

Condensed Phase and Interfacial Molecular Science

Portfolio Description

The Condensed Phase and Interfacial Molecular Science (CPIMS) program emphasizes basic research at the boundary of chemistry and physics, pursuing a molecular-level understanding of chemical, physical, and electron- and photon-driven processes in liquids and at interfaces. With its foundation in chemical physics, the impact of this crosscutting program on DOE missions is far-reaching, including energy utilization, catalytic and separation processes, chemical synthesis, energy storage, and subsurface chemical and transport processes. Experimental and theoretical investigations in the condensed phase and at interfaces elucidate the molecular-scale chemical and physical properties and interactions that govern chemical reactivity, solute/solvent structure and transport. Studies of reaction dynamics at well-characterized 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 understanding of molecular reactivity and dynamical processes in solution and at interfaces. Studies across scales confront the transition from molecular-scale chemistry to collective phenomena in complex systems. Fundamental studies of reactive processes driven by radiolysis in condensed phases and at interfaces provide improved understanding of radiation-driven chemistry in nuclear fuel and waste environments.

Scientific Challenges

Research in Condensed Phase and Interfacial Molecular Science is fundamental to meeting the grand challenges for basic energy sciences, as identified in the report *Directing Matter and Energy: Five Challenges for Science and the Imagination* ([report link](#)). Specific opportunities include: 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 confinement effects; develop a structural basis for understanding gas/surface interactions, encouraging site-specific studies that measure local behavior at both defined sites and transient, complex environments; and understand the molecular origins of condensed-phase behavior and the nature and effects of non-covalent interactions including hydrogen bonding and proton transport.

Projected Evolution

The program will continue to support research using new experimental and theoretical tools that push the horizon of spatial and temporal resolution needed to probe chemical behavior selectively at interfaces and in solution, enabling studies of composition, structure, bonding, and reactivity at the molecular level. The transition from molecular-scale chemistry to collective phenomena in complex systems is also of interest, including the effects of solvation on chemical structure and reactivity, in both aqueous and non-aqueous media. In this manner, the desired evolution for supported research is toward predictive capabilities that span the microscopic to mesoscale domains, enabling the computation of individual molecular interactions as well as their role in complex, collective behavior in the real world. Key targets for greater investment in the near future include a shift away from ideal, perfectly ordered interfaces toward more complex interfaces, including those created with amorphous materials; systems with novel solvents and mixed solvent systems; and experimental and computational studies that extend

molecular-level insight across a range of scales. These new directions are described further in the recent reports entitled *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science* ([report link](#)) and *From Quanta to the Continuum: Opportunities for Mesoscale Science* ([report link](#)).

The CPIMS program does not fund research in continuum fluid mechanics or fluid dynamics, applications such as the development of micro-scale devices, and research that is of principal importance to medical sciences and applications.

Significant Accomplishments

Recent accomplishments in the CPIMS program include the following:

- The pursuit of substrates needed for chemical imaging experiments has led to the first demonstration of borophene.
- Novel multidimensional coherent spectroscopy has enabled the first observation of transient excitons in metals.
- The interfacial radioactive transformation of iodine-125 to an isotope of tellurium in gold layers was demonstrated for the first time, providing a new means to study radiation-driven reactions at liquid/metal interfaces.
- Single atom alloy catalysts were demonstrated on surfaces and as nanoparticle catalysts for hydrogenation reactions, showing high carbon monoxide tolerance.
- A new technique has been invented, in which a single carbon monoxide molecule is attached to the tip of a scanning tunneling microscope, enabling the relationship of the structure and function of single molecules to be further clarified.
- A new, ultrafast mid-infrared spectrometer with unusually broad frequency span (allowing monitoring of stretches and bends simultaneously) led to the discovery of the dominant structure that results when liquid water accommodates extra protons. In a related effort, a cluster of water molecules was shown to incorporate an extra proton in the formation of an aqueous acid, with the extra proton residing on the surface of a cage structure formed by 21 water molecules.
- In a vital insight for tailoring catalytic activity for energy storage, two types of intermediates for the water oxidation reaction, arranged perpendicular and parallel to the surface, were found to be stabilized by water molecules in the electrolyte that reorganize to accommodate them.

Unique Aspects

The CPIMS activity is unique in its long-term support of fundamental chemical science in the condensed phase and at interfaces that is fully integrated with many other BES research activities, and in its integration of capabilities from research universities and DOE national laboratories and user facilities. This enables long-term progress in difficult scientific areas as well as effective coupling to DOE missions. The CPIMS activity emphasizes basic, discovery science rather than use-inspired activities.

Mission Relevance

The CPIMS activity impacts a variety of mission areas by providing a fundamental basis for understanding chemical reactivity and dynamics in transient, complex systems, such as those encountered in energy production and storage. Condensed-phase and interfacial chemical physics

research on dissolution, solvation, nucleation, separation, and reaction provides important fundamental knowledge relevant to 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.

Relationship to Other Programs

Research under this activity complements research supported across BES and coordinates and leverages efforts with other agencies and facilities. There is a strong interaction with other BES programs, including the Solar Photochemistry program (fundamental chemistry and physics of radiolytic processes in condensed media and at interfaces), the Computational and Theoretical Chemistry program (extension of computational methods to larger, more complex chemical systems in solution and at complex interfaces), the Atomic, Molecular, and Optical Sciences program (ultrafast spectroscopies in solution and at interfaces), the Geosciences program (extension of multiscale chemical dynamics imaging for complex, subsurface flows), the Catalysis program (surface chemistry and synthesis in catalysis science), and the Synthesis and Processing Science program (chemical dynamical processes in synthesis and collective effects on reactivity during nanoparticle synthesis). The interaction with BES Nanoscale Science Research Centers (in coordination with the BES Scientific User Facilities Division) is significant, including support for novel interfaces needed in chemical imaging science, studies of novel solvents and electrolytes, and examinations of catalytic water reactions at electrode interfaces. CPIMS-supported scientists include users of the Advanced Photon Source at Argonne National Laboratory, the Linac Coherent Light Source at SLAC National Accelerator Laboratory, and the Advanced Light Source at Lawrence Berkeley National Laboratory.