Spectroscopy, Kinetics and Dynamics of Combustion Radicals

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Spectroscopy, kinetics and dynamics of jet cooled hydrocarbon transients relevant to the DOE combustion mission have been explored, exploiting i) high resolution IR lasers, ii) slit discharge sources for formation of jet cooled radicals, and iii) high sensitivity detection with direct laser absorption methods and near the quantum shot noise limit. What makes this combination powerful is that such transients can be made under high concentrations and pressures characteristic of actual combustion conditions, and yet with the resulting species rapidly cooled ($T \approx 10\text{-}15\text{K}$) in the slit supersonic expansion. Combined with the power of IR laser absorption methods, this provides novel access to spectral detection and study of many critical combustion species. A few selected highlights from work over the granting period are summarized below.

1. Experimental Overview

The Nesbitt group has been extensively involved over the past several years in high resolution IR laser techniques for slit spectroscopy of jet cooled radicals (Fig. 1).¹⁻⁹ The scheme is based on i) a fast 1D slit supersonic pulsed valve, with ii) a 1 mm discharge region struck immediately behind the slit jaws, followed by iii) direct IR laser absorption spectroscopy of the supersonically cooled transients along the slit axis. Low energy electrons in the discharge are used for “rational synthesis” of radicals via rapid dissociative attachment processes ($\text{RX} + e^- \rightarrow \text{R} + \text{X}^-$) proceeding at near Langevin rates.¹⁰ The advantages of a slit jet geometry for high sensitivity direct absorption studies are significant, including i) 100-fold increase in absorption path length, ii) 100-fold radical density enhancement due to linear vs. quadratic drop-off with distance, and iii) 10-fold increase in absorption cross sections due to sub-Doppler collimation of radicals into a single velocity group. Altogether, this offers a remarkable enhancement in detection sensitivity which, for a 20-fold multipass cell and shot noise limited absorbances, translates into minimum

Fig. 1

densities of 10^8 #/cm³ per quantum state for a typical hydrocarbon CH stretch absorption.¹¹ For routine slit jet radical densities in the laser probe region of 10^{12} - 10^{14} /cm³, this implies that high S/N spectra ($> 2000:1$ for optimal systems) can be obtained for highly reactive transients with complete rovibrational and even partial fine/hyperfine sub-Doppler resolution. Most importantly, the nascent radicals are rapidly cooled into low quantum states by the high density slit expansion, achieving rotational temperatures of $T \approx 10$ - 20 K with appreciable cooling also in low frequency vibrational degrees of freedom. This fortuitous confluence of events both i) increases density per quantum state and ii) reduces spectral congestion, thereby greatly extending the range of radical complexity that can be tackled via high resolution IR laser methods.

2. High Resolution IR Spectroscopy of Open Shell Aromatics: Phenyl Radical

As a first highlight, we successfully obtained first high resolution IR spectra¹² of jet cooled phenyl radical, C₆H₅. (see Fig. 2). Phenyl is a highly reactive 6-membered organic hydrocarbon ring intermediate formed from homolytic cleavage of a CH bond in benzene.¹³⁻¹⁵ By virtue of its overall reactivity, this radical plays a central role in combustion, especially for fossil fuels typically rich in aromatics.^{16,17} It is the classic prototype of an open shell aromatic species, achieving partial stabilization of the radical due to resonance structures arising from electron delocalization around the ring. This radical stabilization also makes it a prime target intermediate for ring formation in complex combustion processes, which identifies phenyl as a crucial species in mediating the early stages of soot formation.¹⁸⁻²¹ Rigorous assignment of rotational structure in our gas phase spectra has been obtained via precision 2-line ground state combination differences from radio frequency spectroscopy of Thaddeus and coworkers.¹⁴ The analysis yields rotational constants and vibrational energy for the excited state, the latter of which reveal good agreement with matrix isolation studies by Ellison and coworkers.¹³ It is worth stressing that the ability to obtain rovibrationally resolved spectra for such a large but fundamental aromatic species represents an important milestone for spectroscopic study of highly reactive combustion species, and bodes extremely well for spectroscopic detection and analysis of even more complex radical intermediates.

3. Non-Born Oppenheimer Rovibronic Dynamics in Ethynyl (C₂H) Radical

Ethynyl radical (C₂H) is a particularly important reactive intermediate in combustion as well as interstellar chemistry, specifically postulated to play a role formation of polycyclic aromatic hydrocarbons (PAHs). PAHs are likely a precursor to soot formation, which remains a poorly understood byproduct of many combustion processes. One mechanism involves the reaction of free radical intermediates such as C₂H with other unsaturated molecules (HCCH) to form the first PAH species, followed by rapid sequential aggregation to large solid particulates. What makes C₂H particularly interesting is the presence of low

lying electronically excited states, in which the quantum states due to vibrations of the C_2H framework are imbedded and can lead to anomalously strong vibronic mixing dynamics. In order to explore these non-adiabatic effects, we have undertaken a spectroscopic reinvestigation of C_2H under sub-Doppler conditions of the slit jet apparatus.^{22,23} At typical rms sensitivity levels of 0.003% in a 10 kHz bandwidth, this translates into signal to noise ratios $> 50:1$ on the strongest lines for the $C_2H \tilde{A} (^2\Pi) \leftarrow \tilde{X} (^2\Sigma^+)$ band, as shown in

Fig. 3

Fig. 3. The combination of i) slit-jet cooling ($T_{rot} \approx 12$ K) and ii) sub-Doppler resolution (≈ 60 MHz) permits satellite branches in each $^2\Pi \leftarrow ^2\Sigma^+$ band to be observed and resolved for the first time, helping to clarify parity assignments from previous studies.²²⁻²⁵

