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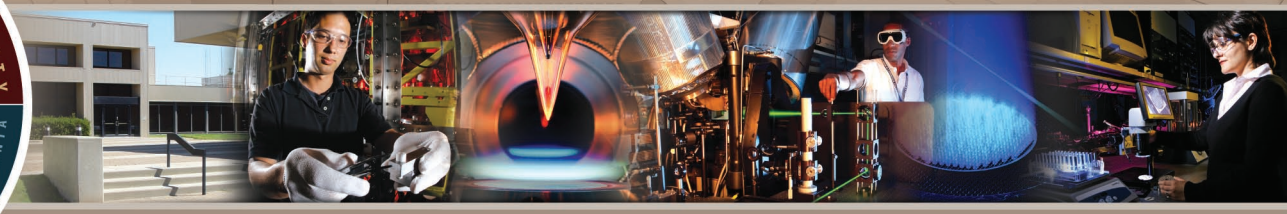

July/August 2008 • VOL. 30, NO. 4

TNF Workshop addresses challenges for collaborative research

The TNF9 Workshop (Ninth International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames), was held July 31 – August 2 in Montreal, Canada, and was attended by 82 researchers from 13 countries. Past workshops have focused on issues of turbulence-chemistry interaction in nonpremixed and partially premixed flames, with collaborative comparisons of measured and modeled results being a centerpiece at each meeting. However, TNF9 was

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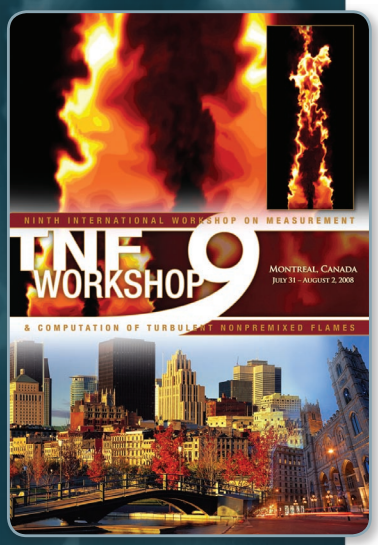

TNF 9 poster representing the event that was held in Montreal, Canada.

Beyond Born-Oppenheimer molecular dynamics

Excited electronic states play an important role in many areas of chemistry from combustion to light harvesting via a variety of elementary chemical mechanisms, including intersystem crossing, photodissociation, internal conversion, and charge transfer. The term "non-Born–Oppenheimer" (NBO) may be generally applied to these processes to emphasize the idea that the Born–Oppenheimer separation of the nuclear (slow) and electronic (fast) time scales breaks down and that electronic surfaces other than the ground surface play a key role in the dynamics. An accurate treatment of the chemistry of NBO systems poses significant conceptual and computational challenges to current theoretical models.

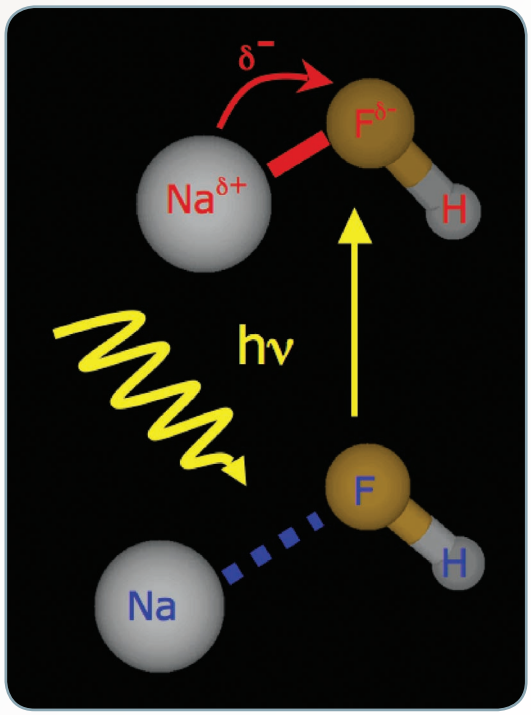

Figure 1. *Upon photoexcitation, charge density is transferred from the Na atom to the F atom, thus strengthening the NaF bond, weaking the HF bond, and enhancing the likelihood of the system fragmenting to the NaF + H products.*

CRF researcher Ahren Jasper, in collaboration with University of Minnesota professor Donald Truhlar, is developing and validating methods for performing quantitative simulations of NBO systems using reactive molecular dynamics (MD), which has traditionally been limited to single surface simulations. NBO MD simulations retain the classical, trajectory-based description of the nuclear motion, while incorporating transitions between the various electronic states based on a quantum mechanical treatment of the electronic degrees of freedom.

