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

The activity supports fundamental molecular level research on interactions of radiation with matter in the condensed phase.

The photochemistry research effort emphasizes fundamental processes aimed at the capture and conversion of solar energy. Biomimetic models (photochemical and photoelectrochemical) seek to mimic the key aspects of photosynthesis – antenna, reaction center, catalytic cycles, and product separation. The research encompasses organic and inorganic photochemistry, photoinduced electron and energy transfer, photoelectrochemistry, biophysical aspects of photosynthesis, and molecular assemblies for artificial photosynthesis.

The radiation sciences effort supports fundamental studies on chemical effects produced by the absorption of energy from ionizing radiation. The radiation chemistry research encompasses heavy ion radiolysis, models for track structure and radiation damage, characterization of reactive intermediates, radiation yields, and radiation-induced chemistry at interfaces. Accelerator-based electron pulse radiolysis methods are employed in studies of highly reactive transient intermediates, and kinetics and mechanisms of chemical reactions in the liquid phase and at liquid/solid interfaces.

Unique Aspects:

This activity is the dominant supporter (85%) of solar photochemistry in the U.S. and the sole supporter of radiation chemistry. Specialized electron pulse radiolysis facilities at Notre Dame, ANL, and BNL serve the academic research community, industrial users, and other national laboratories. A new laser-driven electron accelerator at BNL features a 7 picosecond pulse width and the capability for synchronized electron pulse-laser pump-laser probe experiments.

Relationship to Others:

The solar photochemistry research effort interfaces with activities in BES, including: Energy Biosciences activities in biochemical aspects of photosynthesis; Chemical Physics in theoretical calculations of excited states and computational modeling; Catalysis and Chemical Transformations on electron transfer reactions in homogeneous and microheterogeneous solutions, and advanced catalytic materials; and Materials Sciences fundamental photovoltaics research. The research is relevant to EE activities in the Office of Solar Energy Technologies on photovoltaics, and in the Office of Hydrogen and Superconductivity Technologies on hydrogen production.

The radiation sciences activity interfaces in BES with Catalysis and Chemical Transformations in reaction kinetics in homogeneous solutions, and Materials Sciences in radiolytic damage to glasses and radiation-induced corrosion of structural materials. There are also important

interfaces with EM activities in waste remediation and NE activities on nuclear reactors, and nuclear processing and storage. Radiolytic processes in solution, particularly heavy ion radiolysis, are of interest to the NIH regarding radiation damage to biological systems in medical diagnosis and therapy.

Significant Accomplishments:

Stratospheric ozone depletion by chlorofluorocarbons was predicted by F. Sherwood Rowland of UC, Irvine, in 1974. Professor Rowland's research, solely supported by this activity, involved the chemistry of "hot" chlorine atoms produced by nuclear recoil and complementary photolytic reactions. Rowland was awarded the Nobel Prize in 1995. Radiotracers for nuclear medicine were pioneered by Alfred Wolf at BNL. The "special pair" model for electron donor chlorophyll molecules in photosynthesis was introduced by Joseph Katz and James Norris of ANL. Photosynthetic molecular models for light to chemical energy conversion were developed by Michael Wasielewski of ANL and by Professors Gust, Moore, and Moore of Arizona State University. The "inverted region" in Marcus electron transfer theory was verified in pulse radiolysis experiments by John Miller at ANL.

Mission Relevance:

Solar photochemical energy conversion is a long-range option for meeting the world's future energy needs. An alternative to solid-state semiconductor photovoltaic cells, the attraction of solar photochemical and photoelectrochemical conversion is that fuels, chemicals, and electricity may be produced with minimal environmental pollution and with closed renewable energy cycles. A strong interface with EE solar conversion programs exists at NREL, involving shared research, analytical and fabrication facilities, and a jointly shared project on dye-sensitized solar cells.

Radiation chemistry methods are of importance in solving problems in environmental waste management and remediation, nuclear energy production, and medical diagnosis and radiation therapy. Fundamental studies on radiation-induced processes complement collocated NERI and EMSP projects.

Scientific Challenges:

In solar photoconversion, knowledge gained in charge separation and long-distance electron transfer needs to be applied in a meaningful way to activation of small molecules (CO_2, N_2, and H_2O) via photocatalytic cycles. The major scientific challenge for photoelectrochemical energy conversion is that small band gap semiconductors capable of absorbing solar photons are susceptible to oxidative degradation, whereas wide band gap semiconductors, which are resistant to oxidative degradation in aqueous media, absorb too little of the solar spectrum. Ongoing research activities include multibandgap, multilayer cascade-type semiconductors, photosensitized nanoparticles, and surface coatings that protect against photocorrosion. Experimental and theoretical studies on photosynthetic pigment-protein antenna complexes should lead to advances in design of efficient and robust artificial light-collecting molecular assemblies. Computational chemistry methods incorporating recent advances in calculation of excited states should be developed and applied in design of photocatalysts and molecular dynamics simulations in artificial photosynthesis. Fundamental studies on photochemical

reaction pathways offer opportunities for less energy intensive and more environmentally benign processing of specialty chemicals and high volume industrial intermediates.

