

# Research Needs and Opportunities In Radiation Chemistry Workshop

April 19-22, 1998 • Indian Oaks Conference Center • Chesterton, Indiana

## Final Report



Sponsored by the  
U.S. Department of Energy  
Office of Basic Energy Sciences  
Division of Chemical Sciences

### Front Cover Caption

The figure on the front cover illustrates "dynamic control" of electron transfer rates at short distances. The graph compares existing rates with two theoretical ideas: 1) nonadiabatic theoretical predictions that rates will continue to increase as electronic coupling increases, and 2) dynamical theoretical predictions that rates will be limited by solvent motions. Proposed experiments would measure rates in the region in which the theories differ. (John R. Miller, Argonne National Laboratory)

# **Research Needs and Opportunities In Radiation Chemistry**

## **Final Report**

**of the workshop held  
April 19-22, 1998**

**in**

**Chesterton, Indiana**

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U.S. Department of Energy  
Office of Science  
Office of Basic Energy Sciences  
Division of Chemical Sciences  
Germantown, MD 20874**



## FOREWORD

The U.S. Department of Energy (DOE) Office of Basic Energy Sciences sponsored a workshop on Research Needs and Opportunities in Radiation Chemistry on April 19-22, 1998, to examine new directions, connections, and impacts of radiation chemistry in the context of forefront basic research. The specific goals of the workshop were to explore and document (1) new, exciting frontiers in radiation chemistry, (2) how research activities in the field relate to other scientific undertakings and disciplines, and (3) the ways in which radiation chemistry relates to applications and underpins the development of future energy technologies.

The participants included over 100 chemists, physicists, and engineers from national laboratories, universities, and colleges in the U.S. and abroad. Many of the participants were from the three DOE national laboratories with specialized experimental facilities for radiolytic studies, namely Argonne National Laboratory, Brookhaven National Laboratory, and the Notre Dame Radiation Laboratory.

The workshop included five panels focussed on the following topics:

- A. Fundamental Studies on Effects of Ionizing Radiation: Primary Processes
- B. Instrumentation
- C. Nuclear Energy Production and Environmental Waste Management
- D. Solution Kinetics and Catalytic Processes
- E. Environmental Remediation

An Executive Summary of the panel reports is found in the following section. Detailed reports from the panels can be found in later sections of this report. Appendix I is a list of the workshop participants with addresses and affiliations. Finally, the program for the workshop including a list of the formal lectures and discussion groups is found in Appendix II.

Paul F. Barbara, Chair

## EXECUTIVE SUMMARY

There is a growing urgency for forefront basic research on *ionizing radiation-induced chemical reactions*, due to the relevance of these reactions in such areas of critical national need as environmental waste management, environmental remediation, nuclear energy production, and medical diagnosis and radiation therapy. Fortunately, the emergence of new theoretical and experimental tools for the study of radiation-induced chemical and physical processes, i.e. Radiation Chemistry, makes future progress quite promising. Nevertheless, a recent decline in the number of young investigators in radiation chemistry, as well as a natural obsolescence of large research facilities in radiation chemistry are serious obstacles to further progress.

Understanding radiation-induced processes is of vital significance in such diverse fields as waste remediation in environmental cleanup, radiation processing of polymers and food, medical diagnosis and therapy, catalysis of chemical reactions, environmentally benign synthesis, and nuclear energy production. Radiation chemistry provides for these fields *fundamental quantitative data*, such as reaction rate coefficients, diffusion coefficients, radiation chemical yields, etc. As well as providing useful quantitative information of technological and medical importance, radiation chemistry is also a valuable tool for solving fundamental problems in chemistry and in material sciences. Exploiting the many facets of radiation chemistry requires a thorough and comprehensive understanding of the underlying chemical and physical processes. An understanding of the structure and dynamics of “tracks” produced by ionizing radiation is a central issue in the field. There is a continuing need to study the ultrafast processes that link the chemistry and physics of radiation-induced phenomena. This is especially true for practically important, but less well understood, nonstandard environments such as interfacial systems, supercritical media, and heterogeneous systems. These various goals necessitate the development and application of complementary programs of experiment and theory, and will involve the use of nonconventional radiation sources and the study of novel *homogeneous* and *heterogeneous* chemical systems. There is also a need to upgrade other types of instrumentation used in radiation chemistry in the national laboratories, including high field electron paramagnetic resonance, and modern analytical tools. The development and enhancement of these various tools will allow for a much wider use of the national radiation chemistry facilities.