Because there is no unique way to couple quantum and classical subsystems, practical mixed quantum/classical treatments of quantum mechanical events are necessarily somewhat ad hoc, and several NBO MD methods have been proposed. An important aspect of current research is therefore the quantification and reduction of the errors associated with the additional assumptions and approximations used to model electronic transitions in MD simulations.

A recent target for theoretical treatment was the photodissociation of the Na…FH van der Waals complex. Thermal excitation tends to break the weak van der Waals bond, pro-

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ducing the Na and HF products exclusively. Upon electronic excitation with visible light, however, the complex is promoted to a metastable complex called an exciplex. The exciplex is proposed to exhibit enhanced reactivity to form NaF + H via the "harpooning" mechanism shown in Figure 1.

Analytic representations of the ground and first-excited potential energy surfaces were developed based on high-level quantum chemistry calculations and are shown in Figure 2. The two surfaces are most strongly coupled along a line of avoided crossings occurring at slightly extended HF distances. Avoided crossings typically represent the "shoulder" of a nearby but energetically inaccessible conical intersection.

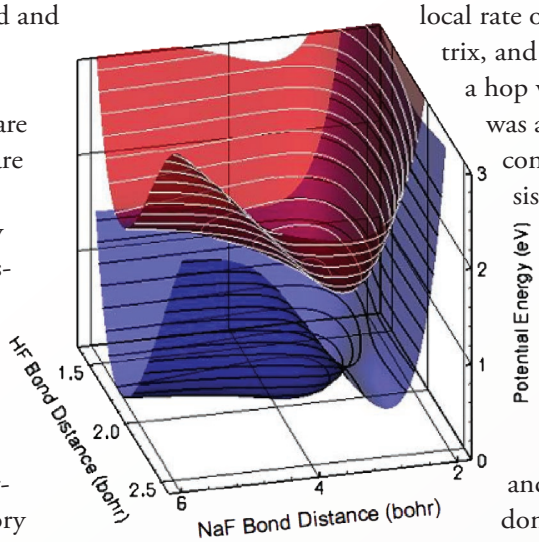

Figure 2. *Ground (blue) and first excited (red) potential energy surfaces of the Na. . . FH system.*

NBO MD simulations were carried out using the fewest switches (FS) surface hopping algorithm. Each trajectory was initially propagated in the excited electronic state with its starting coordinates and momenta selected from a distribution designed to simulate the result of laser excitation. As the trajectory vibrated in the exciplex, a time-dependent electronic density matrix was calculated, representing the nonradiative flow of electronic density between the two states. This flow of electronic density depends on terms in the Hamiltonian that are neglected in the BO approximation but that become significant when the character of the electronic states changes rapidly as a function of nuclear geometry. At each time step along the trajectory, a probability of "hopping" between the states was computed based on the local rate of change of the electronic density matrix, and hops were carried out stochastically. If a hop was called for, the nuclear momentum was adjusted such that total energy was conserved. The NBO simulation consisted of thousands of trajectories, and the results were averaged to obtain product branching probabilities and exciplex lifetimes.

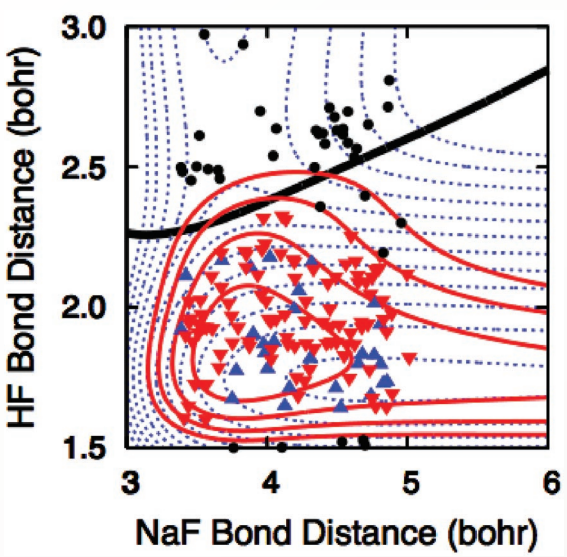

Figure 3. *Ground (blue) and first excited (red) potential energy surfaces. The initial hops down are shown as red triangles. Subsequent successful hops up are shown as blue triangles, and frustrated hops up are shown as black dots. The solid black line is the line of avoided crossings.*

The NBO MD simulations confirmed the enhanced reactivity of the harpooning mechanism, and NaF + H was predicted to be the dominant photodissociated bimolecular product. Quantitatively, however, the FS method was found to overpredict the formation of Na + HF by a factor of four when compared with accurate quantum mechanical results. The lifetime of the exciplex was likewise overestimated by a factor of two.

