectra are fitted by a sum (“Tot”, purple
 151 traces) of a supersonic distribution (“SS”, red traces) and a Maxwell-Boltzmann distribution at the liquid
 152 temperature (“MB”, blue traces) and normalized to the intensity of the total trace.

As either θ_i or θ_f increases, the TOF profiles trend toward faster arrival times and narrower peaks. For example, the maximum in the total fitted curve for the top trace in each plot shifts from 236 μ s at $\theta_i = 45^\circ$ to 191 μ s at $\theta_i = 75^\circ$, and the full width at half maximum drops from 247 μ s to 145 μ s. At greater values of θ_i , collisions become more glancing, leading to an increase in the relative number of particles which impulsively scatter from the surface. The drop in TD signal at larger θ_f is consistent with the $\cos(\theta_f)$ angular distribution expected of molecules evaporating from the surface (also shown in Figure 3).³⁹

Angular distributions of CD₄ scattered from cold salty water are created by plotting the integrated non-normalized intensities of the SS and MB fitted curves as a function of outgoing angle, as shown in Figures 3a–c. The TD component at $\theta_i = 45^\circ$ is approximately aligned with the expected $\cos(\theta_f)$ distribution, indicating that the vapor above the surface of the jet does not significantly distort the energies or trajectories of particles leaving the jet. The IS channel consistently exhibits super-specular scattering, in that the most intense scattering signal is measured at an outgoing angle larger than the specular angle. In all three angular distributions, the IS signal reaches its maximum at the largest measured θ_f .

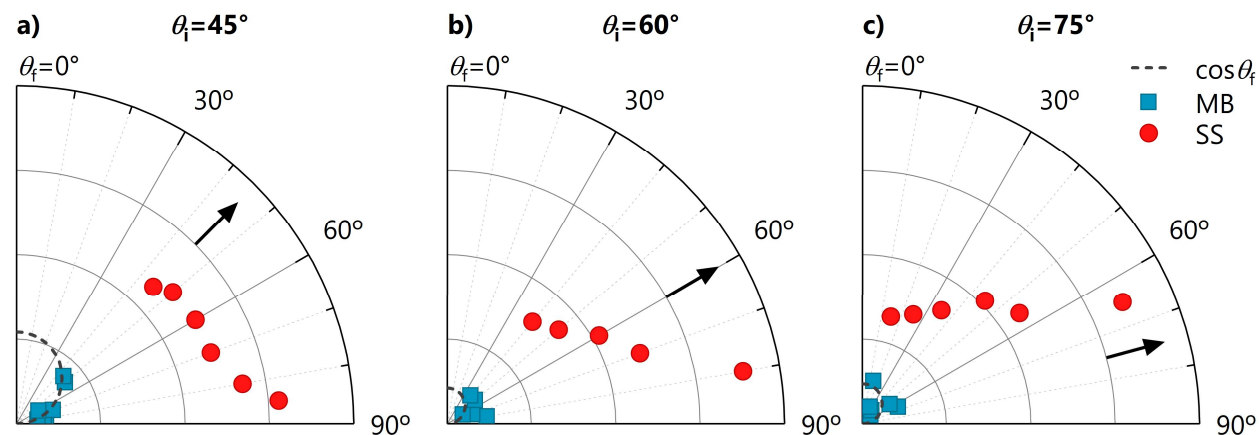
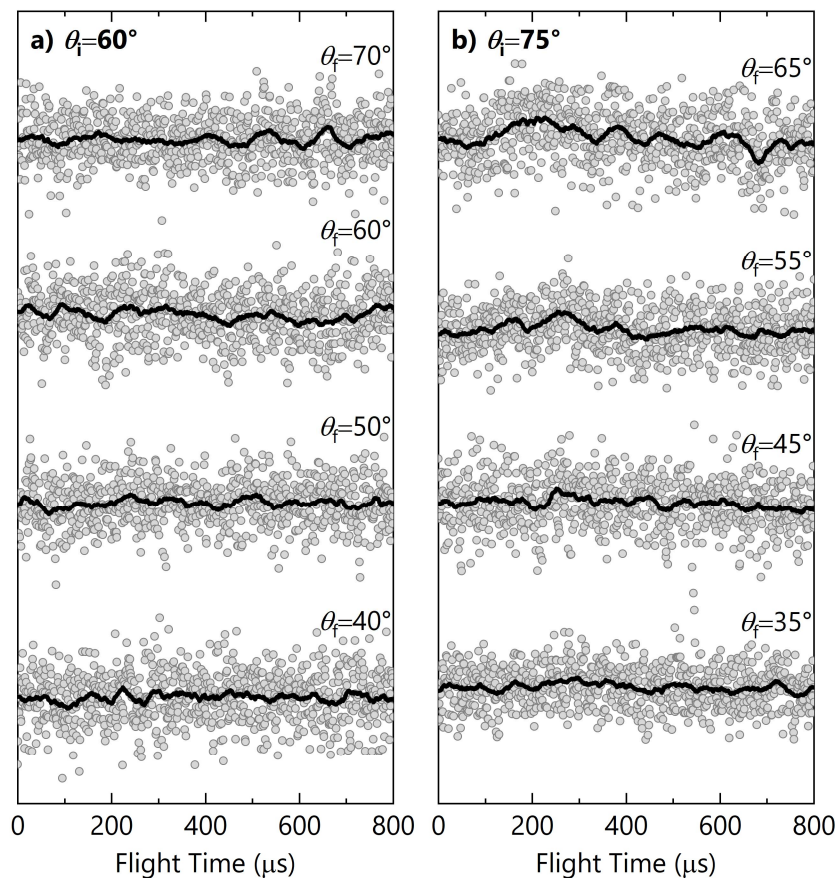