*Instrumentation and Facilities.* There is a continuing need for enhanced experimental capabilities for pulse radiolysis, the central tool in radiation chemistry. There is a particular need to develop national facilities with shorter time resolution in order to directly monitor the complex chemical and physical processes that are induced by ionizing radiation. In the near term this will involve state-of-the-art subpicosecond photocathode based linear electron accelerators, which allow for synchronization of the electron pulse and a femtosecond light pulse. A benefit of laser synchronization is that it allows for powerful, novel, laser based methods for detection of transient species via uv-vis, infrared, Raman, and coherent spectroscopies. In the long term, radiation chemistry will also undoubtedly be advanced by novel sources for radiolysis such as table top laser generation of electron beams, X-rays, etc., as well as novel and ultrasensitive detection schemes such as X-ray absorption and Coulomb explosion. Additionally, the use of synchrotron radiation and free electron lasers in radiation chemistry should be further explored.

*Heterogeneous Systems.* A more fundamental understanding of radiolytic reactions in heterogeneous systems is necessary in order to establish the resultant chemistry and predict the ways with which we can control chemical transformation in complex chemical systems. The radiation chemistry of heterogeneous systems is complex and underdeveloped at a time when incisive and fruitful studies are needed to underpin emerging technologies. For example, Advanced Oxidation Processes using radiation chemistry is a promising strategy for environmental remediation, but we currently lack the ability to predict and control the radiation chemical processes in complex, typically heterogeneous environmental systems. It is important that we understand how the radiation source, intensity, and energy determine reaction rates, mechanisms, and product distribution in heterogeneous systems and address the issue of radiation catalytic effects induced by metal oxide supports. Understanding the basic mechanisms of advanced oxidation processes will allow optimization of the technological processes with respect to versatility and commercial competitiveness. The issues involved here are (1) establishing the mechanisms of free radical reactions such as those applicable to remediation processes and (2) improving the overall efficiency of remediation by controlling the reactivity and the generation of free radicals. It is also necessary to elucidate the roles of secondary radicals generated in competition with the primary oxidation of target contaminants. Many of the same issues arise in the study of effects of radiation in the operation of nuclear reactors, the separation processes of spent nuclear fuel, nuclear wastes in temporary storage, and the waste forms considered for permanent storage.

There are other scientific opportunities for applying radiation chemistry in heterogeneous environments. Microporous and mesoporous oxides in which radiation chemistry can be used to introduce and study metal ions in new valence states, organic radical intermediates, and chemical defect sites are of interest. Such studies are needed to optimize the catalytic properties of these channel- and cage-containing materials already of great significance in industrial heterogeneous catalysis. Additional opportunities include nanoparticles, which can be synthesized and studied by radiation chemistry methods to exploit large band gap semiconductors, and the preparation and development of films and ordered arrays of metals and semiconductors as catalysts. A molecular level understanding of reactive species at surfaces is key in catalysis and the growth and processing of semiconductor structures.

*Homogeneous Systems.* Radiation chemistry studies in homogeneous systems will continue to be one of the most active areas of research in the field. For example, pulse radiolysis provides a uniquely powerful probe of systems of emerging interest: novel, tailored, multifunctional, supramolecular structures; shape and size selective homogeneous catalysts; catalysts for reduction of carbon dioxide; and for oxygen and hydrogen transfer. Radiation chemistry will be invaluable in preparing and characterizing new electronically excited states and in the development of new synthetic organic strategies for free-radical and carbocation-based organic synthesis. There are critical needs for radiation chemical data in a wider range of media such as organic solvents and supercritical fluids, for development and maintenance of databases for kinetic and thermodynamic data, and for enhanced opportunities for university utilization of DOE National Laboratory-based radiation chemical facilities. There is a need for studies which characterize supercritical fluid solvent environments and correlate this characterization with observed reaction dynamics and transport of solute species. Radiation chemistry can provide a

unique tool for the study of such supercritical fluid solvent effects in electron transfer, redox, and free radical reactions.

*Electron Transfer Processes.* Radiation chemistry studies, particularly with ultrafast synchronized accelerator/femtosecond laser sources, are vital to a molecular level understanding of electron transfer in homogeneous and heterogeneous systems. Special opportunities include: very fast electron transfer to test theory for adiabatic reactions; electron transfer in supercritical fluids and other novel media at the extremes of temperature, pressure, and pH; electron transfer involving high energy intermediates, synthetic peptides, and biomolecules; exploitation of the interplay of theory and experiment and the rapid advances in computational power to model electron and nuclear energetics and dynamics.

