State-to-state thermal/hyperthermal collision dynamics of atmospheric species

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Direct absorption IR, LIF, REMPI and velocity map imaging methods developed under AFOSR support have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts over this past year have led to progress in multiple areas: 1) Diode laser and LIF studies of hyperthermal CO2 and NO collisions at the gas-room temperature ionic liquid (RTIL) interfaces. 2) Large scale trajectory simulations for theoretical analysis of gas-liquid scattering studies, 3) LIF data for state-resolved scattering of hyperthermal NO at the gas-molten Ga(l) interface as a function of incident energy and surface temperature, 4) Velocity map ion imaging studies elucidating state-resolved reactive scattering dynamics of HCl from self assembled monolayers (SAMs). 5) Ultrafast plasmon mediated electron ejection dynamics in single Au nanostructures via novel scanning photo-ionization imaging microscopy (SPIM) methods developed in our group.

State-to-state collision dynamics, atmospheric radical kinetics

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Abstract:
Direct absorption IR, LIF, REMPI and velocity map imaging methods developed under AFOSR support have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts over this past year have led to progress in multiple areas: 1) Diode laser and LIF studies of hyperthermal CO2 and NO collisions at the gas-room temperature ionic liquid (RTIL) interfaces. 2) Large scale trajectory simulations for theoretical analysis of gas-liquid scattering studies, 3) LIF data for state-resolved scattering of hyperthermal NO at the gas-molten Ga(l) interface as a function of incident energy and surface temperature, 4) Velocity map ion imaging studies elucidating state-resolved reactive scattering dynamics of HCl from self assembled monolayers (SAMs). 5) Ultrafast plasmon mediated electron ejection dynamics in single Au nanostructures via novel scanning photo-ionization imaging microscopy (SPIM) methods developed in our group.

Summary of research accomplishments (2008-present)
The current granting period has been highly productive; over the last three years, 23 manuscripts from our group have been published on AFOSR-supported projects, with selected highlights summarized below.

A. Surface Temperature Dependent Collision Dynamics at Gas-Liquid Interfaces
As a major thrust over the last granting period, we have refined the technology for quantum state resolved scattering at the gas-liquid interface to an unprecedented level of absorbance sensitivity, which has enabled a number of studies.1-7 For example, energy transfer dynamics at the gas-liquid interface has been investigated as a function of surface temperature (Fig. 1) both by experimental studies of CO2 + perfluorinated polyether (PFPE) and molecular dynamics simulations of CO2 + fluorinated self-assembled monolayers (F-SAMs).6 At low incident energies [E_{inc} = 1.6(1) kcal/mol], CO2 J-state populations and transverse Doppler velocity distributions are in quantitative agreement with the surface temperature (T_{rot} \approx T_{trans} \approx T_S) over the range from 230K – 320K. In contrast, the rotational and translational distributions at high incident energies [E_{inc} = 10.6(8) kcal/mol] show evidence for both trapping-desorption (TD) and impulsive scattering (IS) events. Nevertheless, the populations are surprisingly well characterized by a sum of Boltzmann distributions where one component (TD) is equilibrated with the surface (T_{TD} \approx T_S), while the second (IS) is much hotter than the surface temperature (T_{IS} >> T_S). Support for the superthermal, yet Boltzmann, nature of the IS channel is provided by molecular dynamics (MD) simulations of CO2 + F-SAMs [E_{inc} = 10.6 kcal/mol], which also reveal dual-temperature distributions, sticking probabilities, and angular distributions in remarkably quantitative agreement with the experimental PFPE results. Interestingly, experiments as a function of surface temperature reveal an increase in both sticking probability as well as rotational/translational temperature of the IS component. Such a trend is consistent with increased surface roughness at higher surface temperatures,8 which increases the overall probability of trapping, yet also preferentially leads to greater torque to yield more highly rotationally excited CO2 recoiling impulsively from the surface.