Figure 3. Angular distributions of the IS and TD pathways at incidence angles (a) $\theta_i = 45^\circ$, (b) $\theta_i = 60^\circ$, and (c) $\theta_i = 75^\circ$. Each point is created by integrating the SS (red circles) and MB (blue squares) fitted curves and plotting as a function of outgoing angle. The dashed grey curve represents the $\cos(\theta_f)$ distribution expected for Maxwellian evaporation from the jet. Arrows mark the specular angle.

Figure 4 shows TOF measurements of ND₃ scattered from a cold salty water jet at $\theta_i = 60^\circ$ and 75° . At all scattering angles, there is no discernible signal above the baseline noise. An 80-point Savitzky-Golay filter is applied to the data to guide the eye, so chosen based on the capability of the filter to capture

174 the spectral features of the CD₄/water TOF profiles. It thus appears that ND₃ molecules impinging on the
 175 surface of the jet are dissolved and, most likely, protonated by the liquid. As a result, they do not exhibit
 176 detectable scattering or evaporation signal within the $\sim 150 \mu\text{s}$ viewing window of our detector.



177

178 **Figure 4.** Time-of-flight (TOF) spectra of ND₃ scattered from a flat jet of cold salty water at incidence
 179 angles $\theta_i = 60^\circ$ and 75° . An 80-point Savitzky-Golay filter applied to the data is represented by a black
 180 trace overlaying each spectrum.

181 For CD₄, the portion of detected particles which follow the TD pathway is described by the TD
 182 fraction: $\text{TD}/(\text{TD} + \text{IS})$. Figure 5a shows the TD fractions at incidence angle $\theta_i = 60^\circ$ as a function of
 183 deflection angle χ for CD₄ scattered from cold salty water, as well as Ne scattered from cold salty water
 184 and CD₄, ND₃, and Ne scattered from dodecane for comparison.^{33, 34, 36} The TD fraction for each scatterer–
 185 liquid pair as a function of θ_i is plotted in Figure 5b.