*Research Funding in Radiation Chemistry.* Due to funding limitations there have been relatively few new investigators in the field of radiation chemistry such that the number of active researchers is beginning to decrease. This is a serious obstacle to the future success in this field. Increased funding in the areas of postdoctoral fellowships, academic research, and joint ventures between universities and national laboratories is essential for meeting the challenges of the future.

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## **Panel A: Fundamental Studies on Effects of Ionizing Radiation: Primary Processes**

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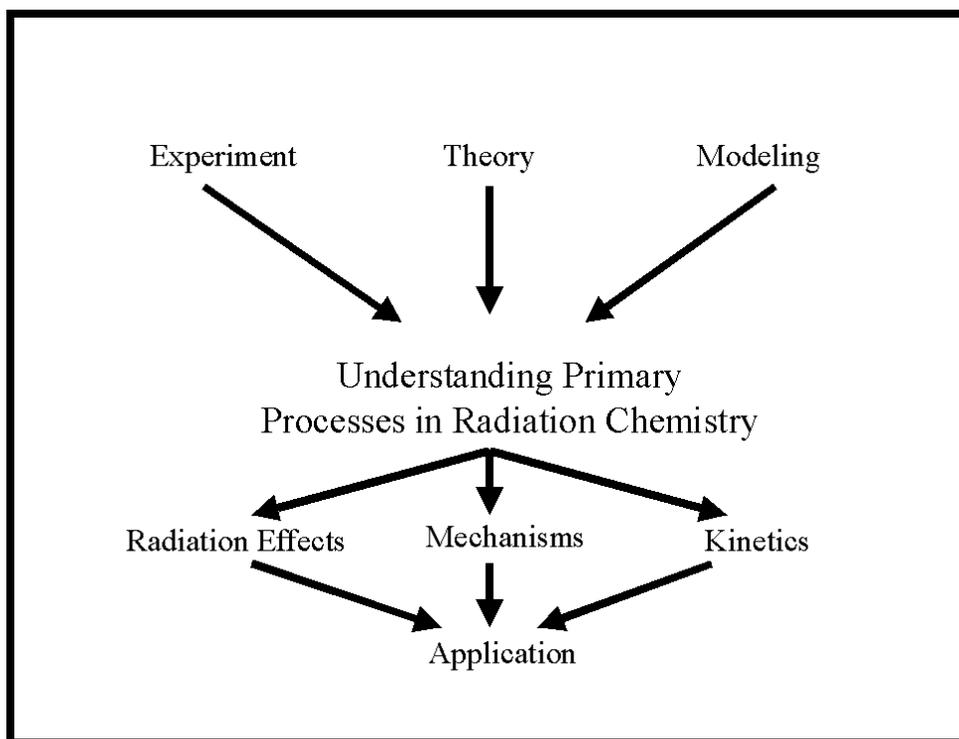
## **I. Summary**

Understanding radiation-induced processes is of significance in such diverse fields as waste remediation and environmental cleanup, radiation processing, and medical diagnosis and therapy. To help elucidate the vagaries of these complex systems, radiation chemistry can provide:

- fundamental quantitative data, such as reaction rate coefficients, diffusion coefficients, radiation chemical yields, etc.
- details about the chemical effects of high Linear Energy Transfer (LET) radiations, such as heavy charged particles, X-rays and low energy electrons
- information on radiation-induced damage to new and/or technologically significant materials like polymers and plastics (hydrocarbons).

As well as providing useful quantitative information of technological and medical importance, radiation chemistry is a valuable tool for solving fundamental problems in chemical and in material sciences. The significance of fundamental studies in radiation chemistry is portrayed in Figure 1. With recent experimental and theoretical advances, it is now feasible to study:

- the fundamental processes that link chemistry with the early time events of physics
- the chemistry and physics at interfaces
- the details of transient chemistry in nonstandard systems like supercritical fluids.