Fig. 1
**B. Incident and Final Angle Resolved Collision Dynamics at the Gas-Liquid Interface**

Quantum state resolved detection by direct IR laser absorption in a tight optical multipass offers exceptional flexibility and control over incident and probe geometries, which can be exploited to probe scattering into a full $2\pi$ solid angle. For example, molecular beam scattering dynamics at the gas-liquid interface has been investigated for CO$_2$ ($E_{\text{inc}} = 10.6(8)$ kcal/mol) impinging on liquid PFPE, with quantum-state ($v, J$) populations measured as a function of incident ($\theta_{\text{inc}}$), and final ($\theta_{\text{scat}}$) scattering angles (Fig. 2). The internal state distributions are well-characterized for both normal and grazing incident angles by a two-component Boltzmann model for trapping desorption (TD) and impulsive scattering (IS) at rotational temperatures $T_{\text{rot}}(\text{TD/IS})$. The angular dependence of the IS flux at normal incidence ($\theta_{\text{inc}} = 0^\circ$) is surprisingly well modeled by a simple $\cos^n(\theta_{\text{scat}})$ distribution with $n = 1.0 \pm 0.2$, while glancing incident angles ($\theta_{\text{inc}} = 30^\circ, 45^\circ$, and $60^\circ$) result in lobular angular IS distributions scattered preferentially in the forward direction. This trend is also corroborated in the TD fraction $\alpha$, which decreases rapidly under non-normal incident conditions as a function of backward versus forward scattering direction. Furthermore, the extent of rotational excitation in the IS channel increases dramatically with angle of incidence, consistent with an increasing rotational torque sampled by the projectile by virtue of molecular scale roughness at the gas-liquid interface.

**C. Reaction Dynamics at the Gas–Liquid Interface: F + Squalane (C$_{30}$H$_{62}$)**

One powerful direction has been to use direct infrared laser absorption spectroscopy to probe fast chemical reactions by colliding a supersonic beam of F atoms [$E_{\text{com}} = 0.7(3)$ kcal/mol] with a continuously refreshed liquid hydrocarbon (squalane) surface under vacuum conditions (Fig. 3). Nascent HF($v \leq 3$) products are formed in a highly non-equilibrium (inverted) vibrational distribution [$\langle E_{\text{vib}} \rangle = 13.2(2)$ kcal/mol], reflecting insufficient time for thermal accommodation with the prior to desorption. Interestingly, populations, though colder, are also excited in a non-Boltzmann [$\langle E_{\text{rot}} \rangle = 1.0(1)$ kcal/mol], which that a substantial fraction of also directly scatter into the gas without rotationally equilibrating surface. Finally, nascent HF recoils liquid surface with excess energy, resulting in Doppler broadened line widths that increase systematically with internal HF excitation. The data are consistent with microscopic branching in HF-surface dynamics following the reactive event, with i) a direct reactive scattering (DRS) fraction of newly formed product molecules leaving the surface promptly and ii) a trapping desorption (TD) fraction that accommodates rotationally (though still not vibrationally) with the bulk liquid. Comparison with crossed molecular beam gas phase H atom abstraction processes in our group (such as F + ethane) reveals a notably hotter HF vibrational distribution than observed at the gas-liquid interface.
interface, suggesting that the liquid acts as a partial but incomplete “heat sink” for vibrational energy flow on the time scale of the chemical reaction event.

D. 3D Quantum State Resolved Collision Dynamics at the Gas-Liquid Interface
A critical synergy over the past granting period has been harnessing theoretical molecular dynamics simulations in parallel with experiment (Fig. 4) in order to elucidate the underlying chemical physics. Specifically, large scale MD trajectory calculations have been performed for collisions of CO$_2$ with a model fluorinated self-assembled monolayer surface (F-SAMs), based on an explicit atom-atom interaction potential obtained from earlier theoretical studies with the Hase group.\textsuperscript{3} Initial conditions for the simulations are chosen to match those in our experimental studies, i.e., with high-energy jet-cooled CO$_2$ molecules ($E_{\text{inc}} = 10.6(8)$ kcal/mol, $\langle E_{\text{rot}} \rangle \approx 10$ cm$^{-1}$) scattered from a 300 K perfluorinated liquid surface over a range of incident angles ($\theta_{\text{inc}} = 0^\circ – 60^\circ$). The nascent CO$_2$ rotational distributions prove to be remarkably well-characterized by a simple two-temperature trapping-desorption (TD) and impulsive scattering (IS) model, with nearly quantitative agreement between experimental and theoretical column integrated densities. Furthermore, three-dimensional (3D) quantum state resolved flux maps for glancing incident angles ($\theta_{\text{inc}} \approx 60^\circ$) reveal broad, lobular distributions peaking strongly in the forward subspecular direction as $\cos^n(\theta_{\text{scat}} – \theta')$, with $n \approx 5.6(1.2)$ and $\theta' \approx 49(2)^\circ$. As expected, the component of the scattered flux that proceeds by trapping desorption is equilibrated to the surface temperature. However, the quantitative success of a dual temperature characterization for rotation is consistent with a broad distribution of collision number and duration even for molecules recoiling in a nominally “impulsive scattering” channel, as further confirmed by detailed analysis of the trajectory statistics.