Of particular dynamical interest is vibronic coupling between the electronically excited $\tilde{A} (^2\Pi)$ state and highly excited vibrational states in the ground state of this radical, which is responsible for the rich complexity observed in the near IR spectrum. To explore this further, a high resolution infrared spectrum of the origin band region near 3600 cm^{-1} of jet-cooled ethynyl radical (C_2H) has been explored and analyzed in detail, which exhibits a strong, parity specific rotational crossing in the excited spin orbit $F_2 ^2\Pi_{1/2}$ state. By incorporating this Σ - Π Coriolis coupling into the unperturbed Hamiltonian model (containing only rotational, spin-rotational, spin-orbit, and lambda-doubling contributions), we are able to fit the observed $^2\Pi$ - $^2\Sigma^+$ origin band to a standard deviation of 15 MHz, i.e., essentially the experimental limit. By virtue of the high frequency precision, these data permitted a direct determination of the band origin (ν_{pert}) and rotational constant (B_{pert}) for the perturbing “dark” $^2\Sigma^+$ state. Furthermore, since the vibrational density of states is still relatively modest in C_2H at 3600 cm^{-1} , we have successfully identified the dark state by comparison with high quality predictions of Tarroni and Carter. Indeed, the results unambiguously indicate the source of strong vibronic coupling arising from a fortuitous near resonant “avoided crossing” between the $F_2 ^2\Pi_{1/2}$ state and the high overtone $^2\Sigma^+ (0,8^0,0)$ state with 8 quanta of CH bending excitation. By way of further confirmation, the rotational constants observed from this high resolution analysis are in excellent agreement with the UV dispersed fluorescence studies of Hsu *et al.*²⁶

4. *Ab Initio* Rovibrational Dynamics of $H_2 + H_2O$

A first principles description of combustion processes requires a detailed understanding of state-to-state collisional energy transfer dynamics, which in turn requires high quality multidimensional intra/intermolecular potential energy surfaces for reactants and products, benchmarked against high quality experimental data. As an important milestone for progress in this direction, we have explored $H_2 + H_2O$ interactions by a synergistic combination of i) *ab initio* calculations, ii) exact multidimensional quantum dynamics and iii) high resolution spectroscopy of the corresponding H_2 - H_2O and D_2 - H_2O complexes.^{27,28} Specifically, jet cooled H_2O - H_2 and H_2O - D_2 complexes are formed by pulsed supersonic expansion through a slit valve and detected via direct absorption of high resolution IR light in the $6.2\text{ }\mu\text{m}$ region corresponding to ν_2 bending of the H_2O chromophore. The stagnation gas is formed by

passing a mixture of H₂ (99.999%) or D₂ (> 99%) and “first run” Ne (70/30 Ne/He) at 260 kPa through a distilled H₂O bubbler at 273 K. Absolute frequencies are determined from H₂¹⁷O and H₂¹⁸O transitions measured also in the slit jet expansion and readily observable in natural isotopic abundance. High resolution rotational structure for each of the H₂O-H₂ and H₂O-D₂ complexes is observed, which can be unambiguously assigned to progressions in the $K_a = 0 \leftarrow 0$ and $1 \leftarrow 1$ manifolds arising from i) overall rotation and ii) large amplitude internal rotor motion in the complex. From a theoretical

perspective, a 5D intermolecular potential is obtained from a state-of-the-art 9 D *ab initio* potential energy surface (PES) by averaging over the ground state vibrational wave functions of H₂O and H₂/D₂. On this PES, we calculate the bound rovibrational levels for total angular momentum $J = 0-3$, based on a coupled free rotor basis for the hindered internal rotations (with permutation/inversion symmetry associated with the para/ortho (p/o) nature of both H₂O and H₂/D₂), and a discrete variable representation (DVR) in the intermolecular distance R . Agreement between experiment and theory proves to be outstandingly quantitative ($< 0.1\%$ in B_{rot}), providing an extremely successful test of the H₂ + H₂O potential energy surface from a fully rigorous, first principles perspective.

4. Isotopic Symmetry Breaking in the C-H Stretching Manifold of Methyl Radical

Methyl (CH₃) represents a critical radical species in the combustion of hydrocarbon fuels, which provides motivation for a detailed understanding of its molecular properties. To address these issues, we have obtained first high resolution sub-Doppler IR spectra of CH₂D radical in both the symmetric/antisymmetric C-H stretching regions. Isotopic “symmetry breaking” in the CH₂D radical by partial H/D substitution has been exploited to localize CD vs. CH vibrational motion, lower the point group symmetry from D_{3h} to C_{2v}, and thereby permit investigation of unimolecular vibrational coupling dynamics in unprecedented detail. At our resolution, the spectral structure is rovibrationally fully resolved and can be fit to a Watson asymmetric top Hamiltonian to yield rotational/centrifugal constants and vibrational band origins. An asymmetric top stick spectrum for the observed rotational lines of CH₂D is shown in Fig. 5 along with residuals from a least squares fit simulation. However, in addition, the transverse velocity distribution along the laser probe direction is collisionally quenched in the slit jet expansion, thus yielding complete sub-Doppler resolution of spin-rotation structure and even partial resolution of nuclear hyperfine structure for each rovibrational line. Global least-squares

fits to the line shapes provide additional information on spin-rotation and nuclear hyperfine constants, which both complement and clarify previous FTIR studies of CH_2D in the out of plane bending region. Of particular interest, we have successfully exploited a harmonically coupled anharmonic oscillator model Hamiltonian for systematic analysis over the entire isotopomeric $\text{CH}_m\text{D}_{3-m}$ series, which now provides a remarkably quantitative framework for predicting in-plane stretching dynamics in this fundamental combustion radical. Furthermore, symmetry breaking allows the molecule to have a weak but non-vanishing dipole moment, which, based on the current high resolution IR data, should enable further study of this radical via microwave/mm wave spectroscopy.

