Chemical Physics Research

Portfolio Description

This activity supports experimental and theoretical investigations in the gas phase, condensed phase, and at interfaces aimed at elucidating the molecular-scale chemical and physical properties and interactions that govern chemical reactivity, solute/solvent structure, and transport. New opportunities to attain predictive understanding of chemical reactivity are also supported, including structural and dynamical studies that emphasize a complete understanding of reactive chemistry at full quantum detail. These activities include the development and implementation of predictive computational modeling and simulation approaches, incorporating advanced theory and experimental validation, for scientific discovery across multiple scales. The impact on DOE missions is far reaching, including energy utilization, catalytic and separation processes, energy storage, and environmental chemical and transport processes.

The Chemical Physics portfolio comprises three program areas: (1) Gas Phase Chemical Physics (GPCP), (2) Condensed Phase and Interfacial Molecular Science (CPIMS), and (3) Computational and Theoretical Chemistry (CTC):

- Gas Phase Chemical Physics (GPCP) research emphasizes studies of the dynamics and rates of chemical reactions at energies characteristic of combustion, and the chemical and physical properties of key combustion intermediates. The overall aim is the development of a fundamental understanding of chemical reactivity enabling validated theories, models and computational tools for predicting rates, products, and dynamics of chemical processes involved in energy utilization by combustion devices. Important to this aim is also the development of experimental tools for discovery of fundamental dynamics and processes affecting chemical reactivity. Combustion models using this input are developed that incorporate complex chemistry with the turbulent flow and energy transport characteristics of real combustion processes.
- Condensed Phase and Interfacial Molecular Science (CPIMS) research emphasizes molecular understanding of chemical, physical, and electron-driven processes in aqueous media and at interfaces. Studies of reaction dynamics at well-characterized metal and metal-oxide surfaces and clusters lead to the development of theories on the molecular origins of surface-mediated catalysis and heterogeneous chemistry. Studies of model condensed-phase systems target first-principles understandings of molecular reactivity and dynamical processes in solution and at interfaces. The approach confronts the transition from molecular-scale chemistry to collective phenomena in complex systems, such as the effects of solvation on chemical structure and reactivity.
- Research in Computational and Theoretical Chemistry (CTC) emphasizes integration and development of new and existing theoretical and computational approaches for the accurate and efficient description of processes relevant to the BES mission. Supported efforts are tightly integrated with the research and goals of the CPIMS and GPCP programs and many have wider crosscutting relevance, advancing goals of other BES chemistry, biochemistry and geochemistry programs. Common to all of these areas is the need for new approaches that go beyond standard representations to address excited-state dynamics, the inclusion of spin-dependent effects, the ability to model extremely anharmonic processes, and the ability to account for all types of energy exchange between various degrees of freedom. Also of

interest are methods that will advance modeling of weakly-bound systems and systems interacting with both polar and nonpolar solvents and/or environments.

Unique Aspects

The BES Chemical Physics Research activity is unique in its long term support of a number of fundamental chemical science areas, and in its integration of capabilities from research universities and DOE national laboratories that sustain long-term progress in difficult scientific areas as well as effective coupling to DOE missions:

- Through the GPCP program, DOE is the principal supporter of high-temperature chemical kinetics and gas-phase chemical reaction dynamics in the nation. This activity also has oversight for several national laboratory programs, including the Combustion Research Facility (CRF), a unique, multi-investigator research laboratory that have a strong collaborative visitor program and that promotes synergism between BES-supported basic research and the applied science and technology programs supported the Office of Energy Efficiency and Renewable Energy (EERE) and industry.
- The CPIMS program is unique is its relevance to DOE mission areas, providing a fundamental basis for understanding chemical reactivity in complex systems, such as those encountered in catalysis, energy storage, separations, and the environmental contaminant transport in mineral and aqueous environments. This program is a major supporter of basic research on chemical reactivity of molecular species in the liquid phase, on metal clusters, and at solid-gas and solid-liquid interfaces. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiolysis effects and radiation-driven chemistry in nuclear fuel and waste environments.
- The CTC program is not a separate program but rather it is fully integrated with other BES research activities, contributing principally to the GPCP and CPIMS elements of the Chemical Physics portfolio, but also providing significant support to efforts spanning BES chemistry, biochemistry and geochemistry research. A unique component of this program is its support for extremely complex research that requires simultaneous development of theoretical and massively parallel computational implementation.

