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

**5. FUNDING NUMBERS**

F49620-03-1-0029

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**12a. DISTRIBUTION / AVAILABILITY STATEMENT**

Approve for Public Release: Distribution Unlimited

**13. ABSTRACT (Maximum 200 Words)**

Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics under single collision conditions. Efforts over this past year have led to significant progress in several areas: i) H atom abstraction dynamics in prototypic atom + diatom (e.g. X + HD → HX(v,J) + D), atom + triatom (e.g. X + H2O → HX(v,J) + OH(v,N)) and atom + polyatom (e.g. X + CH3-CH2) reaction systems, ii) application of novel slit discharge concentration modulation methods for ultrasensitive IR laser based detection of cold ions in supersonic jets, iii) LIF capabilities for stereodynamical studies of aligned collisions in rovibrationally state-selected molecules, iv) first efforts in extending high sensitivity IR absorption methods to reactive scattering at the gas + hydrocarbon liquid interface, which indicate surprisingly “hot”, highly non-statistical product state distributions as well as direct evidence for both “direct” and “trapping/desorption” reaction channels.

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**14. SUBJECT TERMS**

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

Abstract:
Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state reactive scattering dynamics under single collision conditions. Efforts over this past granting period have led to significant progress in several areas: i) H atom abstraction dynamics in prototypic atom + diatom (e.g. X + HD → HX(v,J) + D), atom + triatom (e.g. X + H2O → HX(v,J) + OH(v,N)) and atom + polyatom (e.g. X + CH3-CH3) reaction systems, ii) application of novel slit discharge concentration modulation methods for ultrasensitive IR laser based detection of cold ions in supersonic jets, iii) stereodynamics of aligned collisions in rovibrationally state-selected molecules in crossed jets, iv) development of high sensitivity IR absorption methods to hyperthermal inelastic and reactive scattering at the gas-liquid interface, which indicate the presence of surprisingly “hot”, highly non-statistical product state distributions as well as direct evidence for both “direct” and “trapping/desorption” reaction channels.

4) Accomplishments/New Findings

The work in this last granting period has resulted into 19 papers and over 40 invited talks acknowledging support from the AFOSR. In the interest of brevity, two of the research areas represented by this larger body of work are discussed below.

1) Over the past decade, elegant scattering studies have been performed between high energy molecular beams and low vapor pressure liquid surfaces, such as large chain hydrocarbons, perfluoropolyethers (PFPE), and even liquid metals, based on translational energy loss time of flight mass spectrometry. It has proven more challenging, however, to investigate internal rovibrational degrees of freedom in gas-liquid energy transfer dynamics. As a major building effort over this granting period, we have constructed an apparatus for detailed study of quantum state-resolved inelastic energy transfer dynamics at the gas-liquid interface. The approach relies on supersonic jet-cooled molecular beams impinging on a continually renewable Fenn-type liquid surface in vacuum, exploiting sub-Doppler diode laser absorption methods to probe rotation, vibration and translational distributions in the scattered flux. First results have been obtained for skimmed beams of jet-cooled CO2 (Tbeam ≈ 15 K) colliding at normal incidence with a liquid perfluoropolyether (PFPE) surface at Ecoll = 15 kcal/mol, with tunable Pb-salt diode laser direct absorption on the CO2 asymmetric stretch. Measured rotational distributions in both 000 and 010 vibrational manifolds indicate CO2 inelastically scatters from the surface into a hot, non-
Boltzmann distribution, clearly indicating a lack of thermal equilibration with the liquid. Furthermore, high resolution laser Doppler profiles indicate translational distributions significantly warmer than T, and increasing systematically with J rotational state. Detailed analysis of these rotational and translational distributions support the presence of two distinct collision pathways, i) a Trot ≈ 300 K component due to trapping desorption (TS) events, and ii) a much hotter distribution (Trot ≈ 750 K) due to “prompt” direct inelastic scattering (IS) from the gas-liquid interface. Interestingly, populations in the CO₂ bending vibration are inefficiently excited (Tvib ≈ 230 K) by scattering from the liquid, consistent with slower T-V collisional energy transfer on the time scale of the gas-liquid scattering event.