5. Quantum “Roaming” and 1,2 H atom Shift Dynamics in Vinyl Radical

The vinyl radical C_2H_3 is a critically important species in hydrocarbon combustion,^{29,30} planetary atmospheres,³¹⁻³³ and hydrocarbon plasma chemistry.³⁴ A particularly interesting dynamical feature of the vinyl radical is the presence of multiple global minimum energy configurations connected via first order saddle points. The lowest-lying first-order saddle point is a planar Y-shaped structure of C_{2v} symmetry, i.e., $\text{H}_2\text{C}-\text{C}-\text{H}$, where large amplitude α -CH-rocking motion results in tunneling between the two C_s equilibrium geometries, but without swapping the radical C atom. However, there is also a 1,2 hydride shift pathway at much higher energies (i.e., $18,000\text{ cm}^{-1}$), which does interchange the C radical center.³⁵ What makes these higher isomerization barriers particularly intriguing is that quantum

Fig. 6

tunneling can occur at substantial rates, despite the fact that the 1,2, shift barrier is substantially above the homolytic limit for CH bond cleavage. To address this issue, we have calculated splittings associated with large amplitude 1,2 H-atom migration for vinyl radical via two completely independent approaches, i) full-D *ab initio* potential energy surface (CCSD(T)/aug-cc-pVTZ) and ii) “intrinsic reaction paths” (CCSD(T)/aug-cc-pVnZ/CBS), yielding results in remarkable quantitative agreement over a 10-order dynamic range of tunneling lifetimes. Most importantly, this work predicts tunneling-promoted 1,2 hydride shift dynamics in vinyl radical to exhibit exponential growth with internal vibrational excitation, specifically achieving $> 1\text{ MHz}$ rates relevant to low pressure combustion at energies above $E \approx 7500\text{ cm}^{-1}$, i.e., far below the CH bond dissociation limit. Of particular importance, these results suggest such “quantum isomerization” dynamics to be in competition with “roaming,” which is classically restricted to a narrow window of energies at the dissociation limit. Furthermore, integrated over a Boltzmann distribution of thermal energies, these microcanonical tunneling rates are consistent with sub μsec time scales for 1,2 hydride shift dynamics at $T > 1400\text{ K}$ (see Fig. 6) These results have relevance for combustion modeling of low pressure flames, as well as observations of nuclear spin statistical mixing from high resolution IR/microwave spectroscopy on vinyl radical.

6. Quantum state resolved scattering dynamics at interfaces

The dynamics of gas-surface molecular collisions plays a crucial role in a variety of fundamental combustion processes, ranging from thermal ignition to industrial heterogeneous catalysis. As a first step toward more detailed study of such phenomena in the upcoming granting period, we have developed a novel capability for exploring molecular scattering dynamics at the gas-solid interface via laser ionization coupled with velocity-map imaging (VMI). These first studies are based on state-resolved REMPI of HCl scattering hydrocarbon self-assembled monolayers (SAM) on Au(111)/mica. The resulting velocity maps provide 3D momentum insights into the state-to-state HCl scattering dynamics, revealing for the first time correlations between internal J and translational degrees of freedom. For example, velocity maps at low J are dominated by room-temperature trapping-desorption (TD), but at higher J contain a forward scattered component and provide a first glimpse into impulsive scattering (IS) dynamics (see Fig. 7). Specifically, within the purely-IS HCl region of the velocity maps, the J distributions are found to be remarkably Boltzmann like, but with a temperature ($T_{\text{rot}} \approx 455$ K) significantly higher than the 300 K SAM. By way of contrast, the translational degree of freedom of the IS flux is clearly non-Boltzmann in character, with a strong propensity for in-plane scattering in the forward direction, and yet still exhibiting out-of-plane velocity distributions characterized by a much hotter 690 K temperature. These first data establish prospects for a new class of experimental tools aimed at exploring energy transfer and reactive scattering events on gas-solid and gas-SAMs interfaces with quantum state resolved information on correlated internal and translational distributions.

Publications in last 3 year granting period (* with DOE support)

*207) E. N. Sharp, M. A. Roberts and D. J. Nesbitt, "Rotationally resolved infrared spectroscopy of jet cooled phenyl radical in the gas phase: out of phase symmetric CH stretch excitation," *Phys. Chem. Chem. Phys.* **10**, 6592-6596 (2008).

208) J. L. Fiore, B. Kraemer, F. Koberling, R. Erdmann, and D. J. Nesbitt, "Enthalpy-driven RNA folding: Single-molecule thermodynamics of tetraloop-receptor tertiary interaction," *Biochemistry* **48**, 2550-2558 (2009).

209) B. G. Perkins, Jr. and D. J. Nesbitt, "Toward 3D quantum state resolved collision dynamics at the gas-liquid interface: Experiment and theory", *J. Phys. Chem. A* **113**, 4613-4625 (2009).

