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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. $X + HD \rightarrow HX(v,J) + D$), atom + triatom (e.g. $X + H_2O \rightarrow HX(v,J) + OH(v,N)$) and atom + polyatom (e.g. $X + CH_3\text{-}CH_3$) 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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State-to-state thermal/hyperthermal collision dynamics of atmospheric species

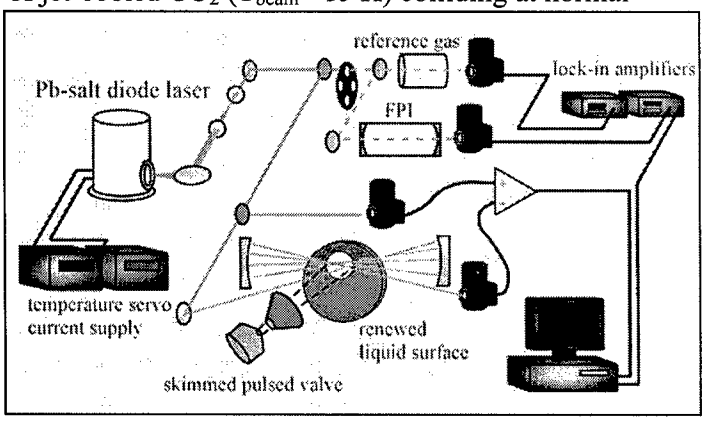
Abstract:

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 + H_2O → HX(v,J) + OH(v,N)) and atom + polyatom (e.g. X + CH_3-CH_3) 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

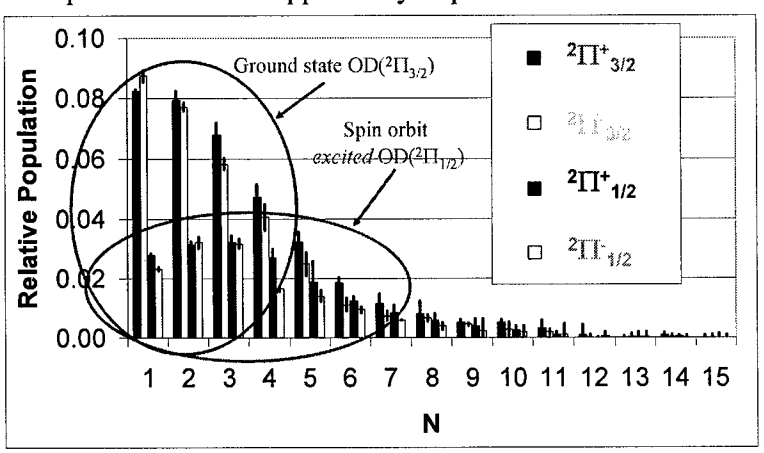
The work in this last granting period has resulted into 19 papers and over 40 invited talks acknowledging support from the AFOSR. In the interest of brevity, two of the research areas represented by this larger body of work are discussed below.

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,[1-3] perfluoropolyethers (PFPE),[4] and even liquid metals,[5,6] 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.[7,8] 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.[9] The approach relies on supersonic jet-cooled molecular beams impinging on a continually renewable Fenn-type[10] 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 CO_2 (T_{beam} ≈15 K) colliding at normal incidence with a liquid perfluoropolyether (PFPE) surface at E_{com} = 15 kcal/mol, with tunable Pb-salt diode laser direct absorption on the CO_2 υ_3 asymmetric stretch. Measured rotational distributions in both 00^00 and 01^10 vibrational manifolds indicate CO_2 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_s 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 $T_{rot} \approx 300$ K component due to trapping desorption (TS) events, and ii) a much hotter distribution ($T_{rot} \approx 750$ K) due to "prompt" direct inelastic scattering (IS) from the gas-liquid interface. Interestingly, populations in the CO_2 bending vibration are inefficiently excited ($T_{vib} \approx 230$ 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[11] (with MRCI+Q, spin orbit interactions included) for hydrogen abstraction reactions in the F + H_2O 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($^2\Pi_{3/2,1/2}$). 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 + $D_2O \rightarrow$ DF + OD has been studied at $E_{com} \approx 5(1)$ kcal/mol in low density crossed supersonic jets, exploiting laser-induced fluorescence for detection of the nascent OD product under single collision conditions.[12] The product OD is found exclusively in the $v_{OD} = 0$ 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 ($^2\Pi_{3/2}{}^{\pm}$), which correlates adiabatically with reaction over a low barrier ($\Delta E^{TS} \approx 4$ kcal/mol). Interestingly, however, significant *excited spin orbit* state formation ($^2\Pi_{1/2}{}^{\pm}$) is also observed (35%), despite a much higher barrier ($\Delta E^{*TS} \approx 25$ kcal/mol) that is *energetically inaccessible* by ≈ 20 kcal/mol in the Born-Oppenheimer approximation. The very presence of spin orbit excited $^2\Pi_{1/2}{}^{\pm}$, therefore, provides unambiguous evidence for *non-adiabatic* surface hopping dynamics between the lowest two electronic surfaces for the F + D_2O atom abstraction reaction. This is in agreement with theoretical predictions of strong non-adiabatic coupling in the post-transition state "bond-making" region,[11] and confirms that reactive scattering, even in "simple" atom + triatom systems, is not necessarily isolated to the ground electronic surface.



