State-resolved Thermal/Hyperthermal Dynamics of Atmospheric Species

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

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Direct absorption IR, LIF, REMPI and velocity map imaging methods have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts 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.

State-to-state collision dynamics, atmospheric radical kinetics

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Abstract:
Direct absorption IR, LIF, REMPI and velocity map imaging methods have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts 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.

Summary of research accomplishments under AFOSR funding (2011-present)
This past granting cycle has been unusually productive, with 18 manuscripts from our group published or submitted over the last three years on AFOSR-supported projects. The complete list of manuscripts is reported later in this report, with selected highlights summarized below.

A. Laser Diode Quantum State Resolved Scattering of CO₂ from Room Temperature Ionic Liquids
As one of the major thrusts over the last granting period, we have refined the infrared laser technology for quantum state resolved scattering at the gas-liquid interface to unprecedented sensitivity levels, which has enabled a large number of dynamical studies.¹⁻⁵ Of particular interest has been probing novel collision dynamics at gas-room temperature ionic liquid (RTIL) interfaces whose bulk chemical/physical properties can be engineered by chemical modification.⁶⁻⁷ For example, we obtained first results (see Fig. 1) on state-resolved scattering studies for seeded CO₂ supersonically cooled molecular beams (E_{inc} = 14.8(10) kcal/mol) from a series of room temperature ionic liquids (RTILs, Cₙ⁻ methylimidazolium cations, BF₄⁻ or Tf₂N⁻ anions), which are of particularly keen interest for molecule specific "filters" in industrial synthesis and carbon sequestration processes.⁸ Final rovibrational quantum state and Doppler velocity distributions from such hyperthermal surface scattering events have been monitored by high resolution diode laser absorption spectroscopy as a function of i) cation alkyl chain length and ii) anion size, and analyzed to yield the propensity for trapping-desorption (TD) vs. impulsive scattering (IS)

Fig. 1

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dynamics. The data reveal fascinating trends in anion vs. cation competition for interfacial sites, for example, i) the clear presence of anions at the surface for sufficiently short alkyl headgroups, as well as ii) inertial “stiffening” effects due to increasing the average surface mass. Most intriguingly, the trapping-desorption probabilities are found to follow the exact opposite trend in “bulk” Henry’s Law solubility constants with respect to anion size, which highlights the intrinsically non-equilibrium dynamics sampled by hyperthermal collisions at the gas-liquid interface.

B. Probing for Ions at the Gas-Liquid Interface by Quantum State-resolved Scattering

There has been a long standing controversy over the free energy propensities for cations vs. anions at the gas-liquid interface, which has important implications for atmospheric and marine boundary layer chemistry, as well as being of fundamental interest to cluster/condensed phase chemical physics communities. To explore this further, we have pursued a novel approach for selectively probing ions at interfaces, based on scattering high energy, jet-cooled molecular projectiles from the surface of hydrogen-bonded liquids (e.g., glycerol) with dissolved alkali halide salts as the source of solvated charges. In particular, we have probed quantum state-resolved scattering studies of CO$_2$ as a function of i) alkali halide concentration (0-5 M), ii) anion identity ($\text{LiX}: X = \text{Cl}^-, \text{Br}^-, \text{I}^-$), and iii) cation identity ($\text{M}^+; M = \text{Li}^+, \text{Na}^+, \text{K}^+$), which reveal clear “signatures” in the final rotational state distributions (see Fig. 2). As a simple physical picture, one might expect interfacial anions to interact strongly with the CO$_2$ quadrupole moment and encourage horizontal collisions with the liquid surface. On the other hand, electrostatic interactions with surface cations could suggest a greater propensity for vertical collisional geometries of the CO$_2$. Experimentally, the scattering CO$_2$ distributions at high rotational energies reveal an unambiguous dependence only on the anion identity, with i) large effects seen for the most polarizable anionic species (e.g., I$^-$), ii) no dependence within experimental uncertainty as a function of monovalent cation, and iii) detailed trajectory calculations providing additional insight into the anticipated vs. observed magnitudes of these experimental trends. The results clearly support a reduced cation vs. anion density in the topmost surface layer, which is consistent with second harmonic generation/x-ray photoelectron studies and could profoundly