- 210) T. A. Baker, J. L. Rouge, D. J. Nesbitt, "Single molecule studies of quantum dot fluorescence intermittency: Evidence for both dark and light-assisted blinking dynamics", *Mol. Phys.* 107, 1867-1878 (2009).
- 211) M. P. Ziemkiewicz and D. J. Nesbitt, "Non-adiabatic reactive scattering in atom + triatom systems: Nascent rovibronic distributions in $F + H_2O \rightarrow HF + OH$ ", *J. Chem. Phys.* 131, 054309 (2009).
- 212) K.-K. Ni, S. Ospelkaus, D. J. Nesbitt, J. Ye and D. S. Jin, "A dipolar gas of ultracold molecules", *Phys. Chem. Chem. Phys.* 11, 9626-9639 (2009).
- 213) B. G. Perkins, Jr. and D. J. Nesbitt, "Stereodynamics at the gas-liquid Interface: Orientation and alignment of CO_2 scattered from perfluorinated liquid surfaces", *J. Phys. Chem. A.* 114, 1398 (2010).
- * 214) E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, "Definition of the hydrogen bond", *International Union of Pure and Applied Chemistry* (2010).
- 215) J. R. Roscioli and D. J. Nesbitt "State-resolved scattering at room temperature ionic liquid-vacuum interfaces: Anion dependence and the role of dynamic vs. equilibrium effects", *J. Phys. Chem. Lett.* 1, 674 (2010).
- 216) H. S. P. Müller, F. Dong, D. J. Nesbitt, T. Furuya and S. Saito, "Tunneling dynamics and spectroscopic parameters of monodeuterated hydronium, H_2DO^+ , from a combined analysis of infrared and submillimeter spectra", *Phys. Chem. Chem. Phys.* 12, 8362 (2010).
- 217) K. Terrill and D. J. Nesbitt, "*Ab Initio* anharmonic vibrational frequency predictions for linear proton-bound complexes $OC-H^+-CO$ and $N_2-H^+-N_2$ ", *Phys. Chem. Chem. Phys.* 12, 8311 (2010).
- * 218) D. J. Nesbitt and M. A. Suhm, "Chemical dynamics of large amplitude motion", *Phys. Chem. Chem. Phys.* 12, 8151 (2010).
- 219) B. G. Perkins, Jr. and D. J. Nesbitt, "High resolution Dopplerimetry of correlated angular and quantum state-resolved CO_2 scattering dynamics at the gas-liquid interface", *Phys. Chem. Chem. Phys.* 12, 14294 (2010).
- 220) E. D. Holmstrom and D. J. Nesbitt, "IR overtone laser temporal control of temperature in picoliter H_2O samples: "Nanobathtubs" for single molecule microscopy", *J. Phys. Chem. Letters* 1, 2264 (2010).
- 221) J. L. Fiore and D. J. Nesbitt, "An entropic origin of Mg^{+2} -facilitated RNA folding", *Proc. Nat. Acad. Sci.* 109, 2902-2907 (2012).

222) V. Schweikhard, A. Grubisic, T. A. Baker and D. J. Nesbitt, "Multi-photon scanning photoionization imaging microscopy for single-particle studies of plasmonic metal nanostructures", J. Phys. Chem. C. 115, 83-91 (2011).

* 223) E. Sharp-Williams, M. A. Roberts, and D. J. Nesbitt, "High resolution slit-jet infrared spectroscopy of ethynyl radical: $^2\Pi-^2\Sigma^+$ vibronic bands with sub-Doppler resolution", J. Chem. Phys. 134, 064314 (2011).

224) J. R. Roscioli, D. Bell, and D. J. Nesbitt, "State-resolved velocity map imaging of surface-scattered molecular flux", Phys. Chem. Chem. Phys. 14, 4070-4080 (2012).

225) C. Savage, F. Dong and D. J. Nesbitt, "High resolution spectroscopy of jet cooled CH_5^+ : Progress", American Institute of Physics, Proceedings International Conference of Computational Methods in Sciences and Engineering (in press).

* 226) A. van der Avoird and D. J. Nesbitt, "Rovibrational states of the $\text{H}_2\text{O}-\text{H}_2$ complex: An *ab initio* calculation", J. Chem. Phys. 134, 044314 (2011).

227) J. R. Roscioli and D. J. Nesbitt, "Quantum state resolved scattering from room temperature ionic liquids: The role of cation vs. anion structure at the interface", J. Phys. Chem. C. 115, 9764-9773 (2011).

* 228) J. R. Roscioli and D. J. Nesbitt, "Quantum state resolved velocity-map imaging spectroscopy: A new tool for collision dynamics at gas/self-assembled monolayer interfaces", Frontiers in Spectroscopy, Faraday Disc. 150/22, 1-9 (2011).

229) M. P. Ziemkiewicz, J. R. Roscioli, and D. J. Nesbitt, "State-to-state dynamics at the gas-liquid metal interface: Rotationally and electronically inelastic scattering of $\text{NO}[^2\Pi_{1/2}(0.5)]$ from molten gallium", J. Chem. Phys. . 134, 234703 (2011).

230) T. A. Baker, O. L. A. Monti, and D. J. Nesbitt, "Kinetic studies of laser generated SERS active silver nanoparticles", J. Phys. Chem. C. 115, 9861-9870 (2011).

231) V. Schweikhard, A. Grubisic, T. A. Baker and D. J. Nesbitt, "Polarization dependent scanning photoionization microscopy: Ultrafast plasmon-mediated electron ejection dynamics in single Au nanorods", ACS Nano 5, 3724-3735 (2011).

* 232) A. van der Avoird, Y. Scribano, A. Faure, M. J. Weida, J. R. Fair, and D. J. Nesbitt, "Intermolecular potential and rovibrational states of the $\text{H}_2\text{O}-\text{D}_2$ complex", Chem. Phys. 399, 28-38 (2012).

* 233) P. Casavecchia M. Brouard, M. Costes, D. J. Nesbitt, E. Bieske and S. Kable, "Molecular collision dynamics", Phys. Chem. Chem. Phys. DOI: 10.1039/c1cp90049h (2011).

