Research Activity:	**Chemical Physics Research**
Division:	Chemical Sciences, Geosciences, and Biosciences
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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 reactivity, solute/solvent structure, and transport. Also supported are studies motivated by new opportunities fostered by predictive understanding of chemical reactivity, including structural and dynamical studies that emphasize a complete understanding of reactive chemistry. 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. Impact on DOE missions is far reaching, including energy utilization, catalytic and separation processes, energy storage, and environmental chemical and transport processes. The activity is implemented as two distinct programs: (1) Gas Phase Chemical Physics (GPCP) and (2) Condensed Phase and Interfacial Molecular Science (CPIMS).

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.

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.

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 portfolio, 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 facility that hosts a strong visitors program for collaborating scientists and promotes synergism between the BES-supported basic research and the applied science and technology programs supported by the Office of Fossil Energy (FE), the Office of Energy Efficiency and Renewable Energy (EERE), and industry.

The CPIMS portfolio 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.

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. There are also 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).

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. 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. These developments have led, in turn, 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 GPCP portion of this activity contributes strongly to the DOE mission in the area of the efficient and clean combustion of fuels, enabling new opportunities fostered by an increasingly predictive understanding of chemical combustion. Since 85 percent of nation's energy use is derived from burning fossil fuels, this activity is motivated by national needs in energy security, economic growth, and environmental preservation. The chemical complexity of combustion has provided an impressive challenge to predictive modeling. Truly predictive combustion models will 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 innovative new devices.

The CPIMS portion of this activity provides fundamental underpinnings relevant to energy production and storage, along with energy-relevant processes such as chemical separations and catalysis. Surface-mediated catalysis, for example, reduces the energy demands of industrial chemical processes by bypassing energy barriers to chemical reaction. The knowledge gained from this research program will aid in the development of a predictive capability for surface chemistry. Basic research with respect to radiation-induced excited species in the condensed-phase provides fundamental knowledge relevant to solar energy production and environmental remediation. This activity also contributes to DOE missions in areas of waste remediation and radiation effects associated with nuclear energy production.

Scientific Challenges:

- 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.

- 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.

Funding Summary:

	Dollars in Thousands		
	FY 2007	FY 2008	FY 2009 Request
Chemical Physics Research (Total)	33,877	34,777	52,764

These funds provide support for about 130 principal investigators along with their graduate students and postdoctoral associates. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by senior scientists and postdoctoral associates. Beginning in FY 2009, this activity assumes oversight of the CRF operational budget of approximately $7.2M per year.

Performer	Funding Percentage
DOE Laboratories	68 %
Universities	31 %
Other	1 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

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, and on 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, and to explore the molecular origins of condensed phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding. 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.