An analysis of the NBO MD trajectories revealed that an important dynamical feature was missing from the FS method. Figure 3 shows contour plots of the excited and ground electronic states, as well as hopping information for a subset of trajectories. More than three-fourths of the trajectories attempted to hop back into the exciplex after their first hop down, but many did so at geometries where the excited state is energetically forbidden. The majority of these so-called "frustrated" hops occur near the line of avoided crossings, a region where the two electronic surfaces have very different shapes. Frustrated hops have previously been identified as a significant source of error in NBO MD surface hopping simulations.

In the quantum mechanical calculation, the nuclear motions associated with divergent parts of the wave function cause the electronic subsystem to decohere, which reduces the likelihood of electronic transitions. Decoherence due to wave packet divergence may be expected to be significant near the line of avoided crossings, as shown schematically in Figure 4. In contrast, the FS method incorrectly treats the electronic

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Combustion Research Facility Visitor Program

These visitors will be leaving the Combustion Research Facility at the completion of their tenure.

Santiago Jimenez
Visiting Researcher
Affiliation: Laboratory for Research in Combustion Technology (LITEC), Zaragoza, Spain
Project: Oxy-fuel combustion
Host: Chris Shaddix

Robert Knaus
PSI intern
Affiliation: University of Illinois
Mentor: Joe Oefelein

Julien Manin
Visiting Researcher
Affiliation: Universidad Politecnica de Valencia
Project: Diesel engine fuel-air mixing
Host: Lyle Pickett

James Martin
Visiting Student Fellow
Affiliation: University of Texas-Austin
Project: Bayesian methods for uncertainty quantifications
Mentor: Youssef Marzouk

Daniel Merthe
PSI Intern
Affiliation: University of San Francisco
Project: Molecular Bean Scattering of Molecules
Mentors: Len Jusinski & Craig Taatjes

Geoff Oxberry
Visiting Student Fellow
Affiliation: MIT
Project: Computational singular perturbation of chemical systems
Mentor: Habib Najm

Adam Ruggles
Visiting Student Researcher
Institution: Cranfield University
Project: Investigating of hydrogen utilization as a future energy carrier
Host: Bob Schefer

Jonathan Scheffe
Visiting Student Researcher
Affiliation: University of Colorado
Mentors: Anthony McDaniel & Mark Allendorf

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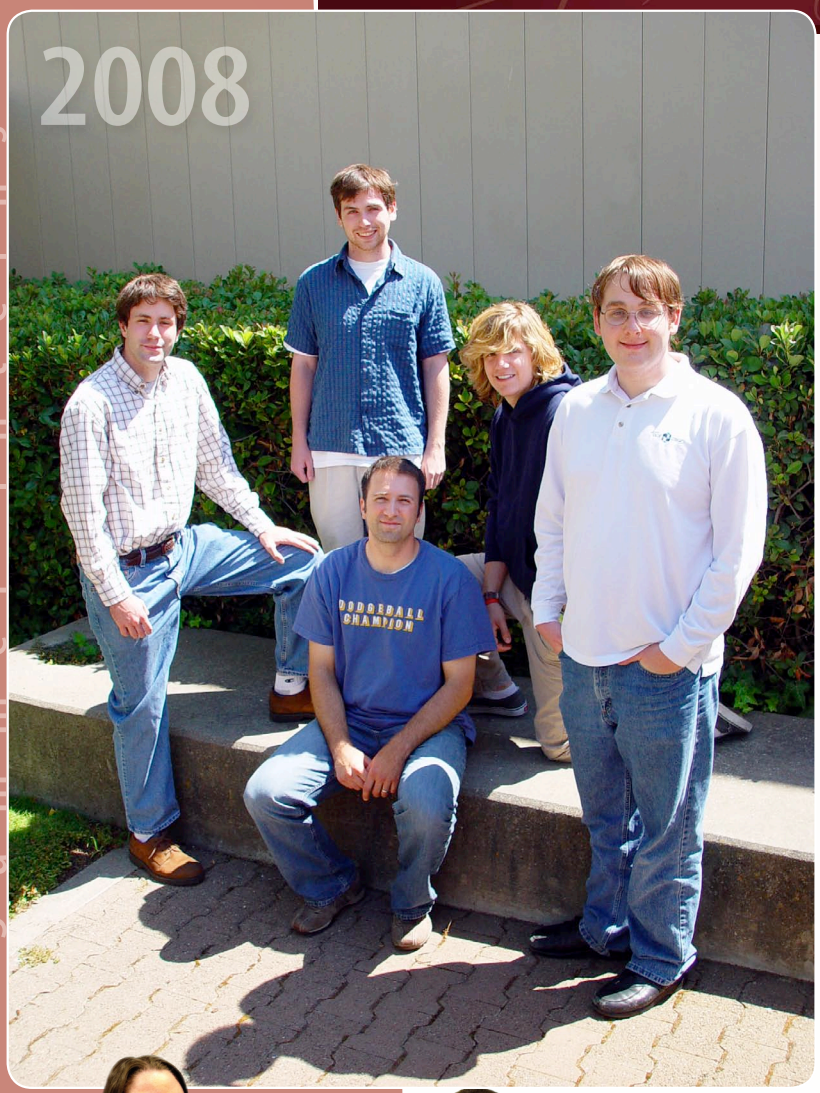
Summer Interns