- * 234) E. N. Sharp-Williams, M. A. Roberts, D. J. Nesbitt, "Dark state vibronic coupling in the $\tilde{A}(^2\Pi) \leftarrow \tilde{X}(^2\Sigma^+)$ Band of ethynyl radical via high resolution infrared absorption spectroscopy", *Phys. Chem. Chem. Phys.* 2011, **13** (39), 17474 - 17483.
- 235) A. Grubisic, V. Schweikhard, T. A. Baker and D. J. Nesbitt, "Coherent Multiphoton Photoelectron Emission from Single Au Nanorods: The Critical Role of Plasmonic Electric Near-Field Enhancement," *ACS Nano* (<http://dx.doi.org/10.1021/nn305194n>) (2013).
- *236) A. R. Sharma, J. M. Bowman, D. J. Nesbitt "Large-amplitude dynamics in vinyl radical: The role of quantum tunneling as an isomerization mechanism," *J. Chem. Phys.* **136**, 034305 (2012).
- 237) L. F. Phillips and D. J. Nesbitt, "The surface of liquid gallium," *Chem. Phys. Lett.* **536**, 61-64 (2012).
- 238) E. D. Holmstrom, J. L. Fiore and D. J. Nesbitt, "Thermodynamic Origins of Monovalent-Facilitated RNA Folding," *Biochemistry* **51**, 3732-3743 (2012).
- *239) 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 [$^2\Pi_{1/2}(0.5)$]," *J. Phys. Chem. C*. <http://dx.doi.org/10.1021/jp212336a> (2012)
- 240) X. Li, G. C. Schatz, and D. J. Nesbitt, "Anion Effects in the Scattering of CO₂ from Room Temperature Ionic Liquids [bmim][BF₄] and [bmim][Tf₂N]: Insights from Quantum Mechanics/Molecular Mechanics Trajectories," *J. Phys. Chem. B* **116**, 3587-3602 (2012).
- *241) M. A. Roberts, C. Savage, F. Dong, E. N. Sharp-Williams, A. B. McCoy, and D. J. Nesbitt, "Sub-Doppler Infrared Spectroscopy of CH₂D Radical in a Slit Supersonic Jet: Isotopic Symmetry Breaking in the C-H Stretching Manifold," *J. Chem. Phys.* **136**, 234308 (2012).
- 242) A. W. Gisler and D. J. Nesbitt, "On Probing Ions at the Gas-Liquid Interface by Quantum State-Resolved Molecular Beam Scattering: The Curious Incident of the Cation in the Night Time," *Faraday Disc.* **157**, 297-305 doi: 10.1039/c2fd20026k (2012).
- 243) L. F. Phillips and D. J. Nesbitt, A "Hot-Spot" model for impulsive scattering at the gas-liquid interface," *Chem. Phys. Lett.* <http://dx.doi.org/10.1016/j.cplett.2012.07.058> (2012).
- *244) M. P. Ziemkiewicz, C. Pluetzer, D. J. Nesbitt, Y. Scribano, A. Faure, A. van der Avoird, "Overtone vibrational spectroscopy in H₂-H₂O complexes: A combined high level theoretical *ab initio*, dynamical and experimental study," *J. Chem. Phys.* **137**, 084301 (2012).
- 245) J. L. Fiore, E. D. Holmstrom, L. R. Fiegland, J. H. Hodak, and D. J. Nesbitt, "The Role of Counterion Valence and Size in GAAA Tetraloop-Receptor Docking/Undocking Kinetics", *J. Mol. Biol.* <http://dx.doi.org/10.1016/j.jmb.2012.07.006> (2012).

246) L. R. Fiegland, A. D. Garst, R. T. Batey, and D. J. Nesbitt, "Single-Molecule Studies of the Lysine Riboswitch Reveal Effector Dependent Conformational Dynamics of the Aptamer Domain," *Biochem.* 51, 9223-9233, doi: 10.1021/bi3007753 (2012).

247) D. J. Nesbitt, "Toward state-to-state dynamics in ultracold collisions: Lessons from high resolution spectroscopy of weakly bound molecular complexes," *Chem. Rev.* dx.doi.org/10.1021/cr300208b (2012).

248) A. Grubisic, E. Ringe, C. M. Cobley, Y. Xia, L. D. Marks, R. P. Van Duyne, and D. J. Nesbitt, "Plasmonic Near Electric Field Enhancement Effects in Ultrafast Photoelectron Emission: Correlated Spatial and Laser Polarization Microscopy Studies of Individual Ag Nanocubes," *Nano Lett.* <http://dx.doi.org/10.1021/nl302271u> (2012).

249) J. L. Fiore and D. J. Nesbitt, "An RNA folding motif: GNRA tetraloop-receptor interactions," *Quart. Rev. Biophys.* (in press).

250) A. Grubisic, V. Schweikhard, T. A. Baker and D. J. Nesbitt, "Multiphoton Photoelectron Emission Microscopy of Single Au Nanorods: Combined Experimental and Theoretical Study of Rod Morphology and Dielectric Environment on Localized Surface Plasmon Resonances," *Phys. Chem. Chem. Phys.* (in press).

*251) M. A. Roberts, E. N. Sharp-Williams, and D. J. Nesbitt, "High-Resolution Direct-Absorption Spectroscopy of Hydroxymethyl Radical in the CH Symmetric Stretching Region," *J. Phys. Chem. A* (in press).

*252) G. T. Buckingham, C.-H. Chang, and D. J. Nesbitt, "High Resolution Rovibrational Spectroscopy of Jet-Cooled Phenyl Radical in the ν_{19} Out-of-Phase Symmetric CH Stretch," *J. Phys. Chem. A* (in press).

253) N. F. Dupuis, E. D. Holmstrom, D. J. Nesbitt, "Single Molecule Kinetics Reveal Cation Promoted DNA Duplex Formation Through Ordering of Single Stranded Helices," *Biophys. J.* (in press).

