

Research Activity: Chemical Physics Research
Division: Chemical Sciences, Geosciences, and Biosciences
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Portfolio Description:

This activity supports experimental and theoretical investigations into the molecular origins of gas-phase chemistry and chemistry at surfaces. Gas-phase chemistry emphasizes the dynamics and rates of chemical reactions at energies characteristic of combustion with the aim of developing validated theories and computational tools for predicting chemical reaction rates for use in combustion models and experimental tools for validating these models. 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. Because of the relevance of gas-phase chemistry to combustion, the program manager for chemical physics is also responsible for oversight of the operation of the Combustion Research Facility.

Unique Aspects:

The Department of Energy 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 program is strongly coupled to the Combustion Research Facility (CRF), Sandia National Laboratories. The facility, through collocation of BES-, DOE Technology Office-, and industry-supported programs, is an effective force for integration of basic and applied research. The latter includes internal combustion engines, coal and biomass combustion, industrial burners for process heat, and high-temperature materials processing and manufacturing. The CRF houses the Nation's foremost fundamental research program on laser-based optical diagnostics for the measurement of chemical and fluid-mechanical parameters. Similarly, chemical physics research supported at PNNL is emerging as a premier program in the application of fundamental molecular research to the environmental management and restoration problems of the Department.

Relationship to Others:

Combustion research is also conducted under various research programs within EE and FE. Linkages with this program vary in formality. In addition, combustion-related chemical physics research is conducted by AFOSR, ONR, ARO, NASA, NIST, and 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 DOE 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:

Nearly 85% of the Nation's energy supply has its origins in combustion and this situation is likely to persist for the foreseeable future. Although an ancient technology, the complexity of combustion—the interaction of fluid dynamics with hundreds of chemical reactions involving dozens of unstable chemical intermediates—has provided an impressive challenge to predictive modeling of combustion processes. 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 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 can be used to find new catalysts for new or existing processes. The knowledge gained from this research program will guide in the development of a predictive capability for surface chemistry.

Scientific Challenges:

The calculation of the electronic structures of open shell systems such as radical reaction intermediates and excited electronic states cannot currently be done with chemical accuracy. This capability is absolutely essential for the calculation of rates of reactions of significance to combustion.

The calculation of the electronic properties of molecules with chemical accuracy scales as the seventh power of the number of electrons. Calculations for molecules with five or more atoms are beyond current and projected computational accuracy. Approximations of proven, reliable accuracy are needed.

Spectra of molecules in high energy states characteristic of combustion are extraordinarily complex and as yet do not yield useful information about the imminent chemical fate of the observed molecule.

The interaction of fluid dynamics with chemistry on the nanoscale is not sufficiently well characterized to provide parameterization of subgrid models.

Molecular dynamics experiments are extraordinarily difficult and yield large amounts of detailed state-to-state reactive and non-reactive data. How can all of these data be made useful?

No equivalent of the Woodward-Hoffmann rules, that have been as useful as predictive tools in organic chemistry, exists for surface chemistry.

Funding Summary:

	Dollars in Thousands		
	<u>FY 2003</u>	<u>FY 2004 Request</u>	<u>FY 2005 Request</u>
Chemical Physics Research	32,097	30,334	31,617
Combustion Research Facility	5,935	5,967	6,169
Chemical Physics Research Total	38,032	36,301	37,786

These funds provide support for ~130 PIs along with their graduate students and postdoctoral associates. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by experienced scientists.

<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 and surface-mediated chemical reactivity of importance to combustion and catalysis. The desired predictive capability spans the microscopic to macroscopic domains – we require the ability to compute the results of individual gas-gas and gas-surface interactions as well as their complex, collective behavior in real-world devices. Currently, we are placing an increased emphasis on theories and computational approaches for structure and dynamics of open shell systems and large molecules and on the interaction of chemistry with fluid dynamics. In surface chemistry, we continue to emphasize the development of a structural basis for gas/surface interactions, encouraging more coupled experimental and theoretical research efforts. Expanding into the future, we plan to initiate efforts on the detailed chemical physics of energy transfer in large molecules, the molecular origins of condensed phase behavior, and the nature and effects of weak interactions including hydrogen bonding. These molecular phenomena impact numerous DOE and national needs.