PSI SUMMER INTERNS

Melissa Harmon is in her second year as administrative intern with Melanie Steadman. She also recently began working with Ali Ratzel as a financial intern. In the fall she will be in her second year at California State University Stanislaus majoring in business.

Ryan Gehmlich is in his fourth year as an intern and his second year working with Lyle Pickett. He is a first year graduate student working on his master's degree at UC Davis, but next year he will be working and studying at RWTH Aachen University, Germany.
Project: Ryan is working with Lyle Pickett on analyzing soot TEM at various conditions.

Sean McNealis is working with Paul Fugazzi and Nils Hansen. He is a sophomore at UC Davis majoring in civil and environmental engineering.
Project: Sean is working on deriving temperature profiles of flames using Laser Induced Florescence (LIF) and learning the workings of the lab from a technologist's standpoint.

Daniel Merthe is an undergradate student in physics and chemistry at the University of San Francisco.
Project: Daniel is working with Len Jusinski in an experimental study of chlorine-initiated butyl + O_2 reaction at low pressure.

Robert Knaus is a second year intern working with Joe Oefelein. He is a second year graduate student in mechanical engineering at the University of Illinois.
Project: Robert is studying the statistics and modeling of scalar dissipation and its relation to the filtered mixture fraction.

Jonathan Scheffe , an intern with Anthony McDaniel and Mark Allendorf, is a third year graduate student in chemical engineering at the University of Colorado.
Project: Jonathan is studying solar water splitting for H_2 production.

Jane Hwang is an intern with Carl Hayden. She is also a US Air Force Academy cadet (Department of Defense intern).
Project: Jane is studying protein binding to membranes.

COMPUTATIONAL SCIENCE GRADUATE FELLOWS (CSGF)

In addition to the PSI interns listed above, there are two Computational Science Graduate Fellow (CSGF) interns at Sandia.

James Martin, a third year graduate student at the University of Texas at Austin, is studying dimensionality reduction for Bayesian Inference Problems with his mentor, Youssef Marzouk.

Geoffrey Oxberry, a graduate student at the Massachusetts Institute of Technology, is working on the analysis and reduction of chemical models and uncertainty with his mentor, Habib Najm.

Physical Science Institute and CSGF summer interns—Top, left to right: Geoffrey Oxberry, Rob Knaus, Ryan Gehmlich, Sean McNealis, James Martin, Bottom, left to right: Melissa Harmon, Jonathan Scheffe, Daniel Merthe, Jane Hwang.

TNF9 (continued)