**Figure 1.** The central role of fundamental studies in radiation chemistry.

Exploiting the many facets of radiation chemistry requires a thorough and comprehensive understanding of the underlying chemical and physical processes. Therefore it is necessary to elucidate:

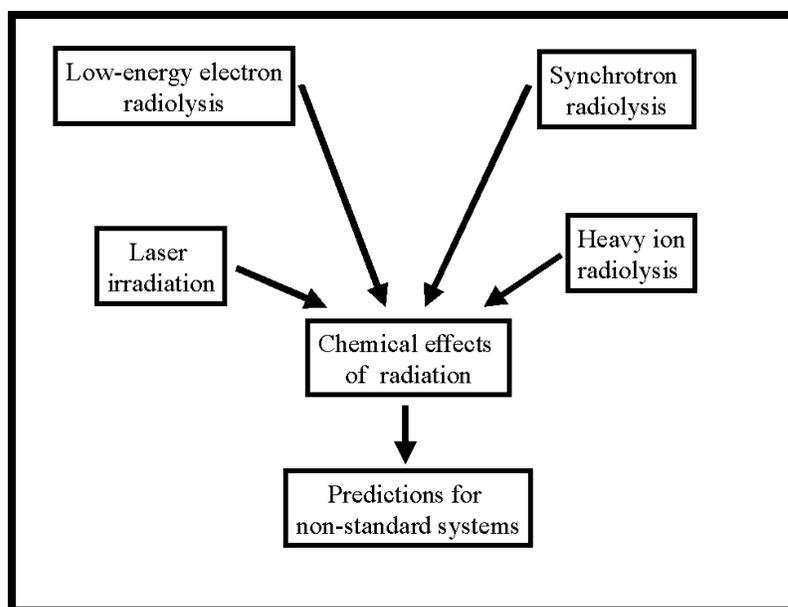
- the structure of the tracks produced by ionizing radiation in condensed matter
- how these tracks evolve in time
- the effects of the track structure and its evolution on radiation-induced damage (chemistry, materials defects, biology, etc.).

It is also important to determine how, when, where, and why radiolysis in the liquid phase differs from or is similar to that in the gaseous and solid phases.

Achieving these goals will necessitate the development and application of complementary programs of experiment and theory, and will involve the use of nonconventional radiation sources and the study of novel homogeneous and heterogeneous chemical systems.

## II. Chemical Effects of Radiation

There is a considerable database of experimental information describing the effects of radiation on a variety of liquids, for example see the Worldwide Web site <http://www.rcdc.nd.edu> of the Radiation Chemistry Data Center. However, there are serious shortcomings in these data. If a complete understanding of radiation damage is to be developed, a variety of complementary experimental and theoretical programs will be necessary. The relevant experimental approaches are shown in Figure 2.



**Figure 2.** Techniques for understanding the chemical effects of radiation.

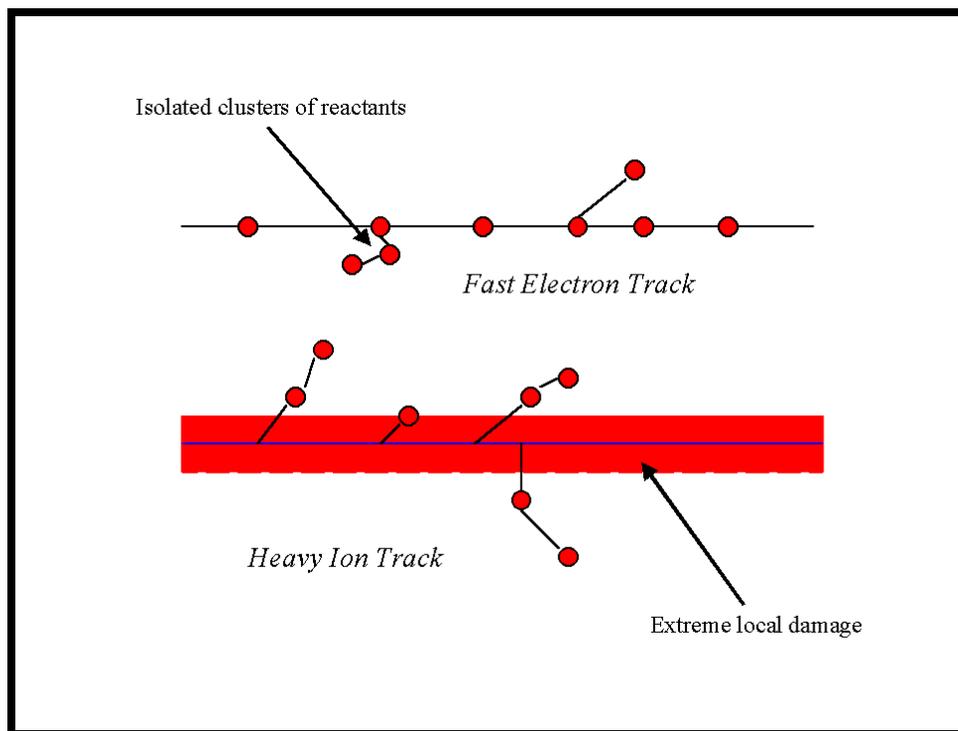
The chemical effects of radiation are largely determined by the track of the radiation particle (H. G. Paretzke, "Radiation Track Structure Theory," in *Kinetics of Nonhomogeneous Processes. A Practical Introduction for Chemists, Biologists, Physicists, and Materials Scientists*, ed. G. R. Freeman, New York: Wiley-Interscience, 1987). Thus an important component in understanding radiation-induced chemistry in complex systems is a detailed, accurate description of how radiation quality and type affects the observed damage.