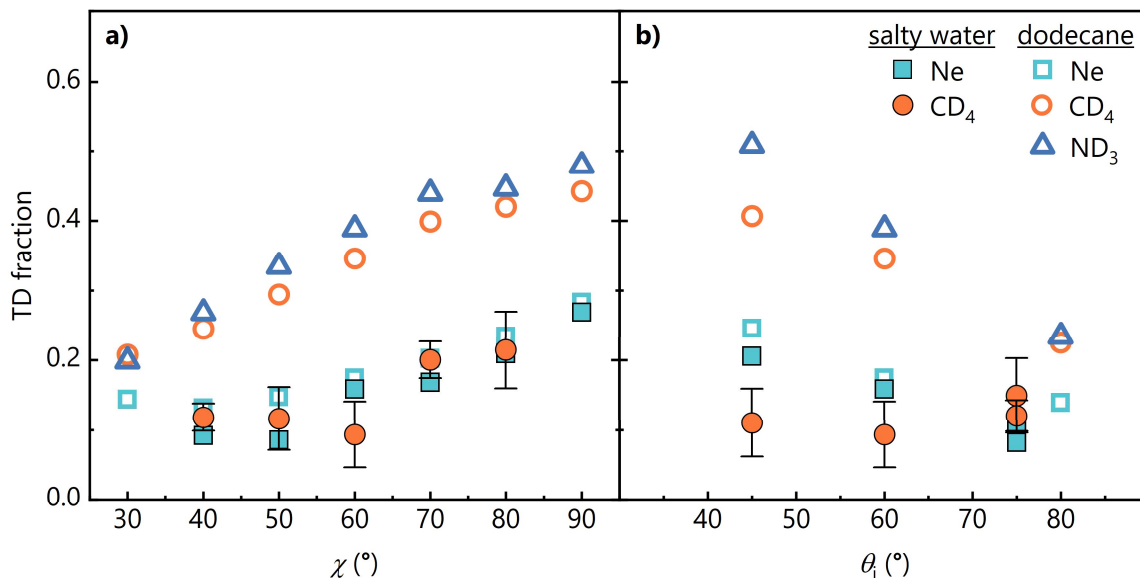


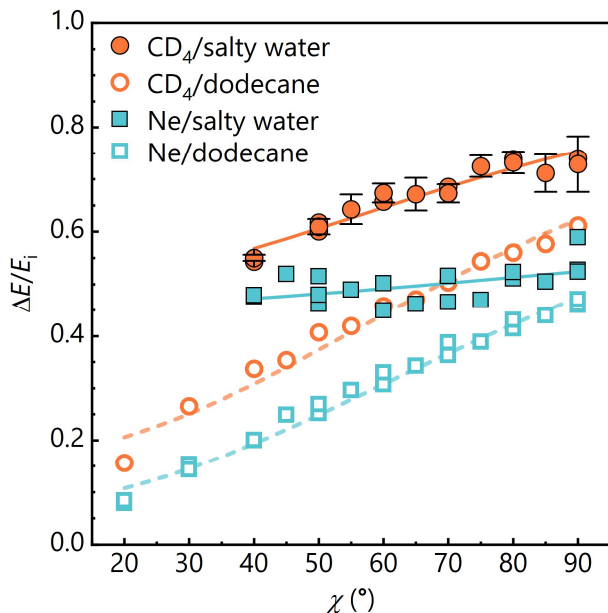
Figure 5. TD fraction for CD₄ and Ne scattered from cold salty water (filled orange circles and teal squares, respectively) and CD₄, ND₃, and Ne scattered from dodecane (empty orange circles, blue triangles, and teal squares) as a function of **a)** deflection angle χ at $\theta_i = 60^\circ$, and **b)** incidence angle θ_i at $\theta_f = 60^\circ$ (all except scattering from cold salty water at $\theta_i = 75^\circ$, which is plotted for $\theta_f = 55^\circ$ and 65°). Ne water data is reproduced from ref. ³⁶; dodecane data is reproduced from refs. ³³ and ³⁴.

The TD fractions for CD₄ scattered from cold salty water at $\theta_i = 60^\circ$ range from 0.09–0.21, whereas the values for CD₄ scattered from dodecane are between 0.21 and 0.44. TD fractions are not reported for ND₃ scattered from water owing to the absence of signal, but the values for ND₃/dodecane lie within 0.2–0.45, similar to those of CD₄/dodecane. For all systems, the TD fraction tends to increase with the deflection angle. While the TD fraction for CD₄ scattered from cold salty water at $\theta_f = 60^\circ$ is relatively consistent across varying incidence angles, the other scattering experiments show a decrease in TD fraction as θ_i increases.