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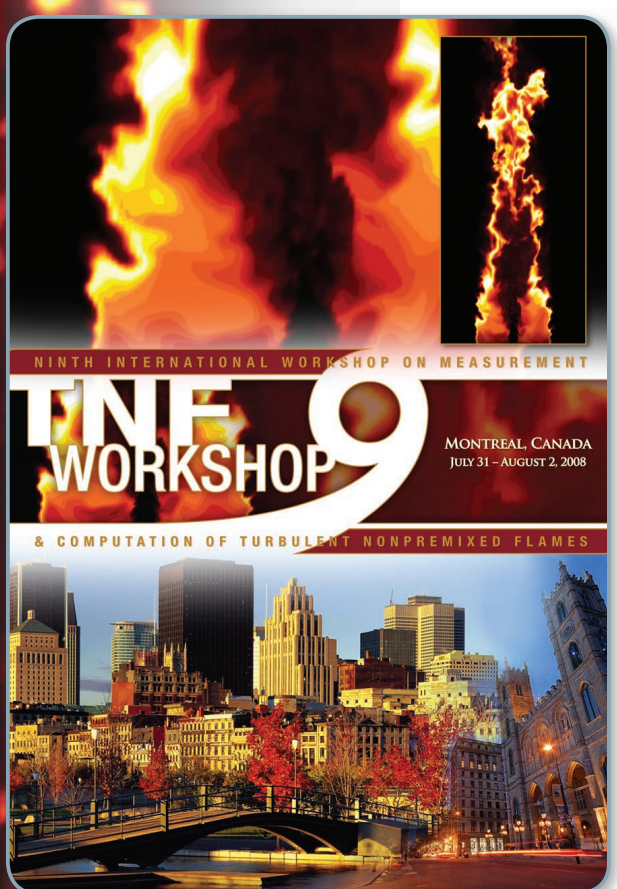
organized to prompt the participants to take a broader view of collaborative research priorities for the next 4 to 6 years. Presentations and discussions were centered on three challenges:

- Development and validation of modeling approaches that are accurate over a broad range of combustion modes and regimes (nonpremixed, partially premixed, stratified, and premixed).
- Extension of quantitative validation work to include more complex fuels (beyond CH_4) and fuel mixtures that are of practical interest.
- Establishment of a more complete framework for verification and validation of combustion large eddy simulation (LES), including quality assessment of calculations, as well as development and utilization of approaches that extract knowledge and understanding from comparisons of detailed experimental measurements with detailed simulations.



Sandians Rob Barlow, Jonathan Frank, and Joe Oefelein helped to coordinate some of the discussion session. Other session coordinators, discussion leaders, and major contributors included Steve Pope (Cornell), Andreas Kempf and Peter Lindstedt (Imperial College of London), Andreas Dreizler and Johannes Janicka (Technical University of Darmstadt), J.-Y. Chen (UC Berkeley), Assaad Masri (Sydney University), and Dirk Roekaerts (Delft University). Bernard Geurts (Twente University) and Graham Goldin (ANSYS) were invited speakers on the topic of LES quality assessment. The Proceedings will be made available soon at http://public.ca.sandia.gov/TNF, and will include a summary of the major discussion points and agreed directions for collaborative research.

Beyond Born (continued)

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motion in this region as fully coherent, independent of the shapes of the potential energy surfaces. This failure of the FS method is due to its artificial separation of the classical nuclear and quantum mechanical electronic motions. A new model for decoherence, called "stochastic decoherence," was developed and introduced into the FS method, resulting in reduced errors associated with frustrated hopping and near quantitative agreement with the quantum mechanical results.

This study represents a step toward a more complete understanding of the complex chemistry of coupled electronic states, including the important role coherence plays in determining the products of laser-induced chemistry. The development of simple models for coherence and multistate dynamics that are readily applicable to large systems may aid in the understanding and design of technologies that seek to exploit these quantum effects for microscopic control.

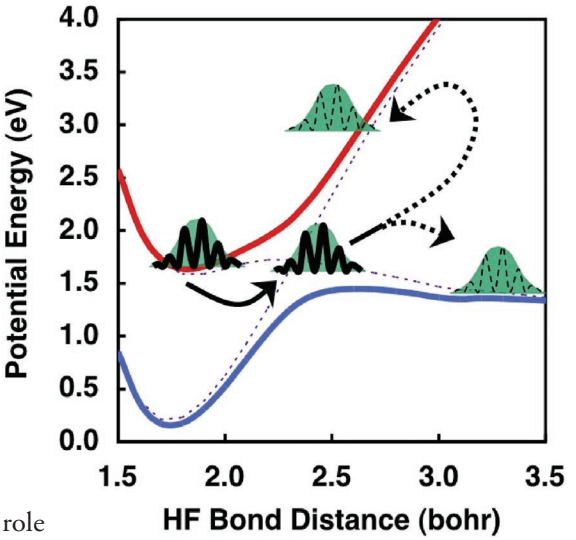

Figure 4. *The stochastic decoherence method accurately treats both coherent motion (the solid arrow) and decoherent motion due to wave packet divergence (the dashed arrows).*

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

CRF News is a bimonthly publication of the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.
ISSN 1548-4300

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