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impact inelastic/reaction dynamics and/or interfacial chemistry on surfaces of atmospheric aerosols.\textsuperscript{14,15}

C. State-resolved Velocity Map Imaging of Surface-Scatterered Molecular Flux

In an important growth area in the upcoming granting period, we have been developing methods to exploit ultrasensitive ion generation/detection methods to probe collision dynamics at gas-solid and gas-self assembled monolayer (SAMs) interfaces. As a critical first step in this direction, we have reported a novel surface-scattering technique, which combines resonance-enhanced multiphoton ionization (REMPI) with velocity-map imaging (VMI) to yield quantum-state and momentum component-resolved distributions in the scattered molecular flux.\textsuperscript{16} As an initial test system, we have explored hyperthermal scattering ($E_{\text{inc}} = 21(5)$ kcal/mol) of jet cooled HCl from Au(111) on atomically flat mica surfaces heated to 500 K. The resulting images clearly reveal 2D ($v_{\text{in-plane}}$ and $v_{\text{out-of-plane}}$) velocity component distributions dominated by two primary features: trapping/thermal-desorption (TD) and a hyperthermal, impulsively scattering (IS) distribution. In particular, the IS component is strongly forward scattered and largely resolved in the velocity map images, which allows us to probe detailed correlations for the first time between rotational and translational degrees of freedom in the IS flux, without any model dependent deconvolution from the TD fraction. Interestingly, such correlation measurements reveal that HCl molecules which have undergone substantial decrease in the incident velocity component parallel to the scattering plane have actually gained the most rotational energy, suggesting a dynamical energy constraint between these two degrees of freedom. More quantitatively, the data can be reduced to a 2D rotational energy map that correlates $\langle E_{\text{rot}} \rangle$ with velocity along and normal to the scattering plane, which reveals that such exchange events occur primarily between rotation and the in-plane kinetic energy component, with $v_{\text{out-of-plane}}$ playing a relatively minor role.

D. Rovibronically Inelastic Scattering of NO($^{2}\Pi_{1/2}(0.5)$) from Molten Gallium

Over the past granting period, we have developed methods for probing quantum state resolved collisions of open shell radicals with molten metals, with initial results suggesting this to be a novel window into non-adiabatic “surface hopping” dynamics of partial electron transfer at the gas-condensed phase interface. Specifically, we have scattered jet cooled NO molecules in the ground ($^{2}\Pi_{1/2}$) spin-orbit state at 45° with respect to a Ga(l) surface ($E_{\text{inc}} = 1.0(3)$ to 20(6) kcal/mol) to probe rotationally and electronically inelastic collisions at the gas-molten metal interface, with final rotational, spin-orbit, and $\lambda$-doublet distributions detected at the specular angle by confocal LIF on the 0-0 and 1-1 A-X bands (see Fig. 4).\textsuperscript{17} Interestingly, NO scattering at near thermal collision energies, where trapping desorption (TD) should dominate, results in
Boltzmann distributions with effective electronic and rotational temperatures consistently lower than the surface temperature \( T_S \), as predicted by the Bowman-Gossage “rotational cooling” model for desorption from a surface rotor state with restricted dimensionality.\(^{18}\) However, increasing collision energy results in a steeper increase in scattered NO rotation vs. spin-orbit electronic temperatures, with the differences between rotational and spin-orbit dynamics discussed in terms of the possible electron-hole pair excitations in the conducting metal. Furthermore, while such electronically non-adiabatic processes could also influence vibrational excitation dynamics in NO + Au(111), the data indicate a sub-thermal \( (< 2.6 \times 10^{-4}) \) probability for collisional formation of NO\( (v = 1) \) at Ga surface temperatures up to 580 K. The propensity for Ga(l) to transform incident translational energy into rotation is notably higher than previous NO scattering studies from single crystal solid surfaces,\(^{19}\) which can be interpreted in terms of temperature-dependent capillary wave excitations introducing microscopic “roughening” at the gas-liquid metal interface.