*254) C.-H. Chang, G. T. Buckingham and D. J. Nesbitt, "Sub-Doppler Spectroscopy of *trans*-HOCO Radical in the OH Stretching Mode," *J. Phys. Chem. A* (in press).

255) K. T. Early and D. J. Nesbitt, "Size-dependent Photoionization in Single CdSe/ZnS Nanocrystals," *Nano Lett* (submitted).

256) A. Grubisic, S. Mukherjee, N. Halas, D. J. Nesbitt, "Anomalously Strong Electric Near-field Enhancing Hot Spots on Silica-Au Core-shell Nanoparticles as Studied by Ultrafast Scanning Photoemission Imaging Microscopy," *J. Chem. Phys. C* (Ron Naaman Festschrift issue) (submitted)

257) T. A. Baker, A. Grubisic, and D. J. Nesbitt, "Plasmonic Electron Photoemission Microscopy of Au Nanoholes and Nanohole Dimers," ACS Nano (submitted).

Invited Talks in the last three years (* indicating DOE support)

* "IR Laser Studies of Molecular Transients: Dynamical Insights Through High Resolution Spectroscopy," Department of Chemistry, Kyushu University, Fukuoka, Japan, October 29, 2008.

* "High Resolution IR Laser Studies of Hydrocarbon Radicals: From Fundamental Spectroscopy to Intramolecular Dynamics," Vinyl Radical Workshop, Kyushu University, Fukuoka, Japan, October 30, 2008.

"Reactive and Inelastic Dynamics at the Gas-Liquid Interface with Quantum State Resolution," Gordon Research Conference on Molecular Energy Transfer, Ventura, CA, January 21, 2009.

* "Novel Optical Windows into Hot Combustion Dynamics at Cold Temperatures," Optical Sciences and Engineering Program Seminar, University of Colorado, Boulder, CO, February 2, 2009.

"Searching for Simplicity: From Collisions at Gas-Liquid Interfaces to Single Molecule RNA Folding," Department of Chemistry, University of Indiana, Bloomington, IN, February 12, 2009.

"Searching for Simplicity: From Gas-Liquid Scattering to Single Molecule RNA Folding," Department of Chemistry, Georgia Tech/Emory University, Atlanta, GA, March 2, 2009.

"Dynamics at Gas-Liquid Interfaces," Physical Chemistry Chemical Physics Editorial Meeting, Barcelona, Spain, April 24, 2009.

"Power Law Behavior in Quantum Dot Blinking: A Novel Role for Biexcitons and Auger Ionization," Department of Physics, Colorado School of Mines, Golden, CO, April 28, 2009.

"Chemistry of Cooking," CU Wizards Program Scientific Outreach, Boulder, CO, June 13, 2009.

"Bimolecular Collision Dynamics: An Overview," Dynamics of Molecular Collisions, Snowbird, UT, July 6, 2009.

* "Laser Studies of Jet Cooled Radicals: High Resolution Spectroscopy to Gas-Liquid Collision Dynamics," 30th International Symposium on Free Radicals, Savonlinna, Finland, July 27, 2009.

“State-resolved reactive scattering: Gas-phase vs. gas-liquid dynamics,” 238th Meeting of the American Chemical Society, Washington, DC, August 17, 2009.

“State-resolved Dynamics at the Gas-Liquid Interface: A High Resolution Perspective,” Department of Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen, The Netherlands, March April 2, 2010.

* “State-Resolved Dynamics from Experimental and Theoretical Perspectives: How a Sabbatical Month with Joachim Changed my Life,” First Principles Quantum Chemistry 2010, Bad Herrenalb, Germany, April 16, 2010.

* “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.

* “High Resolution Spectroscopy and Dynamics: From Jet-Cooled Radicals to Gas-Liquid Interfaces,” 65th International Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, OH, June 23, 2010.

“Nanobathbubs for Single Molecule Microscopy,” Gordon Research Conference on Single Molecule Approaches to Biology 2010, Barga, Italy, June 28, 2010.

“State-Resolved Collision Dynamics and Spectroscopy at Gas-Liquid Interfaces,” Gordon Research Conference on Vibrational Spectroscopy, University of New England, Biddeford, Maine, August 2, 2010.

* “From Combustion Radicals to Gas-Liquid Interfaces: Insights from High Resolution Laser Spectroscopy,” 21st International Conference on High Resolution Molecular Spectroscopy, Poznań, Poland, September 11, 2010.

* “High Resolution Spectroscopy of Jet Cooled CH_5^+ : Progress,” SMILES 2010, Kos, Greece, October 3, 2010.

* “Large Amplitude Quantum Dynamics: A High Resolution Perspective on Unimolecular Rearrangement,” Anharmonic Vibrations of Molecules and Clusters: Experiment and Theory, Pacifichem 2010, Honolulu, HI, December 18, 2010.

“State-to-State Collision Dynamics: New Frontiers at the Gas-Liquid Interface,” Frontiers of State-to-State Dynamics, Pacifichem 2010, Honolulu, HI, December 19, 2010.

“New Advances in Single Particle Microscopy: From Quantum Dots to Biomolecules,” Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL, March 18, 2011.

* “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.

“State-resolved Collision Dynamics at Interfaces: From Insulating Liquids to Molten Metals,” Chemical Reactions and Dynamics at Surfaces, 241st American Chemical Society, National Meeting, Anaheim, CA, March 27, 2011.

* “Quantum State Resolved Velocity-Map Imaging Spectroscopy: A New Tool for Collision Dynamics at Gas/Self-Assembled Monolayer Interfaces,” Frontiers in Spectroscopy, Faraday Discussions 150, Basel, Switzerland, April 8, 2011.

