Gas Phase Chemical Physics Research

Portfolio Description

This program supports research on gas-phase chemical processes important in energy applications. In the past, clean and efficient use of chemical energy was the major focus, such as in combustion processes, and it continues to be a significant driver. The overall goal of this program is to understand energy flow and reaction mechanisms in complex, nonequilibrium, gas-phase environments in which the coupling of chemical and transport processes is poorly understood, such as those encountered in combustion. The program may be divided into four basic science research thrusts described below.

1. *Light-Matter Interactions*. This thrust consists of research in molecular spectroscopy and diagnostics development to probe molecular structure, dynamics and interactions in complex gas-phase systems. This research is expected to provide approaches for chemical and physical analysis of heterogeneous and dynamic gas-phase environments.
2. *Chemical Reactivity*. This thrust includes chemical kinetics and mechanisms, chemical dynamics, collisional energy transfer, and construction of, and calculations on, molecular potential energy surfaces. This research is expected to develop fundamental understanding of energy flows and chemical reactions, which is the basis for determining accurate rate constants and predictive chemical mechanisms, and to develop and validate new theoretical methods to improve accuracy of theoretical chemical kinetics.
3. *Chemistry-Transport Interactions*. This thrust consists of multidimensional, multi-scalar measurements in reacting flows and direct numerical simulation and large eddy simulation modeling of turbulent reacting flows. Research in this area is expected to lead to the development of multiplexed diagnostics that measure many variables simultaneously to overcome irreproducibility associated with turbulence and a better understanding of turbulence-chemistry interactions.
4. *Gas-Particle Interconversions*. This thrusts consists of research on the formation, growth and evaporation of small particulates and aerosols and the transition to supercritical fluids at high pressures. This research is expected to lead to the development of mechanistic models of particle formation and growth, as well as a better understanding of particle evaporation.

Scientific Challenges

Several challenges for the gas phase chemical physics (GPCP) community voiced at research meetings, workshops, and strategic planning sessions are listed below.

- Develop artificial intelligence methodologies to automate gas phase chemical physics modeling and calculations.
- Develop experimental and computational methods that can handle more complex molecules, multi-species, and multi-reaction systems.
- Understand kinetics at high pressures where collisions do not occur as isolated binary events.
- Understand the role of non-thermal kinetics, i.e., the effect of reactions occurring during the thermalization process.
- Understand the transition between gas and condensed phase including transitions from polycyclic aromatic hydrocarbons to stacked polymers and evaporation to sprays.

- Develop experimental and computational methods to characterize rare events and stochastic processes by understanding the critical roles of heterogeneity, non-ideality, and disorder.
- Understand and control the complexity of interacting chemistry and physics via revolutionary advances in models, algorithms and computing.
- Interrogate the relationship of reaction processes across time and length scales via transformative advances in imaging capabilities.

Projected Evolution

Major thrust areas supported by the Gas Phase Chemical Physics program include quantum chemistry, reactive molecular dynamics, chemical kinetics, spectroscopy, predictive combustion models, combustion diagnostics, and soot formation and growth. Currently, increased emphasis in gas-phase chemical physics is on validated theories and computational approaches investigating the effect of non-thermal initial distributions on the reactions of radicals, experimental investigations of radical-radical reactions, better insight into chemical reactions at high pressures, and improved understanding of the interaction of chemistry with fluid dynamics and stochastic in-cylinder processes.

The Gas Phase Chemical Physics program does not support research in non-reacting fluid dynamics and spray dynamics, data-sharing software development, end-use combustion device development, and characterization or optimization of end-use combustion devices.

Significant Accomplishments

Recent accomplishments in the Gas Phase Chemical Physics program include the following:

- Development of new spectroscopic techniques as well as an improved understanding and interpretation of complicated spectra has resulted in a number of significant breakthroughs including the direct observation and kinetics of important intermediates in combustion and atmospheric chemistry including the Criegee intermediate and hydroperoxy alkyl radical (QOOH), and the direct determination of isomerization transition state energy barriers.
- Direct confirmation of the role of hydrogen-abstraction and acetylene-addition processes in the soot formation mechanism was achieved by use of a hot nozzle coupled to a synchrotron (Advanced Light Source).
- Development of single shot multi-species detection was achieved via Raman scattering measurements of 12 species in a dimethyl ether flame.
- Inclusion of the prompt dissociation of HCO, prior to achieving thermal equilibrium, in chemical kinetic modeling has been shown to influence the combustion of important fuels.

Unique Aspects

The Basic Energy Sciences (BES) Gas Phase 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, enabling long-term progress in difficult scientific areas as well as effective coupling to DOE missions. This activity also has oversight for several national laboratory programs, including the Combustion Research Facility (CRF), a unique, multi-investigator research laboratory that has a strong collaborative visitor program that promotes synergy between BES-supported basic research and the applied science and technology programs supported by the Office of Energy Efficiency and Renewable Energy (EERE) and industry.

Mission Relevance

The GPCP activity contributes strongly to the DOE mission in 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 impacts. 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.

Relationship to Other Programs

Research under this activity complements research supported across BES and coordinates and leverages efforts with other agencies and facilities. Strong ties exist between the GPCP program and other programs in the BES Chemical Sciences, Geosciences, and Biosciences Division. Development of computational methods for potential energy surfaces are carried out by investigators supported by both the GPCP program and the Computational and Theoretical Chemistry program. The Condensed Phase and Interfacial Molecular Science program and the GPCP program support research in high pressure gas-liquid interfaces. The Atomic Molecular and Optical Sciences program and the GPCP program use several of the same DOE facilities and leverage experimental techniques developed in the programs. The GPCP program and DOE EERE support coordinated combustion research efforts at the CRF and at Argonne National Laboratory. The GPCP program works with several federal research agencies as an active member of the Multi-Agency Coordinating Committee on Combustion Research to host an annual Fuels Research Review.