E. Confocal Microscopy/Photogeneration Kinetics of Highly SERS Active Ag Nanoparticles

Nanoscale metal materials can exhibit novel optical and electronic properties that differ dramatically from the bulk, with Au, Ag and Cu of particular interest due to collective surface plasmon resonances (SPR) that can be excited in the near ultraviolet and visible. The convenience of visible laser sources coupled with the strong size, shape and proximity dependence on the spectral properties make such nanoscale plasmonic materials a powerful research tool from biophysics to nanooptics, but with a significant challenge of producing such nanostructures with high activity and reproducibility. Toward this end, we have developed simple yet robust laser based methods for photogeneration of diffraction limited, intensely Raman active silver nanoparticles from AgClO\(_4\) dispersed in a thin polymer film (see Fig. 5).\(^{20}\) The emission is resolved both spectrally and temporally to
demonstrate that the signal is prompt (< 1 ps) and arises from surface enhanced Raman scattering (SERS) from multiple silver nanoparticles generated in the diffraction limited spot. The time evolution of the SERS signal is sigmoidal in shape and well described by cooperative Avrami phase transformation kinetics. The rate constant for this Avrami transformation is found to depend linearly on illumination intensity, consistent with single photon photoreduction of the AgClO₄ starting material as the limiting step to form silver nanoparticles. Avrami analysis of the kinetics indicates that transformation is constrained to 2D, consistent with the hexagonal platelike structures observed from correlated high resolution SEM images of the samples. The technique presented provides a novel route to systematic generation of large scale periodic molecular sensor arrays with long term stability, diffraction limited resolution (< 1 μm), and laser based spatial/temporal control of the formation kinetics.

F. Multiphoton Scanning Photoionization Imaging Microscopy of Plasmonic Nanostructures

Efforts over the last granting period have been successful in developing and extending our capabilities in scanning photoionization imaging microscopy (SPIM) for detailed studies of plasmonic nanomaterials. As first results in this exciting area, ultrafast photoemission studies of single Au and Ag metal nanostructures have been reported, based on 4-photon ultrafast (30 fs) excitation at 840 nm in a homebuilt in vacuo Galliean microscope to yield high signal-to-noise 2D photoelectron images for a variety of nanomaterials from photolithographically patterned gold to crystalline Au nanorods and polycrystalline silver nanospheres. At the single nanoparticle level, striking differences in the photoemissive properties of individual nanoparticles are observed that would escape detection in ensemble studies. Under 840 nm excitation, for example, each Au nanorod on a Pt substrate exhibits a strongly anisotropic \( \cos^8(\theta - \theta_0) \) dependence of photoemission strength on the angle between laser polarization (\( \theta \)) and the rod axis (\( \theta_0 \)), clearly consistent with 4-photon electron photoemission initiated by multiphoton excitation of the long-axis dipolar plasmon resonance for that specific nanorod geometry (see Fig. 6). Surprisingly, strongly polarization-dependent photoelectron signals are also observed for nominally spherical Ag nanoparticles, with varying degrees of anisotropy for different particles. One possibility indicated by the data and supported by later studies is that localized regions of concentrated electric fields (i.e., “hot-spots”) or local variations of the emission propensity in these polycrystalline particles are responsible for the strong polarization anisotropy. In summary, the strong wavelength, intensity and angular sensitivity of the SPIM signals provides a promising alternative technique for probing local electric field enhancement and plasmonic properties of individual metallic nanostructures.
G. SPIM Photoemission from Au Nanorods: Critical Role of Plasmonic Near-Field Enhancement