E. Molecular Beam Reactive Scattering Dynamics via IR Direct Absorption
The quantum state resolved IR methods described above have also demonstrated extraordinary power in studying reactive scattering dynamics of F + H$_2$O $\rightarrow$ HF + OH under single-collision, crossed supersonic jet conditions (Fig. 5).\textsuperscript{11} Nascent HF($v,J$) rovibrational populations ($v \leq 2$, $J \leq 17$) at 5.4(1.3) kcal/mol are found to be highly inverted, with 75(2)$\%$ and 21(5)$\%$ of the observed HF product formed in $v = 1$ and 0, respectively. Small but finite branching [5(1)$\%$] into the $v = 2$ manifold is observed, which is accessible only via the additional center of mass collision energy provided by the crossed jet collision geometry. Despite energy constraints associated with substantial vibrational excitation, the reaction dynamics also lead to rotationally hyperthermal HF, with populations observed up to near the energetic limit for each of the $v = 0,1,2$ vibrational manifolds. The trends in these nascent product rovibrational distributions support a strongly bent,
early barrier transition state with long-range dipole-dipole interactions in the exit channel, in excellent agreement with high level MCSCF/MRCI surfaces calculated in our group.\textsuperscript{12}

F. Non-Adiabatic Reaction Dynamics in Atom + Triatom Systems

Reactive collision dynamics in open shell systems offers even more sensitive methods for probing nascent quantum states of the radical product. For example, we have also explored crossed supersonic jet studies of $F + H_2O \rightarrow HF + OH(^3\Pi_{3/2}, ^1\Pi_{1/2})$ under low density, single collision conditions at $E_{\text{com}} = 6(2)\text{ kcal/mol}$, exploiting laser induced fluorescence (LIF) methods to yield rotational, vibrational, and spin-orbit state distributions in the nascent OH.\textsuperscript{13} Of critical dynamical interest is the Wigner non-crossing rule, which predicts the lowest adiabatic reaction barriers on the ground and first excited electronic surfaces at $\Delta E \approx 4\text{ kcal/mol}$ and $\Delta E \approx 25\text{ kcal/mol}$ for formation of OH($^3\Pi_{3/2}$) and OH($^1\Pi_{1/2}$), respectively. In contrast, despite the fact that only reactions on the ground state potential are Born-Oppenheimer allowed at our experimental collision energy, both ground and excited spin-orbit OH products are observed in a substantial ($^3\Pi_{3/2} : ^1\Pi_{1/2} = 69(1)\% : 31(1)\%$) branching ratio. This indicates unambiguously the presence of strong non-adiabatic surface hopping interactions,\textsuperscript{14-16} in agreement with previous results for $F + D_2O \rightarrow DF + OD$.\textsuperscript{17}

Interestingly, despite clear differences in the rotational distributions between $F + H_2O$ and $F + D_2O$ isotopic reactions, the overall electronic branching into spin-orbit manifolds is nearly identical for both OH and OD products. Furthermore, when plotted versus total electronic + rotational energy (Fig. 6), the nascent OH and OD populations each lie on single curves, with pronounced kinks in the Boltzmann plots suggestive of microscopic branching in the reaction dynamics. Such an equivalence of electronic and rotational energy release in the OH/OD products is consistent with nonadiabatic processes taking place in the immediate post transition state region rather than asymptotically in the exit channel.

G. IR Laser Polarization Studies of Stereodynamics at the Gas–Liquid Interface

By way of contrast with the isotropically averaged environment of bulk liquids, the gas-liquid interface offers a fascinating window into non-isotropic collision dynamics. Specifically, stereodynamics at the gas–liquid interface has been investigated by molecular beam scattering of CO$_2$ from liquid PFPE at $E_{\text{inc}} = 10.6(8)\text{ kcal/mol}$, $\theta_{\text{inc}} = 60^\circ$, with internal quantum state populations and $M_J$ distributions probed by high resolution, polarization modulated infrared laser spectroscopy.\textsuperscript{4}