Relationship to Other Programs

Research under this activity complements research supported across the Office of Basic Energy Sciences, including Catalysis Science, Separations and Analysis, Heavy Element Chemistry, Atomic and Molecular Optical Science, Solar Photochemistry, and Geosciences. There is a particularly strong coupling between the CPIMS and Solar Photochemistry programs in the fundamental chemistry and physics of radiolytic processes in condensed media and at interfaces. The CTC program co-funds efforts with the Office of Advanced Scientific Computing Research (ASCR) where appropriate for the BES and ASCR missions, and has supported a number of Scientific Discovery through Advanced Computing (SciDAC) efforts. There are numerous linkages with combustion research conducted under various research programs within DOE EERE and DOE FE as well as combustion-related chemical physics research conducted by the Air Force Office of Scientific Research (AFOSR), Office of Naval Research (ONR), Army Research Office (ARO), National Aeronautics and Space Administration (NASA), National Institute of Standards and Technology (NIST), and the National Science Foundation (NSF). These linkages include common PIs and industry relationships in a number of programs, as well as the couplings described above fostered by the CRF. This activity provides substantial support

for basic research to scientists at PNNL who utilize the William R. Riley Environmental Molecular Sciences Laboratory (EMSL), a national user facility operated by the DOE/SC Office of Biological and Environmental Research (BER). Experiments concerning ultrafast chemical imaging are supported at the Center for Nanoscale Materials at Argonne National Laboratory in coordination with the BES Scientific User Facilities Division. In FY 2009, support was provided for the following Gordon conferences: Dynamics at Surfaces, Time-Resolved Vibrational Spectroscopy, Electronic Spectroscopy and Dynamics, and Laser Diagnostics in Combustion. In FY 2010, support was provided for the Gordon conferences on Water Aqueous Solutions and Radiation Chemistry.

Significant Accomplishments

Impacts in fundamental science include the development of crossed molecular beams and ion imaging techniques that have spawned a generation of experiments in state-to-state chemical reaction dynamics and energy transfer, much of which has been supported by the chemical physics program. In addition, support from this activity resulted in the development of molecular beam and laser sputtering techniques for the study of atomic clusters as prototypical models for catalysis. More recently, ultrafast laser spectroscopy has provided important insights into hydrogen bonding and proton transport in water in nano-confined geometries. Support has yielded for the first time a conclusive link between the size of catalytic particles on a surface, the particle electronic properties, and the ability of particles to speed chemical reactions. Furthermore, recent advances in low-temperature scanning tunneling microscopy (STM) have been combined with temporally and spatially resolved spectroscopic tools such as ultrafast, two-photon photoemission, resulting in the discovery of long-lived electronic surface states that could lead to new ways to induce and control electronic excitation at surfaces, and have yielded an unprecedented view of the coupling of electronic and vibrational motion within a single molecule. Advanced probes of combustion environments have also yielded recent discoveries, such as the direct observation of reactions important in incipient soot formation and the recent discovery of the importance of enols in flame chemistry. This activity has played a major role in the development of quantum chemistry methodologies for accurate predictions of chemical properties. Advances in high resolution time-resolved spectroscopy have yielded information on intermediates and product state distributions with unprecedented isomeric specificity. These developments have led to theories and computer codes for the calculation of thermodynamic properties and chemical reaction rates in the gas phase as well as the properties of complex molecular systems in the condensed phase.

Mission Relevance

- The gas-phase portion of this activity contributes strongly to the DOE mission in the area of the efficient and clean combustion of fuels. The coupling of complex chemistry and turbulent flow has long challenged predictive combustion modeling. Truly predictive combustion models enable the design of new combustion devices (such as internal combustion engines, burners, and turbines) with maximum energy efficiency and minimal environmental consequences. In transportation, the changing composition of fuels, from those derived from light, sweet crude oil to biofuels and fuels from alternative fossil feedstocks puts increasing emphasis on the need for science-based design of modern engines.
- The condensed-phase and interfacial portions of this activity impacts a variety of mission areas by providing a fundamental basis for understanding chemical reactivity in complex

systems, such as those encountered in catalysis and environmental processes, along with activity that provides fundamental underpinnings relevant to energy production and storage. Surface-mediated chemistry research in this activity complements more directed efforts in heterogeneous catalysis. Condensed-phase and interfacial chemical physics research on dissolution, solvation, nucleation, separation, and reaction provides important fundamental knowledge relevant to the environmental contaminant transport in mineral and aqueous environments. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiolysis effects in nuclear fuel and waste environments.