We have extended the above studies to explore electron emission from individual Au nanorods deposited on indium-tin-oxide (ITO) following excitation with femtosecond laser pulses near the rod longitudinal plasmon resonance, with the measured electron signals found to strongly depend on the excitation laser polarization and wavelength.\(^{21,23}\) Correlated secondary electron microscopy (SEM) and dark-field microscopy (DFM) studies of the same nanorods unambiguously confirm that maximum electron emission results from i) laser polarization aligned with the rod long axis and ii) laser wavelength resonant with the localized surface plasmon resonance. The experimental results are in excellent agreement with quantitative predictions for a coherent multiphoton photoelectric effect, which is identified as the predominant electron emission mechanism for metal nanoparticles under the excitation conditions studied (see Fig. 7). Due to the high order (n = 4) dependence on laser intensity and the enhancement of the incident electromagnetic E field in the particle near-field, the multiphoton photoemission rate is shown to be increased by over 10 orders of magnitude in the vicinity of a localized surface plasmon resonance. As supported by detailed theoretical COMSOL calculations of the plasmonic electromagnetic fields, these findings identify multiphoton photoemission as an extremely sensitive metric of local electric fields (i.e., “hot spots”), which in turn can be exploited for direct quantitation of the near-electric field enhancement factors in more complex plasmonic nanoparticle architectures.

H. Spatial/Polarization Microscopy of Ag Nanocubes: Role of Coherent Plasmon Excitation

One critical question in such electron photoemission studies has been the role of optical coherence in the multiphoton plasmon state, i.e., is the electron ejection event due to sequential absorption of multiple incoherent photons, or does it require a coherent collective excitation? To address this in detail, we have explored\(^{24}\) electron emission from single, supported Ag nanocubes (see Fig. 8) excited with ultrafast laser pulses (\(\lambda = 800\ nm\)) via spatial and polarization correlated (i) dark field scattering microscopy (DFM), (ii) scanning photoionization microscopy (SPIM), and (iii) high-resolution transmission electron microscopy (HRTEM). In
complete contrast with the perfectly isotropic behavior predicted in a 1-photon absorption spectrum for any absorber with a rotational axis of 3-fold (or higher), the SPIM signals are found to be highly dependent on polarization vector, peaking strongly for alignment parallel to the cube diagonals. Most importantly, the observed anisotropy rules out incoherent thermionic emission models for electron heating ejection and serves to highlight the critical influence of plasmonic near-field enhancement of the incident electric field on the overall electron yield. For laser pulses with photon energy below the metal work function, coherent multiphoton photoelectron emission (MPPE) is therefore identified as the most probable mechanism responsible for electron emission from Ag nanocubes and likely for metal nanoparticles/surfaces in general.

References
Personnel Supported:
1) Tom Baker (graduate student)
2) Amelia Zutz (graduate student)
3) Mike Ziemkiewicz (graduate student)
4) Andrew Gisler (graduate student)
5) Rob Roscioli (postdoctoral student)
6) Andrej Grubisic (postdoctoral student)

Papers published/submitted during the 2011-2014 granting period acknowledging AFOSR support:


10) M. P. Ziemkiewicz, A. Zutz, and D. J. Nesbitt, “Inelastic scattering of radicals at the gas-ionic liquid interface: Probing surface dynamics of [bmim][Cl], [bmim][BF₄], and [bmim][Tf₂N] by rovibronic scattering of NO [²Π₁/₂(0.5)],” J. Phys. Chem. C. 
DOI: 10.1021/jp212336a (2012)


Interactions/Transitions:
Invited talks during the 2011-2014 granting period acknowledging AFOSR support:

“In Search of Simplicity: From Spectroscopy of Radicals to Collisions at the Gas-Liquid Interface,” Department of Chemistry, University of Virginia, Charlottesville, VA, March 25, 2011.


“From Spectroscopy of Hot Radicals at Cold Temperatures to Collisions at the Gas-Liquid Interface,” University of Georgia, Department of Chemistry, Athens, GA, April 17, 2012.


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“From Single Molecule RNA Folding to Ultrafast Nanoparticle Plasmonics: The Beauty of One at a Time,” Department of Chemistry, Purdue University, April 30, 2014.


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Abstract
Direct absorption IR, LIF, REMPI and velocity map imaging methods have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts 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.

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Technical Summary

Funding Summary by Cost Category (by FY, $K)

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