B. Energy Transfer

Figure 6 shows the average fractional energy loss as a function of deflection angle for impulsively scattered CD₄ and Ne for cold salty water and dodecane liquid jets. ^{33, 36} The fitted curves generated by the soft-sphere kinematic modeling of the data are also provided. The values of $\Delta E/E_i$ vary from 0.54 to 0.74 for CD₄ scattered from cold salty water, notably exceeding the fractional energy loss seen for other comparable gas–liquid systems studied in our laboratory and elsewhere. ^{32–34, 36, 43–45} This observation agrees with trends identified previously; polyatomic scatterers outpaced Ne when scattered from

206 dodecane, and cold salty water facilitated more energy transfer than dodecane in Ne scattering
 207 experiments.^{33, 34, 36} In all cases, $\Delta E/E_i$ depends only on χ , irrespective of θ_i and θ_f . The fractional energy
 208 loss generally increases with the deflection angle, though to varying extents. The correlation between
 209 $\Delta E/E_i$ and χ for CD₄/salty water is stronger than that of Ne/salty water, and weaker than for CD₄/dodecane
 210 (which is nearly identical to ND₃/dodecane). For both CD₄ and Ne, $\Delta E/E_i$ exhibits less χ -dependence when
 211 scattered from cold salty water compared to dodecane.



212

213 **Figure 6.** Average fractional energy loss for all incidence angles as a function of deflection angle χ for
 214 impulsively scattered CD₄ and Ne from cold salty water and dodecane.³³ Fitted curves generated by a
 215 soft-sphere kinematic model are represented by solid and dashed lines for water and dodecane scattering,
 216 respectively. Select error bars are reported; error bars for all other CD₄/salty water points are comparable
 217 to those shown.

218 Table 1 gives the parameters extracted from the soft-sphere model — total internal excitation E_{int} and
 219 effective surface mass m_{eff} — as well as the incident beam energy E_i for each of the experiments under
 220 discussion. Analysis of CD₄ scattered from cold salty water yields $E_{\text{int}} = 14.2 \text{ kJ mol}^{-1}$ and $m_{\text{eff}} = 78 \text{ amu}$.
 221 While the fitted curves capture the overall behavior of each dataset, there are limitations in interpreting
 222 the information derived from the soft-sphere model, as discussed in previous work.³⁶ Determining
 223 appropriate error bars for E_{int} and m_{eff} is nontrivial due to their significant correlation with one another,

and a method for addressing this challenge was described in ref. ³⁶. Implementing that approach, error bars of +0.9/−1.0 kJ mol^{−1} and +15/−10 amu were obtained for E_{int} and m_{eff} , respectively.

Table 1. Values of total internal excitation E_{int} , effective surface mass m_{eff} , and beam energy E_i .

Scatterer/Liquid	E_{int} (kJ mol ^{−1})	m_{eff} (amu)	E_i (kJ mol ^{−1})
CD ₄ /salty water	14.2	78	28.9
CD ₄ /dodecane ^a	5.3	52	29.3
Ne/salty water ^b	11.8	190	24.3
Ne/dodecane ^a	2.1	61	23.7
ND ₃ /dodecane ^c	5.8	54	28.8

^a Taken from ref. ³³.

^b Recalculated from data in ref. ³⁶ including only values for deflection angles included in CD₄/salty water analysis.

^c Taken from ref. ³⁴.