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(2) Saecker, M. E.; Nathanson, G. M. *Journal of Chemical Physics* **1993**, *99*, 7056.
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(8) Kelso, H.; Kohler, S. P. K.; Henderson, D. A.; McKendrick, K. G. *Journal of Chemical Physics* **2003**, *119*, 9985.
(9) Perkins, B. G.; Haeber, T, Nesbitt, D. J. *Journal of Physical Chemistry B 34, `16396-16405,* **(2005)**
(10) Sinha, M. P.; Fenn, J. B. *5th Int. Symposium on Molecular Beams* **1975**.
(11) Deskevich, M. P.; Nesbitt, D. J.; Werner, H. J. *Journal of Chemical Physics* **2004**, *120*, 7281.
(12) Ziemkiewicz, M.; Wojcik, M.; Nesbitt, D. J. *Journal of Physical Chemistry A* **2005**, (in press).

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:

M. K. Kuno, D. P. Fromm, S. T. Johnson, A. Gallagher and D. J. Nesbitt, "Modeling distributed kinetics in isolated semiconductor quantum dots," Phys. Rev. B 67, 125304 (2003).

S. A. Nizkorodov, M. Ziemkiewicz, T. L. Myers and D. J. Nesbitt, "Vibrationally-mediated dissociation dynamics of H_2O in the v_{OH}=2 polyad," J. Chem. Phys. 119, 10158 (2003).

H. F. Hamann, M. Larboard, S. Barzen, T. Brown, A. Gallagher and D. J. Nesbitt, "Extinction near-field optical microscopy," Optics Communications 227, 1-13 (2003).

O. L. A. Monti, J. T. Fourkas and D. J. Nesbitt, "Visible light-induced generation of silver nanoparticles," J. Phys. Chem. B 108, 1604-1612 (2004).

M. P. Deskevich, H. J. Werner, and D. J. Nesbitt, "Dynamically weighted MCSCF: Multistate calculations for $F+H_2O \rightarrow HF+OH$ reaction paths," J. Chem. Phys.120, 7281-7289 (2004).

V. V. Protasenko, A. Gallagher and D. J. Nesbitt, "Factors that can influence confocal apertureless near field scanning optical microscopy," Optics Communications 233, 45-56 (2004).

O. Votava, S. R. Mackenzie, and D. J. Nesbitt, "Intracluster stereochemistry in van der Waals complexes: Steric effects in UV photodissociation of state-selected Ar-HOD/H_2O," J. Chem. Phys. 120, 8443-8452 (2004).

S. A. Nizkorodov, M. Ziemkiewicz and D. J. Nesbitt, "Vibrationally-mediated dissociation of H_2O dimer and Ar-H_2O in the v_{OH}=2 manifold," J. Chem. Phys. 122, 194316-194327 (2005).

E. S. Whitney, A. M. Zolot, A. B. McCoy, J. Francisco and D. J. Nesbitt, "Impulsive model scattering dynamics in atom + polyatomic systems: $F + C_2H_6 \rightarrow HF(v,J) + C_2H_5$," J. Chem. Phys. 122, 124310-124320 (2005).

F. Dong, D. Uy, S. Davis, M. Child and D. J. Nesbitt, "Molecular ions in a slit-jet discharge: High-resolution infrared spectroscopy and tunneling dynamics of HD_2O^+," J. Chem. Phys. 122, 224301-224314 (2005).

M. P. Deskevich and D. J. Nesbitt, "Large amplitude quantum mechanics in polyatomic hydrides: I. Particles-on-a-Sphere model for XH_n," J. Chem. Phys. 23, 84304 (2005).

