

**Research Activity:**

Division:

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Team Leader:

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**Chemical Physics Research**

Chemical Sciences, Geosciences, and Biosciences

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**Portfolio Description:**

This activity supports experimental and theoretical investigations in the gas phase, in condensed phases, and at interfaces aimed at elucidating the chemical and physical interactions that govern combustion, surface reactivity, and solute/solvent structure, reactivity, and transport. Gas-phase chemical physics 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 validated theories and computational tools for predicting chemical reaction rates for use in combustion models and experimental tools for validating these models. Combustion models using this input are developed that incorporate complex chemistry with the turbulent flow characteristic of real combustion processes. The surface, interfacial, and condensed-phase chemical physics portion of this activity is focused in two areas. The study of chemistry at well characterized surfaces and the reactions of metal and metal-oxide 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 a first-principles understanding of molecular reactivity in solution and at interfaces; often, this approach confronts the transition from molecular-scale chemistry to collective phenomena in complex systems.

**Unique Aspects:**

The Department of Energy (DOE) is the largest supporter of basic research in combustion in the federal government. This program is the principal supporter of high-temperature chemical kinetics and gas-phase chemical physics in the nation. This activity also has oversight for the Combustion Research Facility (CRF), a BES user facility for the study of combustion science and technology. In-house BES supported efforts at the CRF combine theory, modeling, and experiment including diagnostic development, chemical kinetics, and simulations of reactive, turbulent flows. Several innovative non-intrusive diagnostics are being developed to characterize gas-phase processes, including high-resolution optical spectroscopy, time-resolved Fourier transform infrared spectroscopy, picosecond laser-induced fluorescence, and photoionization mass spectrometry using tunable synchrotron radiation. Benchmark numerical simulations of turbulent combustion are conducted on Office of Science leadership class platforms and a CRF mid-range computing cluster. The CRF provides outreach and organization to the broader combustion community through activities such as the semi-annual, turbulent non-premixed flame (TNF) workshop. Interactions with the Office of Fossil Energy (FE), the Office of Energy Efficiency and Renewable Energy (EERE), and industry are enhanced at the CRF through the co-location of their applied research projects with BES-supported fundamental research.

The surface chemistry work in this activity focuses on identifying, characterizing, and manipulating individual reactive sites on surfaces or clusters of relevance to heterogeneous catalysis, providing an underpinning for work supported in the BES Catalysis and Chemical Transformations activity. The condensed phase and interfacial research on electron-driven processes and reaction dynamics in this activity is relevant to chemistry initiated by ionizing radiation that is studied within the BES Photochemistry and Radiation Research activity. Solute/solvent dynamics and transport phenomena studied in this activity are well connected to DOE mission needs in the area of waste remediation, particularly through the experimental and theoretical condensed phase chemical physics programs at Pacific Northwest National Laboratory.

The Scientific Discovery through Advanced Computing (SciDAC) thrust within the chemical physics program addresses two fundamental application software development efforts: (1) chemically reacting flows and (2) the chemistry of unstable species and large molecules. Each of these efforts is carried out by a team of related scientists working with the appropriate Integrated Software Infrastructure Centers supported under SciDAC by the Office of Advanced Scientific Computing Research within the Office of Science.

### **Relationship to Other Programs:**

Combustion research is also conducted under various research programs within EERE and FE. Linkages with this program vary in formality. In addition, combustion-related chemical physics research is 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 National Science Foundation (NSF). The AFOSR and NASA programs support research in propulsion. NASA and NIST programs investigate fire propagation. ONR and ARO research focuses on organic waste remediation. NSF supports basic research. Surface science is supported through several federal programs, both applied and basic.

### **Significant Accomplishments:**

Within the last ten years, theories and computer codes for the calculation of chemical properties and, in particular, chemical reaction rates, have achieved a high degree of accuracy and reliability for systems of a few atoms. The theoretical developments have been inspired and validated by nearly a quarter of a century of molecular beam, spectroscopy, dynamics, and kinetics research on the detailed measurement of reactions as functions of collision energy and internal energies of reactants and products. Research in the Chemical Physics program has played a prominent role in this development. Professor Y. T. Lee, one of three recipients of the 1986 Nobel Prize in Chemistry for molecular-beam chemical dynamics research, was supported by the Chemical Physics program for his entire U.S. research career. Continuing laser-based experimental research and computationally intensive theoretical work provide the fundamental basis for developing a predictive capability for chemically reacting flows.

### **Mission Relevance:**

The molecular-level studies in this activity are motivated by energy security, environmental preservation, and new opportunities fostered by a predictive understanding of chemical reactivity. Since 85 percent of nation's energy use is derived from burning fossil fuels, the gas-phase portfolio strives to acquire the fundamental information necessary to develop predictive combustion models. Such models are required for optimal design and operation of next-generation combustion and pollution-abatement devices so as to maximize energy efficiency and minimize deleterious impact on the global environment. This thrust complements the more applied combustion programs in FE and EERE. The chemical physics program supports the development of theories and computational algorithms to predict the rates of chemical reactions at temperatures characteristic of combustion. It supports the development and application of experimental techniques for characterizing gas-phase reactions in sufficient detail to develop, test, and validate predictive models of chemical reaction rates. Predicted and measured reaction rates will be used in computer models for the design of new combustion devices with maximum energy efficiency and minimum, undesired environmental consequences.

The research supported by the chemical physics program for the molecular characterization of chemical dynamics at surfaces is aimed at developing predictive theories for surface-mediated chemistry such as is encountered in industrial catalysis or environmental processes. Surface-mediated catalysis reduces the energy demands of industrial chemical processes by bypassing energy barriers to chemical reaction. Surface-mediated catalysis is used to remove pollutants from combustion emissions. At the molecular level, surface-mediated catalysis is not well understood. New catalysts are few; improvements come principally from modification of known catalytic materials. There is no body of organized knowledge such as exists for the field of organic chemistry that may be used to find new catalysts for novel or existing processes. The knowledge gained from this research program will guide in the development of a predictive capability for surface chemistry.

### **Scientific Challenges:**

- Improve and expand experimental measurement of key reaction rates of transient species at elevated temperatures.
- Develop spectroscopic probes of highly energetic, unstable molecules in complex reacting and radiating mixtures.
- 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 computations on large molecules.

- Improve 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.
- Improve the time-to-impact of fundamental insights in chemical physics on next-generation devices and processes.
- Develop and apply new experimental methods for characterizing site structure and reaction mechanisms at interfaces.
- Characterize high-energy electron- and photon-stimulated processes at environmental interfaces.
- Design quantitative models for condensed-phase solvation that include polarization and charge-transfer 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

	<u>FY 2005</u>	<u>FY 2006</u>	<u>FY 2007 Request</u>
Chemical Physics Research	32,946	31,866	37,813
Combustion Research Facility	6,437	6,251	6,805
Chemical Physics Research (Total)	39,383	38,117	44,618

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.

<u>Performer</u>	<u>Funding Percentage</u>
DOE Laboratories	72 %
Universities	27 %
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, and environmental preservation. The desired predictive capability spans the microscopic to macroscopic domains—required is the ability to compute the results of individual molecular interactions as well as their complex, collective behavior in real-world devices. Currently, an increased emphasis is on 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 emphasize 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, emphasize 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; initiate efforts that examine the reactivity of heteroatom-containing molecular building blocks of coal; and probe the chemical physics of energy transfer in large molecules, the molecular origins of condensed phase behavior, and the nature and effects of non-covalent interactions including hydrogen bonding. These molecular phenomena impact numerous DOE and national needs.