

**Research Activity:** **Photochemistry and Radiation Research**  
Division: Chemical Sciences, Geosciences, and Biosciences  
Primary Contact: Mary E. Gress ([mary.gress@science.doe.gov](mailto:mary.gress@science.doe.gov); 301-903-5827)  
Team Leader: Eric A. Rohlfing  
Division Director: Eric A. Rohlfing (Acting)

### **Portfolio Description:**

This activity supports photochemical studies relevant to capture and conversion of solar energy, and fundamental studies in radiation chemistry. The solar photochemistry research encompasses physical chemical aspects of natural photosynthesis, charge separation by donor-acceptor models and nanoscale inorganic/organic assemblies, photocatalytic fuel-forming reactions, photoelectrolysis of water for solar hydrogen production, and photoelectrochemistry. Bioinspired photosynthetic models seek to mimic the key aspects of photosynthesis: the antenna, reaction center, catalytic cycles, and product separation. Research in radiation chemistry investigates fundamental chemical effects produced by the absorption of energy from ionizing radiation. Highly reactive transient intermediates, and the kinetics and mechanisms of their chemical reactions, are explored in the liquid phase and at liquid/solid interfaces. Research is supported on heavy ion radiolysis, models for track structure and radiation damage, free radical reactions in supercritical fluids, and radiolytic reactions in ionic liquids. Specialized accelerator facilities for electron pulse radiolysis are supported at Argonne National Laboratory (ANL), Brookhaven National Laboratory (BNL), and the Notre Dame Radiation Laboratory. A novel Terawatt Ultrafast High Field Facility under development at ANL will offer capability for ultrafast electron-pulse radiolysis.

Solar photochemical energy conversion is an important long-range option for meeting future energy needs. Increasing worldwide demands for energy will need to be met with technologies such as solar photoconversion that do not produce greenhouse gases. An attractive alternative to semiconductor photovoltaic cells, solar photochemical and photoelectrochemical conversion processes produce fuels, chemicals, and electricity with minimal environmental impact and with closed renewable energy cycles. Artificial photosynthesis can be coupled to chemical reactions for generation of fuels such as hydrogen, methane, or complex hydrocarbons. The work in this activity is complementary to and coordinated with studies of natural photosynthesis within the BES activity Molecular Mechanisms of Natural Solar Conversion. A strong interface with the Office of Energy Efficiency and Renewable Energy (EERE) solar energy technology programs exists at the National Renewable Energy Laboratory (NREL), involving shared research, analytical, and fabrication facilities. Fundamental studies of radiation chemistry are of importance in understanding chemical reactions that occur in radiation fields of nuclear reactors, including in their fuel and coolants, and in the processing, storage, and remediation of nuclear waste. Such understanding is required for effective nuclear waste remediation and for design of next-generation nuclear reactors that might employ special media, such as supercritical fluids as coolants. The radiation chemistry of ionic liquids is relevant to their use as fuel-cycle separation solvents. The fundamental research in this activity coordinates with that performed in the BES Chemical Physics activity and is relevant to the Office of Nuclear Energy, Science and Technology (NE). Radiation-induced chemistry is also of importance in biological damage from nuclear weapons, from natural radiation sources, and in therapeutic uses of radiation.

### **Unique Aspects:**

This activity is the dominant supporter (85%) of solar photochemistry in the United States 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 Department of Energy (DOE) national laboratories. A laser-driven electron accelerator at BNL features a 10 picosecond pulse width and the capability for synchronized electron pulse-laser pump-laser probe experiments.

### **Relationship to Other Programs:**

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

The radiation sciences activity interfaces in BES with Catalysis and Chemical Transformations in reaction kinetics in homogeneous solutions and Mechanical Behavior of Materials and Radiation Effects in radiolytic damage to glasses and radiation-induced corrosion of structural materials. There are also important interfaces with NE activities on nuclear reactors, and nuclear waste processing and storage. Radiolytic processes in solution, particularly heavy ion radiolysis, are of interest to the National Institutes of Health (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 EERE solar conversion programs exists at NREL, involving shared research, analytical and fabrication facilities.

Radiation chemistry methods are of importance in solving problems in environmental waste management and remediation, nuclear energy production, and medical diagnosis and radiation therapy.

### **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 ( $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ ) 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" 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 subpicosecond electron accelerator under development at ANL will 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

<u>FY 2005</u>	<u>FY 2006</u>	<u>FY 2007 Request</u>
30,446	25,489	32,007
<u>Performer</u>	<u>Funding Percentage</u>	
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 53 university grants supporting about 53 graduate students, 50 postdoctoral research associates, and partially supporting about 59 faculty. There are nine programs at DOE national laboratories supporting 45 senior staff and 46 graduate students and postdoctoral research associates. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by senior scientists and postdoctoral associates. In photochemistry, major research groups are supported in inorganic photochemistry and electron transfer at BNL; in photoelectrochemistry at NREL, Notre Dame, and Pacific Northwest National Laboratory (PNNL); and in photosynthesis at ANL and Lawrence Berkeley National Laboratory (LBNL). Many of the research efforts at the national 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 use 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.