B. G. Perkins, Jr., T. Haeber and D. J. Nesbitt, "Inelastic energy transfer dynamics at the gas-liquid interface: High resolution IR diode laser studies of quantum state-resolved CO_2 scattering from polyfluorophenyl ether (PFPE)", J. Phys. Chem. B 34, 16396-16405 (2005)

M. Ziemkiewicz, M. Wojcik and D. J. Nesbitt, "Direct evidence for non-adiabatic dynamics in atom + polyatom reactive scattering: $F + D_2O \rightarrow DF + OD$," J. Chem. Phys. 123, 224307 (2005).

O. L. A. Monti, T. A. Baker and D. J. Nesbitt, "Imaging nanostructrures with scanning photoionization microscopy", J. Chem. Phys. (submitted).

M. Y. Hayes, M. P. Deskevich, D. J. Nesbitt, K. Takahashi and R. T. Skodje, "A simple picture for the rotational enhancement of the rate for the $F + HCl \rightarrow HF + Cl$ reaction: A dynamical study using a new *ab initio* potential energy surface", J. Phys. Chem. A 110, 436-444 (2006).

F. Dong, S. Davis and D. J. Nesbitt, "Slit Discharge IR Spectroscopy of Jet-Cooled Cyclopropyl Radical: Structure and Intramolecular Tunneling Dynamics", J. Phys. Chem B (in press).

T. Haeber, A. C. Blair, M. D. Schuder and D. J. Nesbitt, "Hyperconjugation dynamics in alkyl radicals: High-resolution spectroscopy of the ethyl CH stretch manifold", J. Chem. Phys. 124, 54316 (2006).

X. Huang, A. B. McCoy, J. M. Bowman, L. M. Johnson, C. Savage, F. Deng and D. J. Nesbitt, "Quantum deconstruction of the infrared spectrum of CH_5^+", Science 311, 60-63 (2006).

M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje and D. J. Nesbitt, "Multireference configuration interaction calculations for the $F(^2P) + HCl \rightarrow HF + Cl(^2P)$ reaction: A correlation scaled ground state ($1^2A'$) potential energy surface", J. Chem. Phys. (in press).

7) Interactions/Transitions:

Invited talks during the2003-2005 granting period acknowledging AFOSR support:

"Quantum Dot Power Law Kinetics," University of Heidelberg, Heidelberg, Germany, February 27, 2003.

"Jet Cooled Radicals and Blinking Quantum Dots," Argonne National Laboratory, Argonne, IL, March 10, 2003.

"Power Law Kinetics in Single Semiconductor Quantum Dots," 225th National ACS Meeting New Orleans, LA, March 25, 2003.

"Fluorescence Kinetics of Single Quantum Dots: What Your Graduate Kinetics Professor Never Told You," Chemical Physics Seminar Series, JILA, University of Colorado, Boulder, CO, April 18, 2003.

"Quantum State resolved Reaction Dynamics: IR and UV Laser Studies," 3rd Annual Network Meeting For Reaction Dynamics, Nijmegan, Netherlands, May 9, 2003.

"Probing Dynamics with Quantum State Resolution," 3rd Annual Network Meeting For Reaction Dynamics, Nijmegan, Netherlands, May 10, 2003.

"Chemical Dynamics: Gas Phase Radicals to Single Molecule Microscopy," Department of Chemistry, University of Chicago, May 12, 2003.

"Quantum State Resolved Spectroscopy and Reaction Dynamics with IR Lasers," DAMOP, Boulder, CO, May 22, 2003.

"Quantum State Resolved Reaction Dynamics: IR and UV Laser Studies," XX International Symposium on Molecular Beams, Lisbon, Portugal, June 12, 2003.

"Transition State Resonance and Non-Adiabatic Dynamics in Quantum State Resolved Scattering," Conference on Molecular Energy Transfer, El Escorial, Spain, June 15, 2003.

"Time-Dependent Power Law Fluorescence Dynamics in Semiconductor Quantum Dots," Excited State Processes in Electronic and Bio-Nano-Materials, Los Alamos, NM, August 12, 2003.

"IR Laser Studies in Slit Supersonic Jets: Dynamical Insights from High Resolution Spectroscopy," 18th Colloquium on High Resolution Spectroscopy, University of Bourgogne, Dijon, France, September 12, 2003.

"From Single Collisions to Single Molecules," Department of Chemistry, U.C. Irvine, Irvine, CA, October 28, 2003.