2) There is currently intense interest in the role of multiple potential energy surfaces and non-adiabatic dynamics for chemical reactions in the upper atmosphere. We have pursued extensive ab initio theoretical studies\(^1\) (with MRCI+Q, spin orbit interactions included) for hydrogen abstraction reactions in the F + H₂O system, which predict a simple adiabatic correlation of the lowest two F(²P\(_{3/2}\)) surfaces with the two lowest spin orbit states of OH(²Π\(_{3/2,1/2}\)). This provides a novel opportunity to probe the fraction of reactive events that occur by non-adiabatic pathways. Specifically, the state-resolved reactive scattering dynamics of F + D₂O → DF + OD has been studied at E\(_{\text{com}}\) ≈ 5(1) kcal/mol in low density crossed supersonic jets, exploiting laser-induced fluorescence for detection of the nascent OD product under single collision conditions.\(^2\) The product OD is found exclusively in the ν₀D = 0 state with only modest rotational excitation, consistent with weak coupling of the reaction exothermicity into the “spectator” bond degrees of freedom. As expected, the OD is formed predominantly in the ground spin orbit state (²Π\(_{3/2}\)), which correlates adiabatically with reaction over a low barrier (ΔE\(^{TS}\) ≈ 4 kcal/mol). Interestingly, however, significant excited spin orbit state formation (²Π\(_{1/2}^\pm\)) is also observed (35%), despite a much higher barrier (ΔE\(^{TS}\) ≈ 25 kcal/mol) that is energetically inaccessible by ≈ 20 kcal/mol in the Born-Oppenheimer approximation. The very presence of spin orbit excited ²Π\(_{1/2}^\pm\), therefore, provides unambiguous evidence for non-adiabatic surface hopping dynamics between the lowest two electronic surfaces for the F + D₂O atom abstraction reaction. This is in agreement with theoretical predictions of strong non-adiabatic coupling in the post-transition state “bond-making” region,\(^1\) and confirms that reactive scattering, even in “simple” atom + triatom systems, is not necessarily isolated to the ground electronic surface.


(10) Sinha, M. P.; Fenn, J. B. 5th Int. Symposium on Molecular Beams 1975.


5) Personnel Supported:
1) Erin Whitney (graduate student)
2) Tom Baker (graduate student)
3) Alex Zolot (graduate student)
4) Brad Perkins (graduate student)
5) Michael P. Deskevich (graduate student)
6) Oliver Monti (postdoctoral student)
7) Thomas Haeber (postdoctoral student)
8) Feng Dong (postdoctoral student)

6) Papers published/submitted during the 2003-2005 granting period acknowledging AFOSR support:


7) Interactions/Transitions:

Invited talks during the 2003-2005 granting period acknowledging AFOSR support:


“IR/UV Crossed Beam Studies of Nonadiabatic Dynamics: The Road Taken or Not Taken,” 227th National ACS Meeting, Anaheim, CA, April 1, 2004.


“In Search of Simplicity: From Reaction Dynamics to Quantum Dots,” Department of Chemistry, University of Bern, Bern, Switzerland, June 8, 2004.


“Optical Physics at the Single Molecule Level: From Quantum Dots to Docking of RNA”, Lehrstuhl für BioMolekulare Optik, Department für Physik, Ludwig Maximilians Universität, München, Germany, April 12, 2005.


“Spectroscopy on a Mission: Reaction Dynamics and Highly Reactive Chemical Intermediates,” 60th International Symposium on Molecular Spectroscopy, Columbus, OH, June 20, 2005.

“Molecular Splashes and Molecular Pretzels”, Physical and Theoretical Chemistry Laboratory, Oxford University, Oxford, UK, July 20, 2005.


Consulting/Advisory Functions:

Advisory interactions with colleagues at Air Force Research Laboratory (Dr. James Dodd, Dr. Steve Lipson) regarding their radical kinetics program relevant to “airglow” in the upper atmosphere. Several discussions with Skip Williams, AFRL, regarding long pass length Off-Axis ICOS techniques.

Advisory committee, Molecular Spectroscopy Symposium,
Advisory committee, International Meeting on Near Field Optics,
Advisory committee, International Conference on Quantum Dots
Organizer for OSA-ILS symposium on single molecule detection/near field imaging,

ACS Program Chair for Physical Chemistry (2004)
ACS Program Committee member for Physical Chemistry (2000-05)
Editorial Board, Journal of Chemical Physics
Editorial Board, Journal of Physical Chemistry
Editorial Board, Molecular Physics
Advisory Board, Phys Chem Chem Phys
Review Panel, Journal of Chemical Physics

8) Inventions and Patent disclosures:
None

9) Honors, Awards or Fellowships received (2002-2005)
Alexander von Humboldt Fellowship, Humboldt Foundation (2000-present)
American Physical Society Fellow
National Institute of Standards and Technology Fellow (2005)
Fellow of the Royal Society of Chemistry, UK (2005)