A recent workshop "Research Needs and Opportunities in Radiation Chemistry" has identified new directions, connections, and impacts of radiation chemistry. A common theme is the need to explore radiolytic processes that occur across solid-liquid and solid-gas interfaces, where surface chemistry can be activated and changed by radiolysis. Solid-liquid interfaces abound in nuclear reactors and high level radioactive wastes. Colloidal particles participate in gas production, gas retention, and in organic degradation of high level wastes. In regard to environmental remediation, radiation chemistry is one of the most promising advanced oxidation processes for degradation of organic pollutants. A more fundamental understanding of radiolytic reactions in heterogeneous media is needed in order to predict and control radiation chemical transformations in complex environmental systems. A proposed subpicosecond electron accelerator at ANL would enable investigation of the primary events in radiation chemistry, now virtually unknown except for theoretical models, wherein fundamental processes link physics to the chemistry of radiolysis.

Funding Summary:

Dollars in Thousands

FY 2003	FY 2004	FY 2005 Request
24,853	28,502	29,477

Performer	Funding Percentage
DOE Laboratories	67 %
Universities	33 %

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The program provides funding for 49 university grants supporting about 46 graduate students, 51 postdoctoral research associates, and partially supporting about 56 faculty. There are nine programs at DOE laboratories supporting 45 senior staff and 46 graduate students and postdocs. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by experienced scientists. In photochemistry, major research groups are supported in inorganic photochemistry and electron transfer at BNL; in photoelectrochemistry at NREL and NDRL; and in photosynthesis at Ames, ANL, and LBNL. Many of the research efforts at the DOE laboratories involve strong collaborative interfaces with university and industrial communities. The radiation chemistry effort is centered at specialized electron pulse radiolysis facilities at Notre Dame, ANL, and BNL. The Notre Dame Radiation Laboratory serves as the primary radiation research user facility, hosting approximately 40 users/year from academia and industry.

Projected Evolution:
In solar photochemistry, an increased emphasis on solar water splitting will explore new semiconductor, molecular, and hybrid systems for photoconversion. Modern combinatorial techniques will broaden and accelerate the search for new semiconductor and molecular structures. Novel quantum size structures, such as hybrid semiconductor/carbon nanotube assemblies, fullerene-based linear and branched molecular arrays, and semiconductor/metal nanocomposites, will be examined that will allow for more complete utilization of the solar energy spectrum. Unresolved basic science issues in photocatalysis will be explored in coupling photoinduced charge separation to multielectron, energetically uphill redox reactions. Photoconversion systems will be investigated that are based on organic semiconductors and conducting polymers, which are inexpensive and easy to manufacture. An enhanced theory and modeling effort is needed for rational design of artificial solar conversion systems. Of particular interest is the calculation of factors controlling photoinduced long-range electron transfer, charge injection at the semiconductor/electrolyte interface, and photoconversion in biomimetic assemblies for solar photocatalytic water splitting.

Electron pulse radiolysis methods will investigate reaction dynamics, structure, and energetics of short-lived transient intermediates in the condensed phase. Radical ion excited states will be studied in novel synchronized electron pulse-laser pump-laser probe experiments. Fundamental studies on reactivity of nitrogen oxides in aqueous solution are pertinent to understanding radiolytic degradation of nuclear tank waste. Studies of solvent effects on free radical reaction rates in supercritical fluids are relevant to next-generation supercritical water-cooled nuclear power plants. Subpicosecond electron pulse radiolysis is being developed at ANL based on a table top terawatt laser system. Electron pulses are produced by focusing terawatt laser pulses into a supersonic helium gas jet. The approach is different from the laser-driven photocathode method employed at pulse radiolysis facilities at BNL, Osaka, and Paris; where the time resolution is 7 ps, 0.2 ps, and 2 ps, respectively. Electron pulse radiolysis studies on the previously unexplored femtosecond time scale are proposed on solvation and thermalization of electrons in water; the dynamics of solvation and prethermalized species; solvation in confined media such as mesoporous silica and micelles; and charge injection into metal oxides. In the more distant future, the ability with the terawatt ultrafast high field facility to generate simultaneously subpicosecond electrons and x-rays will be exploited for detection of structural changes upon electron injection.