"IR/UV studies of state-to-state reaction dynamics: From A + BC to Atom + Polyatom Systems," Symposium on Atomic, Surface and Cluster Physics, La Thuile, Italy, February 4, 2004.

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

"Single Molecule Kinetics: From Biopolymers to Quantum Dots," Department of Chemistry, U. C. Davis, Davis, CA, May 4, 2004.

"Power-Law Blinking and Fluorescence Dynamics in Semiconductor Quantum Dots," Quantum Dots 2004, Banff, Alberta, May 10, 2004.

"Reaction Dynamics, Gas-Liquid Interfaces and Nanoparticle Spectroscopy," Molecular Dynamics AFOSR Contractors Meeting, Newport, RI, May 25, 2004.

"Catching Molecules On the Fly: Laser Spectroscopy of Radicals," Ecole Polytechnique Federale de Lausanne/Institut des Science et Ingeniere Chimiques, Lausanne, Switzerland, June 7, 2004.

"State-to-state Reaction Dynamics: From A+BC to Atom + Polyatom," Ecole Polytechnique Federale de Lausanne/Institut des Science et Ingeniere Chimiques, Lausanne, Switzerland , June 7, 2004.

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

"Spectroscopy and Intramolecular Dynamics: Clusters, Radicals, Molecular Ions," Department of Chemistry, University of Basel, Basel, Switzerland, June 9, 2004.

"Single Molecule Kinetics: From Quantum Dots to RNA Folding," Ecole Polytechnique Federale de Lausanne/Institut des Science et Ingeniere Chimiques, Lausanne, Switzerland, June 10, 2004.

"Intermolecular Dynamics and Spectroscopy: Single Frequencies, Single Molecules," Department of Physical Chemistry, Eidgenössiche Technische Hochschule, Zürich, Switzerland, June 11, 2004.

"Real Time FRET Studies of Single RNA Folding," 228th National ACS Meeting, Philadelphia, PA, August 26, 2004.

"Splashing" Molecules Off Liquids: Quantum State-Resolved Scattering Dynamics at the Gas-Liquid Interface," Molecular Energy Transfer Conference XV, Nunspeet, Netherlands, September 7, 2004.

"From Confocal Fluorescence to Photoionization Microscopy of Nanostructures," 229th National ACS Meeting, San Diego, CA, March 15, 2005.

"Time Dependent Fluorescence and Blinking Dynamics in Semiconductor Quantum Dots," ACS 229th National Meeting, San Diego, CA, March 17, 2005.

"Reaction Dynamics with Quantum State Resolution: Finding the Physics Behind the Chemistry", Department of Chemistry, Wayne State University, Detroit, MI, March 23, 2005.

"Fluorescence Studies at the Single Molecule Level: From Quantum Dot Blinking to RNA Folding", Single Molecule Workshop, U. S. Department of Energy, Rockville, MD, April 11, 2005.

"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.

"Dynamics with Quantum State Resolution: Finding the Physics Behind the Chemistry," Department of Theoretical and Physical Chemistry, Universitaet Stuttgart, April 19, 2005.

"Time Dependent Fluorescence and Blinking Dynamics in Semiconductor Quantum Dots," Los Alamos National Laboratory, June 17, 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.

"Landscapes in elementary F + diatom and triatom reactions: Potential surfaces and state-resolved experiments", ACS 230th National Meeting, Washington, DC, August 30, 2005.

"Long range electron ejection dynamics in quantum dots: To blink or not to blink", ACS 230th National Meeting, Washington, DC, August 31, 2005.

"Spectroscopy and Dynamics of Jet-Cooled Molecular Transients", 28th International Symposium on Free Radical, Leysin, Switzerland, September 8, 2005.

"Hydrogen Bonding, Spectroscopy and Dynamics: From H_3O^+ to RNA", International Union of Pure and Applied Chemistry", Pisa, Italy, September 9, 2005.

"Spectroscopy One Molecule at a Time: From RNA Folding to Quantum Dots", Department of Chemistry, University of Puerto Rico-Mayaguez, October 13, 2005.

"Spectroscopy One Molecule at a Time: From RNA Folding to Quantum Dots", Department of Chemistry, University of Puerto Rico-Rio Piedras, October 14, 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
Bourke Medal, Royal Society of Chemistry, Faraday Division (2002)
National Institute of Standards and Technology Fellow (2005)
Fellow of the Royal Society of Chemistry, UK (2005)