“Quantum State Resolved Dynamics at the Gas-Liquid Interface,” Department of Chemistry, University of Washington, Seattle, WA, April 20, 2011.

“Searching for Simplicity: From Quantum State Resolved Collision Dynamics at the Gas-Liquid Interface to Single Molecule RNA Folding,” Department of Chemistry, University of Oregon, Eugene, OR, May 2, 2011.

* “In Search of Simplicity: From IR Laser Spectroscopy of Combustion Radicals to Thermodynamics/Kinetics of Single Molecule RNA Folding,” 2010-2011 Frost Lecture, Department of Chemistry, Kingston, Ontario, Canada, May 13, 2011.

“Thermodynamics at the Single Molecule Level: RNA Folding in Laser Nanobathtubs,” Technische Universitaet Dresden, Dresden, Germany, June 10, 2011.

“Role of Multiple Exciton Generation and External Fields in Quantum Dot Blinking Dynamics,” Optical Probes 2011/Excited State Processes 2011, Santa Fe, New Mexico, June 21, 2011.

“Probing Non-Equilibrium Collision Dynamics at the Gas-Liquid Interface with Quantum State Resolution,” 2011 National Meeting, American Chemical Society Denver, CO, August 29, 2011.

“Energy Transfer Dynamics at the Gas-Liquid Interface: A Quantum State Resolved Perspective,” COMET 2011, Oxford University, Oxford, UK, September 15, 2011.

“Searching for Simplicity: From Collisions at Gas-Liquid Interfaces to Single Molecule RNA Folding,” Department of Chemistry, University of Pennsylvania, Philadelphia, PA, November 10, 2011.

“Watching Chemistry at the Single Molecule Level,” Frederick Kaufman Memorial Lecture Series, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, November 21, 2011.

* “In Search of Simplicity: From Spectroscopy of Radicals to Collisions at the Gas-Liquid Interface,” Frederick Kaufman Memorial Lecture Series, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, November 22, 2011.

* “An Overview: Reactions and Radicals in Clusters,” Gordon Research Conference on Molecular and Ionic Clusters, Ventura, CA, Jan 29, 2012.

“Probing Room Temperature Ionic Liquids via Molecular Beam Scattering Studies at the Gas-Liquid Interface,” Ionic Liquids: Science and Applications Symposium, Division of Industrial and Engineering Chemistry, American Chemical Society 243rd National Meeting, San Diego, CA, March 25, 2012.

“Physical Chemistry of Separations at Gas-Liquid Interfaces: Insights from Quantum State-resolved Scattering Studies,” Physical Chemistry of CO₂ Separation Symposium, Division of Physical Chemistry, American Chemical Society, 243rd National Meeting, San Diego, CA March 25, 2012.

*“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.

“On Probing Ions at the Gas-Liquid Interface by Quantum State-resolved Molecular Beam Scattering (or) The Curious Incident of the Cation In the Night Time,” Faraday Discussions 157, Assisi, Italy, June 25, 2012.

“From RNA Folding to Nanoparticle Microscopy: The Beauty of One at a Time,” Symposium in Physical Chemistry,” Institute of Chemistry Chinese Academy of Sciences, Beijing, China, Sept 28, 2012.

“From RNA Folding to Nanoparticle Microscopy: The Beauty of One at a Time,” MANA Symposium: Nanotechnology, Materials and Physical Chemistry, International Center for Materials Nanoarchitectonics, Tsukuba, Japan, October 1, 2012.

“From RNA Folding to Nanoparticle Microscopy: The Beauty of One at a Time,” Korean Society of Chemistry Symposium, Seoul National University, Seoul, Korea, October 4, 2012.

*“High Resolution Laser Spectroscopy in Slit Supersonic Jet Discharges: Near-IR Stepping Stones Toward Far-IR Astronomy,” Molecular Spectroscopy in the Era of Far-IR Astronomy, Emory University, Atlanta, GA, October 30, 2012.

Complex RNA folding dynamics in the tRNA-like structure (TLS) domain of Brome Mosaic Virus,” 7th Biennial Conference on Single Molecule Biophysics, Aspen, CO January 8, 2013.

“Energy Transfer at Surfaces and Interfaces: An Introduction,” Gordon Research Conference on Molecular Energy Transfer, Ventura, CA, January 14, 2013.

“From quantum dots to plasmonic nanomaterials: Insights from single nanoparticle fluorescence and scanning photoionization microscopy,” Indian Institute of Science, Bangalore, India, February 7, 2013.

“Spectroscopy/dynamics at the single nanoparticle level: From quantum dots to plasmonic nanomaterials,” Council of Scientific and Industrial Research (CSIR)-National Chemical Laboratory, Pune, India, February 11, 2013.

“Chemistry of Cooking,” CU Wizards Science Outreach Program, University of Colorado, Boulder, CO, February 23, 2013.

*“State-to-State Dynamics in Ultracold Collisions: Insights From High Resolution Spectroscopy of Weakly Bound Molecular Complexes,” Conference on New Physics with Ultracold Molecules, Kavli Institute for Theoretical Physics, U. C. Santa Barbara, Santa Barbara, CA, March 13, 2013.

“From Single Molecule RNA Folding to Single Nanoparticle Plasmonics: The Beauty of One at a Time,” Advanced Distinguished Lecture Series, Department of Chemistry, Kansas State University, Manhattan, KS, March, 28, 2013.

“Molecular Physics and Bioscience: Connections and Prospects,” Symposium on Physics Applied To Advances In Measurement Technology (in honor of Dr. Katharine B. Gebbie), NIST, Boulder, CO, May 10, 2013.

“State-Resolved Molecular Beam Scattering at Gas-Liquid Interfaces,” International Symposium on Molecular Beams 2013, Prague, Czech Republic, June 7, 2013.

