Heavy Element Chemistry

Portfolio Description

This activity supports basic research on the fundamental chemistry of the elements beyond actinium (those elements with an atomic number greater than 89); typically uranium, neptunium, plutonium, americium, and curium. The goal of this activity is to understand the underlying chemical and physical principles that determine the behavior of the actinides and transactinides elements. The unique molecular bonding of the heavy elements is explored using theory and experiment to elucidate electronic and molecular structure as well as reaction thermodynamics. Emphasis is placed on resolving the *f*-electron challenge; the chemical and physical properties of these elements to determine solution, interfacial, and solid-state bonding and reactivity; fundamental transactinide chemical properties; and the fundamental science underpinning the extraction and separation of the actinides. While the majority of the research supported by this activity is experimental, theoretical proposals are considered such as more adequately describing quantum-mechanically spin-orbit interactions and relativistic effects, which integrate closely with existing experimental research. Synthetic research is pursued within this this activity on molecules that contain heavy elements and on ligand development to separate and sequester heavy elements. Spectroscopic research on the chemical bonding and reactivity of all manner of energy-relevant molecules is also pursued within this activity. Capital equipment funding is provided for items such as instruments used to characterize actinide materials and equipment to handle the actinides safely in laboratories and at user facilities.

Unique Aspects

This activity represents the only Federal, non-applied research program focused primarily on the chemistry of the actinide elements. All of the research sponsored through this activity is peer-reviewed and unclassified. Federal support of heavy element chemistry began with the Manhattan Project as the elements beyond uranium were unknown before then. Since then, this activity has been continuously supported in some manifestation throughout the Atomic Energy Commission years up to the present-day Department of Energy due to its importance to energy and defense. The long term support of this activity to researchers investigating the fundamental properties of the actinides has been crucial to maintain U.S.-based leadership in this critical field. Actinide researchers are supported through other Federal programs (such as the NSF and DOD), but aside from this activity, there is no program that identifies fundamental heavy element chemistry as a research thrust.

Relationship to Other Programs

- Improved knowledge of the fundamental properties of the heavy elements has a direct positive impact on many other Department of Energy missions, including but not limited to advanced nuclear energy, nuclear proliferation detection, defense program stewardship, and environmental remediation.
- This activity uniquely supports unclassified basic research on all the actinide and transactinide elements, while the more applied programs (nuclear energy, environmental, nuclear forensics, stockpile stewardship) limit their investigations to the chemical and material properties of specific elements and systems of strategic programmatic interest.

- This activity is closely coordinated with the BES Separations and Analysis activity, and is highly synergistic with the Catalysis program and Computational and Theoretical Chemistry program, as well as the Subsurface Biogeochemical Research program in the Office of Biological and Environmental Research and to nuclear fuel cycle research funded through the Office of Nuclear Energy.
- This activity sponsors research that is performed at many BES User Facilities; typically the Advanced Light Source (ALS), the Stanford Synchrotron Radiation Lightsource (SSRL), and the Advanced Photon Source (APS). Computational research is also supported that makes use of ASCR User Facilities.
- Related actinide nonproliferation research is pursued within the Office of Nonproliferation R&D of the National Nuclear Security Administration, the Basic Research program of the Defense Threat Reduction Agency, and at the National Technical Nuclear Forensics Center at the Department of Homeland Security.
- Based on programmatic priorities, this activity program does not fund research on: the processes affecting the transport of subsurface contaminants, the form and mobility of contaminants including wasteforms, projects aimed at optimization of materials properties including radiation damage, device fabrication, or biological systems, which are all more appropriately supported through other Department of Energy programs.

Significant Accomplishments
Early goals of this activity were to discover new elements and to determine their chemical and physical properties from microscale and tracer experiments, similar to the techniques that must still be used for the heaviest of elements due to their low-production rate. For the elements heavier than einsteinium in the periodic table, tracer techniques and one-atom-at-a-time chemistry have been developed and carried out to determine chemical properties. Organometallic chemistry has been enriched by discovery of many unique organoactinide compounds. Continual progress has been made on elucidating the novel and unique chemistry of the elements directly relevant to energy-production (the major actinides).