### A. High LET Radiolysis

High Linear Energy Transfer (LET) radiations create extreme conditions. The rate of energy loss is fast and consequently the local density of radiation-induced reactants is high. These properties result in very different chemistry from that observed in high-energy electron

radiolysis (R.H. Schuler, J.A. LaVerne, "Current Status of Radiation Chemical Studies with Heavy Ions," Proc. Advisory Group Meeting, International Atomic Energy Agency, Bologna, Italy, 1988). This is illustrated in Figure 3. A variety of different nonconventional radiation sources offers opportunities to address problems associated with high LET radiolysis that are not accessible by other means, as follows.

*Heavy Charged Ions.* Radiolysis due to highly charged particles, such as  $H^+$ ,  $He^{2+}$ ,  $C^{6+}$ ,  $Fe^{n+}$ ,  $Kr^{n+}$ , and  $Xe^{n+}$ , is important in many fields of interest to DOE. Problems range from describing chemistry in reactors, to transuranic waste storage and handling, to health physics, to the health effects of radon, to space research, etc. Fundamental studies to determine the chemical effects of track structure will produce a database of knowledge useful for developing track models that can then be used to explain the heavy ion radiolysis of these complex systems of technological importance. In heavy ion radiolysis, extremely high concentrations of excited states and other transient species are produced that cannot be formed or examined with other types of radiation. Because of the complex nature of heavy ion tracks, further advances in radiation chemistry studies with these ions will only come about by use of sophisticated techniques. It is of particular importance to examine the time dependence of the decay and formation of the radiation-induced species as the kinetics are the most direct route to the fundamental processes occurring in the track (J.A. LaVerne, *Nucl. Instrum. Methods Phys. Res., Sect. B* **107**, 302-307 (1996)). In particular, the ionic and excited state dissociation processes need to be examined. For a given energy loss, it is not known if the interaction of a highly charged particle induces the



**Figure 3.** A pictorial representation of the differences between heavy ion (high LET) and fast electron (low LET) radiolysis.

same processes as observed with fast electrons or gamma rays. In addition, ionization processes involving multiple ionizations are poorly understood.

Performing time-resolved optical experiments and other basic studies on ionization and fragmentation processes will require the construction and development of sophisticated equipment on *dedicated beamlines* on heavy particle accelerators. Time on current accelerators is very limited. Such facilities are essential to continued progress, and it is strongly recommended that suitable resources be constructed.

*Synchrotron Radiation from Vacuum Ultraviolet to X-Rays.* Almost all radiation effects are observed as an integration of a distribution of many different energy deposition events. Even the tracks of low-LET high-energy electrons are composed of various sizes of energy deposition events. The chemical consequences of these individual deposition events are of fundamental importance for describing radiation damage in many fields, including X-ray imaging, radiobiology, and radiotherapy.

The chemical effects due to low-energy electrons can be probed using monochromatic X-rays and by examining the energy dependence of observed radiation effects (R.A. Holroyd, *et al.*, *J. Phys. Chem.* **96**, 7438 (1992); R.A. Holroyd, *et al.*, *Radiat. Res.* **135**, 312 (1993)). To obtain useful information that can be applied generally, experiments must focus on fundamental radiation chemical processes. Key areas of interest include:

- measurement of the energy dependence of W-values (the average energy required to produce an ion pair) and radiation chemical yields
- determining the chemistry associated with the Auger cascade by tuning of photon energies across K-edges.

An intense monochromatic photon source is necessary to examine radiation chemistry induced by vacuum ultraviolet to X-ray radiation. These studies would best be facilitated by the construction of a dedicated beamline or experimental station for the study of synchrotron radiation chemistry, for instance, at the National Synchrotron Light Source at Brookhaven National Laboratory.