“State-Resolved Molecular Beam Scattering at Gas-Liquid Interfaces,” Dynamics of Molecular Collisions, Granlibakken, Lake Tahoe, NV, July 10, 2013.

References

- ¹ D. T. Anderson, S. Davis, T. S. Zwier, and D. J. Nesbitt, Chem. Phys. Lett. **258**, 207 (1996).
- ² W. B. Chapman, B. W. Blackmon, and D. J. Nesbitt, J. Chem. Phys. **107**, 8193 (1997).
- ³ W. B. Chapman, B. W. Blackmon, S. Nizkorodov, and D. J. Nesbitt, J. Chem. Phys. **109**, 9306 (1998).
- ⁴ S. Davis, D. T. Anderson, G. Duxbury, and D. J. Nesbitt, J. Chem. Phys. **107**, 5661 (1997).
- ⁵ S. Davis, D. Uy, and D. J. Nesbitt, J. Chem. Phys. **112**, 1823 (2000).
- ⁶ S. Davis, M. Farnik, D. Uy, and D. J. Nesbitt, Chem. Phys. Lett. **344**, 23 (2001).
- ⁷ M. Farnik, S. Davis, M. A. Kostin, O. L. Polyansky, J. Tennyson, and D. J. Nesbitt, J. Chem. Phys. **116**, 6146 (2002).
- ⁸ S. A. Nizkorodov, W. W. Harper, W. B. Chapman, B. W. Blackmon, and D. J. Nesbitt, J. Chem. Phys. **111**, 8404 (1999).
- ⁹ D. Uy, S. Davis, and D. J. Nesbitt, J. Chem. Phys. **109**, 7793 (1998).
- ¹⁰ D. Smith and P. Spaniel, in *Advances in Atomic, Molecular, and Optical Physics*, Vol 32 (1994), Vol. 32, pp. 307.
- ¹¹ C. M. Lovejoy and D. J. Nesbitt, Rev. Sci. Instrum. **58**, 807 (1987).
- ¹² E. N. Sharp, M. A. Roberts, and D. J. Nesbitt, Phys. Chem. Chem. Phys. **10**, 6592 (2008).
- ¹³ A. V. Friderichsen, J. G. Radziszewski, M. R. Nimlos, P. R. Winter, D. C. Dayton, D. E. David, and G. B. Ellison, J. Am. Chem. Soc. **123**, 1977 (2001).
- ¹⁴ R. J. McMahon, M. C. McCarthy, C. A. Gottlieb, J. B. Dudek, J. F. Stanton, and P. Thaddeus, Astrophys. J. **590**, L61 (2003).
- ¹⁵ J. G. Radziszewski, M. R. Nimlos, P. R. Winter, and G. B. Ellison, J. Am. Chem. Soc. **118**, 7400 (1996).
- ¹⁶ J. Y. Niu and J. Y. Hu, Marine And Petroleum Geology **16**, 85 (1999).
- ¹⁷ O. P. Strausz, T. W. Mojelsky, J. D. Payzant, G. A. Olah, and G. K. S. Prakash, Energy & Fuels **13**, 558 (1999).
- ¹⁸ G. L. Agafonov, I. Naydenova, P. A. Vlasov, and J. Warnatz, Proc. Combust. Inst. **31**, 575 (2007).
- ¹⁹ J. A. Miller and C. F. Melius, Combust. Flame **91**, 21 (1992).
- ²⁰ N. M. Marinov, W. J. Pitz, C. K. Westbrook, M. J. Castaldi, and S. M. Senkan, Combust. Sci. Technol. **116**, 211 (1996).
- ²¹ H. Wang and M. Frenklach, J. Phys. Chem. **98**, 11465 (1994).
- ²² E. N. Sharp-Williams, M. A. Roberts, and D. J. Nesbitt, J. Chem. Phys. **134** (2011).
- ²³ E. N. Sharp-Williams, M. A. Roberts, and D. J. Nesbitt, Phys. Chem. Chem. Phys. **13**, 17474 (2011).
- ²⁴ W. B. Yan, J. L. Hall, J. W. Stephens, M. L. Richnow, and R. F. Curl, J. Chem. Phys. **86**, 1657 (1987).
- ²⁵ W.-B. Yan, C. B. Dane, D. Zeitz, J. L. Hall, and R. F. Curl, Jr., J. Mol. Spectrosc. **123**, 486 (1987).
- ²⁶ Y.-C. Hsu, Y.-J. Shiu, and C.-M. Lin, J. Chem. Phys. **103**, 5919 (1995).

- 27 A. van der Avoird, Y. Scribano, A. Faure, M. J. Weida, J. R. Fair, and D. J. Nesbitt,
Chem. Phys. (in press).
- 28 A. van der Avoird and D. J. Nesbitt, J. Chem. Phys. **134**, 044314 (2011).
- 29 B. K. Carpenter, J. Phys. Chem. **99**, 9801 (1995).
- 30 J. A. Miller, R. J. Kee, and C. K. Westbrook, Annu. Rev. Phys. Chem. **41**, 345
(1990).
- 31 A. Fahr, P. S. Monks, L. J. Stief, and A. H. Laufer, Icarus **116**, 415 (1995).
- 32 G. R. Gladstone, M. Allen, and Y. L. Yung, Icarus **119**, 1 (1996).
- 33 W. H. Ip, Astrophys. J. **362**, 354 (1990).
- 34 R. K. Janev and D. Reiter, Phys. Plasmas **11**, 780 (2004).
- 35 A. R. Sharma, B. J. Braams, S. Carter, B. C. Shepler, and J. M. Bowman, J. Chem.
Phys. **130**, 174301 (2009).