IV. DISCUSSION

TOF spectra obtained for CD₄ scattering from cold salty water (Figure 2) exhibit both IS and TD channels, thus enabling analysis through the same framework established in the literature for other beam/liquid scattering experiments. ^{25, 30, 32-36, 44-46} The measured TOF profiles of ND₃ (Figure 4) show no detectable signal, indicating that all incident ND₃ is taken up by the jet and has a residence time in the liquid longer than the viewing window of our detector, ca. 150 μs. ³⁶ Previous gas–liquid scattering studies have identified that the collision energy as well as the free energy of solvation for a scatterer in the liquid sample correlate with the TD fraction. ^{36, 45} Since the incidence energies of the CD₄ and ND₃ molecular beams are similar, (28.9 and 30.3 kJ mol^{−1}, respectively), our results are therefore consistent with ND₃ having a much higher bulk solubility than CD₄ in cold salty water. This is to be expected given the room temperature solubilities of NH₃ and CH₄ in pure water ($\Delta G_{\text{solv}} = -10.2$ kJ mol^{−1} and 16.3 kJ mol^{−1}, respectively). ^{47, 48} Additionally, the absence of scattering signal for ND₃ delineates the range of incident and outgoing angles over which the molecular beam is completely blocked by the jet and measurements are free of contamination from beam leakage (see Supplementary Material). ³⁶

246 To our knowledge, there are no literature values for the free energy of solvation for either methane or
247 ammonia in a cold, highly concentrated LiBr solution. Molecular dynamics simulations of CH₄ dissolved
248 in aqueous NaCl solutions showed that the solubility of methane increased at lower temperatures, as is
249 typical for the solvation of gases in liquids, and decreased at higher salt concentrations due to the salting-
250 out effect of NaCl, an effect that became more pronounced at temperatures below ca. 250 K.⁴⁹
251 Extrapolation of the solvation energies provided by ref.⁴⁸ at 230 K out to 7 M NaCl (the approximate
252 molarity of 8 m LiBr) yields an estimated ΔG_{solv} of 18.5 kJ mol⁻¹.^{50, 51} The uptake of NH₃ by aqueous
253 surfaces has been measured for different solution compositions, including pure water and solutions
254 containing H₂SO₄ and NaOH, at temperatures of 260–300 K.⁵²⁻⁵⁴ Values range from 0.1 to 1, depending
255 strongly on both temperature and pH. Thermodynamic modeling of ammonia solubility in aqueous
256 solutions produced an expression for the temperature-dependent Henry's law constant of NH₃ in pure
257 water, which gives an estimated ΔG_{solv} of -15.7 kJ mol⁻¹ at 230 K.⁵⁵ While NaCl once again had a salting-
258 out influence, LiBr notably caused a strong salting-in effect, which would further decrease the free energy
259 of solvation of ammonia in the cold salty water jet. In any case, the absence of IS from ND₃ is consistent
260 with the high solubility of ND₃ in water.

261 In contrast to CD₄, any ND₃ that dissolves in our cold salty water jet will exist largely in its protonated
262 form. The pK_a of NH₄⁺ is 9.25, meaning the ammonium ion dominates over neutral aqueous ND₃ when
263 the pH is below that value.⁵⁶ The LiBr solution is prepared at neutral pH and thus nearly all dissolved
264 ND₃ will become protonated to form ND₃H⁺, significantly reducing the TD signal from ND₃ evaporation.
265 Both the high solubility of ND₃ in water and the protonation of dissolved ND₃ thus contribute to the
266 disappearance of ND₃ in our scattering experiments. The former likely eliminates the IS channel, while
267 the latter reduces any possible TD signal below our detection limit. The extent to which protonation of the
268 incident ND₃ happens at the interface rather than in the bulk liquid is an open and interesting question that
269 cannot be readily addressed in our experiment.

270 The TOF profiles of CD₄ scattered from cold salty water are fitted with curves representing
271 contributions from both IS and TD scattering (Figure 2). For all incidence angles, plotting the area under
272 each curve as a function of outgoing angle shows that impulsively scattered CD₄ leaves the surface of the
273 jet at a larger angle than the initial collision angle (Figure 3). Such super-specular scattering has been
274 documented in other gas–liquid scattering experiments, attributed to anisotropic momentum transfer
275 favored along the surface normal, and we interpret our results analogously.^{32-34, 36} In this framework, a
276 CD₄ molecule striking the surface of cold salty water has incoming momentum that can be broken down
277 into components parallel (X) and perpendicular (Z) to the surface. Preferentially transferring momentum
278 along the surface normal reduces the magnitude of the Z component, and only upon total depletion of Z
279 is the magnitude of the X component diminished. In this way, molecules which transfer a sufficiently large
280 fraction of their incoming translational energy will leave the surface of the jet approaching $\theta_f = 90^\circ$. This
281 effect results in angular distributions for CD₄ that are similar to those observed for Ne scattered from cold
282 salty water.³⁶ We note that this explanation is kinematic in nature; it remains to be seen if similar angular
283 distributions appear in classical trajectory calculations, for example.