Recent accomplishments in the program include:
- Interpretations of spectroscopic results have provided thermodynamic quantities such as oxidation-reduction potentials and enthalpies of reactions.
- Molecular-level information on the geometry and energetics of bonding can now be obtained at synchrotron light sources and from multi-photon laser excitation studies. These tools enable studies of actinides in the gas phase, as clusters, and at interfaces between solutions and surfaces of minerals and colloids in solution.
- Measurements show the light actinide metals have delocalized 5f orbitals and resemble d-orbital transition metals, whereas the 5f electrons become localized at americium (halfway down the actinide series), resembling the rare-earth elements; although recent studies have shown divergent properties that indicate this largely uninvestigated field of chemistry is not a straightforward extrapolation from lighter actinide to heavier.
- The nuclear magnetic resonance of plutonium-239 has finally been measured, which could be the beginnings of the brand-new, fruitful field of plutonium NMR research.
- The exceptional computational challenge imposed by so many electrons and relativistic electron energies has spurred the development of innovative theoretical treatments.

Mission Relevance
This activity is broadly mission relevant to the Department of Energy and represents the nation's only program focused uniquely on the fundamental research on the elements beyond actinium. Knowledge of the chemical characteristics of the heavy elements under realistic conditions provides a basis for advanced fission fuel cycles. Fundamental understanding of the chemistry of these long-lived radioactive species is required to accurately predict and mitigate their transport and fate in the environment. Knowledge of the physical properties of defense-relevant elements is required to develop technologies to counter proliferation of weapon-useable nuclear material. Better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces is motivated by improving the separations processes that are essential for improved nuclear fuel cycles.

Scientific Challenges
The role of 5f electrons in bond formation remains the fundamental topic in actinide chemistry and is the central focus for this program. Resolving the role of the f-electrons is one of the three grand challenges identified in *Basic Research Needs for Advanced Nuclear Energy Systems* report of the Basic Energy Sciences Workshop (2006) and echoed in the report from the Basic Energy Sciences Advisory Committee: Science for Energy Technology: Strengthening the Link between Basic Research and Industry (August 2010). The 5f orbitals participate in the band structure of metallic and ceramic materials that contain the light actinides. Theory and experiment show that 5f orbitals participate significantly in molecular actinide compounds, for example, compounds required for advanced nuclear energy systems. The majority of this activity is pursued at the national laboratories or coordinated directly with them because of the infrastructure needed to handle these materials safely. Research in heavy element chemistry at universities through single-investigator grants is supported, encouraging collaborations between university and laboratory projects. Sophisticated quantum mechanical calculations that treat spin-orbit interactions accurately need further development so that they can predict the properties of molecules that contain actinides and predict the migration of radioactive species. Experimental validation of the theoretical properties of models will be the key to understanding the role of the 5f electrons.

Projected Evolution
Support of research to understand the chemical bonding of elements that have 5f electrons leads to fundamental understanding of separations processes and to the design and synthesis of preorganized chelating agents for the separations of particular actinide ions. Research in bonding, reactivity, and spectroscopic properties of molecules that contain heavy elements and of actinides in environmentally-relevant species aids the development of ligands to sequester actinides in the environment and to remove toxic metals from the human body. Better characterization and modeling of the interactions of actinides at liquid-solid and liquid-liquid interfaces, including mineral surfaces under environmentally relevant conditions, improve separations processes that are essential for advanced nuclear fuel cycles. At the frontier of the periodic table, theoretical chemists predict the properties of actinides and transactinides using modern calculation tools. Sophisticated quantum mechanical calculation techniques that take into account both spin-orbit and relativistic effects of actinide compounds and actinide species in environmental media are being developed.