- The computational and theoretical portions of the portfolio aim to advance the Chemical Physics goals just described, and in addition to advance mission areas across the BES. For example, supported activates advance next-generation solar energy, sunlight-to-fuels, and energy storage concepts.

Scientific Challenges

Research in Chemical Physics is fundamental to meeting the grand challenges for basic energy sciences, as identified in the recent report on this topic from the Basic Energy Sciences Advisory Committee. Specific opportunities are to:

- Improve and expand experimental measurement of highly energetic, unstable molecules to diagnose complex reacting flows and, in more controlled environments, to determine molecular dynamics and reaction rates at elevated temperatures and pressures.
- Develop computational approaches of acceptable precision for the calculation of potential energy surfaces for ground and excited electronic states and their conical intersections for chemically important species including free radicals.
- Improve scaling with number of atoms to facilitate computation of properties and reactions of large molecules.
- Improve accuracy and throughput of methods for calculating chemical reaction rates from detailed chemical dynamics, including reactions without barriers for which statistical theories do not apply.
- Develop improved multiscale methods for dealing with systems exhibiting many orders of magnitude differences in spatial and temporal scales such as those found in turbulent combustion, catalysis, and condensed phase processes.
- Develop fundamental understanding of the mechanisms that underlie assembly of atoms into clusters and larger nanosystems for the rational design and synthesis of cluster-based nanoarchitectures with desired properties.
- Develop and apply new experimental methods for characterizing chemically active molecular scale structures and reaction mechanisms at interfaces.
- Characterize high-energy electron- and photon-stimulated processes at complex interfaces.
- Design quantitative models for condensed-phase solvation that include polarization, charge-transfer, and nano-confinement effects.
- Develop new theoretical time-domain and frequency-domain simulation tools for computing structural, transport, and optical properties of nanoscale systems.
- Develop methods to computationally determine how to externally control energy-, charge- and matter- transfer processes in chemical and molecular systems with low-energy sources of radiation or applied fields, small thermal swings, and/or relatively minor changes in the external environment.

- Determine how such energy exchange, even when rare, is accomplished through resonant, nonresonant and dissipative processes
- Develop a means that addresses the manifestation of these effects over many temporal and spatial scales

Projected Evolution

The focus of the chemical physics program is the development of a molecular-level understanding of gas-phase, condensed-phase, and interfacial chemical reactivity of importance to combustion, catalysis, energy conversion and storage, and environmental preservation. The desired evolution is to predictive capabilities that span the microscopic to macroscopic domains enabling the computation of individual molecular interactions as well as their role in complex, collective behavior in real-world devices. Currently, increased emphasis in gas-phase chemical physics is on validated theories and computational approaches for the structure, dynamics, and kinetics of open shell systems, experimental measurements of combustion reactions at high pressures, better insight into soot particle growth and an improved understanding of the interaction of chemistry with fluid dynamics. In surface chemistry, continued emphasis is on the development of a structural basis for gas/surface interactions, encouraging site-specific studies that measure local behavior at defined sites. At interfaces, emphasis is on aqueous systems and the role of solvents in mediating solute reactivity. Expanding into the future, plans are to enhance the use of computer-generated mechanisms and models in combustion science, broaden efforts to molecular building blocks of emerging fuels, probe the chemical physics of energy transfer in large molecules, to explore the molecular origins of condensed phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding, and to investigate temporally resolved interfacial chemical dynamics and charge transfer using advances in chemical imaging. Computational and theoretical efforts will continue to expand in scope, to span BES mission-relevant research in chemical sciences, geosciences and biosciences, while at the same time remaining tightly integrated with these efforts. A continuing emphasis on DOE mission impact will guide the selection of research opportunities, development of predictive capabilities, and interactions with other programs and organizations.