284 TD fractions of CD₄ scattered from both cold salty water and dodecane illustrate the selectivity of each
285 surface (Figure 5). The TD fractions for CD₄ and Ne from cold salty water are similar and are significantly
286 lower than CD₄ from dodecane; the TD fraction for Ne is about the same for both liquids.³⁶ CD₄ is much
287 better accommodated by dodecane than in aqueous solution owing to its higher solubility in the alkane
288 ($\Delta G_{\text{solv}} = 11.8 \text{ kJ mol}^{-1}$).³³ Alongside these scatterer preferences, the liquid surfaces themselves
289 demonstrate selectivity toward different molecules. Dodecane is a similarly accommodating surface to
290 both CD₄ and ND₃, whereas cold salty water exhibits molecule-specific interactions, capturing ND₃
291 entirely while reflecting CD₄ and Ne.

292 Fractional energy loss in the IS channel is shown as a function of deflection angle χ in Figure 6 for
293 CD₄ and Ne scattered from cold salty water and dodecane. CD₄ scattered from cold salty water exhibits a
294 much higher degree of fractional energy loss compared to dodecane, as was observed for Ne, and may

295 similarly be attributable to strong coupling with a hydrogen-bonded network in the liquid. The mechanism
 296 driving χ -dependence appears to be less influential for cold salty water than dodecane, leading to flatter
 297 $\Delta E/E_i$ distributions that are more sensitive to differences between scatterers. Although both scatterers are
 298 neutral species with the same mass (20 amu), they differ in size and polarizability; CD₄ and Ne have radii
 299 of 2.0 and 1.5 Å and polarizabilities of 2.56 and 0.39 Å³, respectively.⁵⁷⁻⁶¹ It is plausible that the polar
 300 nature of water leads to stronger interactions with the more polarizable CD₄ compared to Ne, leading to a
 301 notable difference in the $\Delta E/E_i$ vs χ slope for molecules of varying polarizability, whereas the nonpolar
 302 dodecane surface responds more similarly to both species in comparison.

303 Analysis of the measured $\Delta E/E_i$ values with the soft-sphere model (eq. 3) yields a total internal energy
 304 E_{int} of 14.2 kJ mol⁻¹ and an effective surface mass m_{eff} of 78 amu.⁴⁰ In concept, m_{eff} can be interpreted as
 305 a proxy for how many surface atoms are involved in the collision with a gas particle. Viewed in this way,
 306 the fact that m_{eff} is larger than the mass of water (18 amu) would suggest that the collision with CD₄
 307 involves more than one H₂O molecule or that surface-active Br⁻ anions (80 amu) are participating. The
 308 surface propensity of aqueous bromide is a topic that has yet to be conclusively resolved; however, the
 309 extremely high ionic strength of our solution may increase the likelihood of Br⁻ existing in the interfacial
 310 region.⁶²⁻⁶⁴ In practice, limitations of the soft-sphere model (e.g. high degree of correlation between m_{eff}
 311 and E_{int} , does not account for multiple-bounce collisions) may manifest in nonphysical values of m_{eff} .³⁶
 312 In the soft-sphere expression, m_{eff} is principally related to the slope of the curve, and E_{int} the vertical offset.
 313 CD₄/dodecane and Ne/dodecane have effective surface masses of 52 and 61 amu, respectively, and the
 314 relationship between $\Delta E/E_i$ and χ is visibly very similar for both systems. Likewise, CD₄/salty water has
 315 both a lower m_{eff} (78 amu) and stronger χ -dependence than Ne/salty water (m_{eff} = 190 amu).