Experimentally, polarization modulation of a single mode diode laser is combined with lock-in detection to measure circular/linear IR polarizance due to CO$_2$ scattering from the surface and probed over a series of final scattering angles. The differential absorption intensities are related through Fano-Macek theory to the three lowest multipole moments ($A_0$, $A_2$, and $O_1$) which describe collisionally
induced orientation and alignment at the liquid surface. The total scattering population reflects both trapping desorption (TD) and impulsive scattering (IS) components, with a strong positive anisotropy in the M\textsubscript{J} distribution that indicates preferential CO\textsubscript{2} scattering from the surface with a forward (i.e., “top-spin”) sense of end-over-end tumbling. Interestingly, the magnitude of the orientation/alignment parameters increases monotonically from zero as a function of final J state (Fig. 7a). This is consistent with the correspondence principle (i.e., J=0 can only be M\textsubscript{J} =0) as well as a simple physical picture of greater torque on the projectile at the liquid interface resulting in both greater rotational excitation and alignment. Theoretical trajectory simulations provide 3D CO\textsubscript{2} flux and J state distributions scattering from fluorinated self-assembled monolayers (F-SAMs), which can be compared with experimental results as a function of final rotational state. Trends in the theoretical orientation/alignment moments are in remarkable agreement over the full range of J-states but with values consistently overpredicted by 2-fold, which provides clear evidence for a higher level of local ordering in F-SAMS vs. PFPE liquid interfaces.

H. State Resolved Scattering at Room-Temperature Ionic Liquid-Vacuum Interfaces
Room-temperature ionic liquids represent a novel class of “green” solvents with nearly zero vapor pressure, high solubility for specific molecules, and therefore of keen industrial interest as possible carbon-sequestration and CO\textsubscript{2} scrubbing agents in natural gas reforming processes. Furthermore, due to their high charge density and electrical conductivity, RTILs are proving to be of considerable use in ionic thrusters for microsatellite propulsion and positioning. We have recently initiated state-resolved scattering studies (Fig. 8) of CO\textsubscript{2} from alkylimidazolium-based RTIL surfaces, containing either BF\textsubscript{4}⁻ or Tf\textsubscript{2}N⁻ anions, a direction which will be explored further in this granting period. The scattered CO\textsubscript{2} exhibits a two-temperature rotational distribution, well described in the context of a trapping-desorption/impulsive-scattering (TD/IS) model. We find that the scattering dynamics for short alkyl chains are highly dependent upon the anion identity, implying that the anions are present at the interface and may play a critical role in the gas-liquid collisions. However, trends in the trapping-desorption fractions are in stark opposition with trends in the bulk Henry’s Law solubility constants, clearly highlighting the critical role of non-equilibrium interfacial dynamics over equilibrium bulk solubility properties in these high-energy collisions.

I. High Resolution Dopplerimetry Scattering at the Gas – Liquid Interface
The high resolution (Δν ≈ 0.0001 cm\textsuperscript{-1}) of the IR probe laser also provides an exceptionally detailed map of the quantum state specific recoil vector velocities in the gas-liquid scattering event. By way of example, full three dimensional (3D) translational distributions for quantum state-resolved scattering dynamics at the gas-liquid interface have been explored for experimental and theoretical studies of CO\textsubscript{2} + perfluorinated surfaces (Fig. 9). Experimentally, high resolution absorption profiles are measured as a function of incident (θ\textsubscript{inc}) and scattering (θ\textsubscript{scat}) angles for CO\textsubscript{2} that has scattered from a 300 K PFPE surface with an incident energy of E\textsubscript{inc} = 10.6(8) kcal/mol. Line shape analysis of the absorption profiles reveals non-equilibrium dynamics that are characterized by trapping-desorption (TD) and impulsive scattering (IS) components, with each channel characterized by an effective Doppler temperature that agrees surprisingly well with analysis based solely on rotational distributions. Molecular dynamics (MD) simulations of CO\textsubscript{2} + fluorinated self-assembled monolayer surface (F-SAMs) yield trajectories parsed by the scattering angle θ\textsubscript{scat} and J, with the results corrected by rigorous flux-to-
density transformation and providing comparisons in remarkably quantitative agreement with experiment. 3D flux and velocity distributions obtained from MD simulations are also presented to illustrate the importance of in- and out-of-plane scattering. It is worth noting that such an experimental capability provides data for scattering into the “full $2\pi$” solid angle, which is one of many powerful advantages of high resolution direct absorption laser methods.

References


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“IR Laser Studies of Rovibrationally State-Resolved Reactive Scattering,” Frontiers in Physical Chemistry, Academia Sinica and National Taiwan University, Taipei, Taiwan, October 20, 2008.

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“Large Amplitude Motion and Roaming Dynamics: What Radicals May Have to Say at High Resolution,” Workshop on Roaming-Radical/Multiple-Mechanisms, Argonne National Laboratory and JILA, University of Colorado, May 7, 2010.


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