316 The parameter E_{int} describes the amount of translational energy that has been converted into excitation
 317 of internal modes of the scatterer and liquid, without distinguishing between them. This partitioning can
 318 be estimated by comparison to E_{int} of an atom scattering from the same liquid surface. A total internal
 319 excitation of 11.8 kJ mol⁻¹ was found for Ne/salty water scattering, which is sufficient to excite several

bulk water modes including intermolecular motions in the THz region and librational bands in the far infrared.^{65, 66} In relating to E_{int} for CD₄/salty water, 14.2 kJ mol⁻¹, one may assume that the degree of surface excitation is the same and that the increase in E_{int} for CD₄ (2.4 kJ mol⁻¹) is from rotational excitation. The internal excitation of CD₄ scattered from dodecane was found to be a comparable value of 3.2 kJ mol⁻¹.³³ Further comparison of CD₄ and Ne shows that scattering from water results in a higher E_{int} than dodecane for both scatterers. The CD₄ and Ne scattering experiments thus determine that cold salty water is a softer surface than dodecane regardless of scatterer.

V. CONCLUSIONS

Our experiments reveal that IS and TD channels are seen for scattering Ne and CD₄ from cold salty water, whereas no detectable scattering of ND₃ in either channel is observed. The latter result is attributed to the high solubility and efficient protonation of ND₃ in water. In contrast, IS and TD for all three scatterers are seen in dodecane experiments, with similar TD fractions and fractional energy loss for ND₃ and CD₄. The likelihood of surface trapping appears to have a causal relationship with the solubility of each scatterer in the respective liquid, lending support to the hypothesis that bulk properties can govern interfacial behaviors.

The angular distribution for IS scattering of CD₄ from cold salty water is strongly super-specular, as was also seen for Ne. In both cases, this effect is attributed to favored anisotropic momentum transfer along the surface normal. Collisional energy transfer for CD₄ is overall greater for scattering from cold salty water than dodecane, and the dependence of $\Delta E/E_i$ on deflection angle varies with both scatterer and surface. Soft-sphere modeling calculates an effective surface mass of 78 amu, which may be indicative of multiple water molecules or bromide anions participating in the collision or instead result from breakdowns in the soft-sphere model that do not account for atypical scattering events. Kinematic analysis additionally yields a total internal excitation of 14.2 kJ mol⁻¹, a quantity compatible with the excitation of several low-frequency bulk water intermolecular and librational modes as well as rotational excitation of CD₄.

345 The ability of cold salty water to selectively trap and reflect ND₃ and CD₄ delivers insight into the
346 fundamental dynamics underpinning interactions between gases and liquids at the air–water interface and
347 provides a basis for future studies. Understanding these principal mechanisms is needed to inform both
348 large-scale models — such as atmospheric systems that necessarily take into account gas transfer across
349 liquid surfaces — as well as smaller, more specialized models that specifically examine cold, concentrated
350 salt solutions like those in evaporating microdroplets. Additional experimental and theoretical work on
351 the solubility of gases in liquids at extreme conditions would enable future gas–liquid scattering studies
352 to investigate the relationship between molecular selectivity and bulk solubility, and whether macro-scale
353 thermodynamics can be used to reliably predict interfacial behavior.

354 **SUPPLEMENTARY MATERIAL**

355 Time-of-flight spectra of ND₃ at outgoing angles for which beam leaking is present can be found in
356 the Supplementary Material.

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362 **AUTHOR DECLARATIONS**

363 **Conflict of Interest**

364 The authors have no conflicts to disclose.

365 **Author Contributions**

366 **Madison M. Foreman:** Conceptualization (equal); Data curation (lead); Formal analysis (lead);
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368 (equal)

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370 (equal); Methodology (equal); Writing – review & editing (equal)

371 **Tiffany C. Ly:** Data curation (supporting); Formal analysis (supporting); Investigation (supporting);
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392 **DATA AVAILABILITY**

393 The data that support the findings of this study are available from the corresponding author upon
394 reasonable request.

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