*Positrons/Muons.* The significance of track-ends in determining radiation damage in biological systems is well established. It is reasonable to expect that these entities, given the high local concentration of reactants, are of similar importance in technologically significant situations relevant to DOE. The dynamics of the production of positronium (muonium) at the end of a positron (muon) track is a direct probe of the radiation chemistry at the track-end where energy loss events are very close together (O. E. Morgensen, *Positron Annihilation in Chemistry*, Springer-Verlag, 1995). Radiolysis experiments with these unusual ion types have the potential to provide a large amount of insight into the effect of the track-end on observable damage. Unfortunately, at present there is no acceptable theoretical model with which to describe the limited experimental data available.

*Low Energy Electrons.* Low energy electrons (< 100 eV) are ubiquitous in radiation chemistry. As the majority of the energy of a high-energy radiation particle ends up as low energy electrons, the chemistry due to these particles is fundamental to all radiation chemical systems. Recently, a

number of experiments has been developed using low energy electrons to irradiate ices. It is crucial to extend these novel techniques to study liquids, in particular water and hydrocarbons.

Given the extensive literature on the radiolysis of these liquids with high energy electrons, low-energy electron studies will significantly advance the understanding of the physical and short-time chemical factors that determine radiation damage (L. Sanche, *et al.*, "Low Energy Electron Interaction with Condensed Matter" in *Atomic and Molecular Data for Radiotherapy and Radiation Research* (IAEA-TECDOC-799), IAEA, 1995).

## **B. Model Radiation Chemical Systems**

Many recent applications of radiation chemical techniques and data are in systems where there are high concentrations of solutes. In these systems the chemistry is complex and involves short-lived, highly-excited species. To understand these complex systems it is necessary to use short time experiments and/or ultrasensitive analytical techniques not normally used in radiation chemistry. In addition, it is of particular importance to move from the dilute solution regime into systems where the scavenging capacity of the solute is large, that is  $\sim 10^9 \text{ s}^{-1}$  and higher, and to mixed phase systems.

*Water and Aqueous Systems.* A significant research effort has already been spent on considering the radiation chemistry of water and dilute aqueous solutions; however, less attention has been given to the radiation chemistry of concentrated solutions (J.W. Spinks, R.J. Woods, *An Introduction to Radiation Chemistry*, Wiley, 1990). Solutions with high concentrations of solutes are of primary importance in the mixed systems found in waste applications and in biological systems. In these complicated systems, it is necessary to understand the chemistry at extremely short times. In fact, most of fundamental properties of the radiolysis of liquid systems can only be understood when the early time dynamics of the transients are known (S.M. Pimblott, N.J.B. Green, "Recent Advances in the Kinetics of Radiolytic Processes" in *Research in Chemical Kinetics* Vol. 3, eds. Compton, R.G. and Hancock, G., Elsevier, 1995). The kinetics of the hydrated electron in water are reasonably well explained; however, information on the decay of the hydroxyl radical, and on the production of molecular hydrogen and hydrogen peroxide is limited. This knowledge needs to be extended. It is especially important to examine the radiation chemical kinetics processes on a picosecond time scale to probe the fundamental boundary between chemistry and physics. This type of work will complement the large amount of information on excited states becoming available from photochemical studies and help to address the nature of the species initially produced by the passage of ionizing radiation through the medium.

*Hydrocarbons and Plastics.* While most radiation chemical studies have been performed on water or aqueous solutions, there are many basic research questions and practical applications in the fields of hydrocarbon and polymer radiolysis that have received very little attention. From the DOE standpoint, hydrocarbons and polymeric materials are commonly encountered in nuclear waste, coolants, and structural components.

While the radiation chemistry of several hydrocarbons has been studied in depth, general information is unfortunately limited. The effects of radiation on different types of hydrocarbon are not (necessarily) the same. Extensive studies are needed to provide a knowledge base of

basic radiation chemical yields and to correlate the fundamental ionization and excitation processes with final chemical species.

The understanding of the radiolysis of polymers is more limited than that of hydrocarbons. Polymer synthesis induced by ionizing radiation is a poorly explored area, as is the relationship between radiation damage to monomers and to polymers. In addition, examination of the radiolysis of polymers with molecular techniques is highly desired to allow the construction of a model describing radiation damage to resins and plastics.

*Supercritical Fluids.* Supercritical fluids are increasingly used as alternative solvents. They are of potential interest to DOE for use in the extraction and oxidative destruction of components of selected hazardous waste systems. Practically no fundamental information is known about the chemical processes occurring in supercritical fluids. The unique ability to vary density and pressure within supercritical fluids provides new opportunities for measuring physical properties like partial molar volumes and for exploring the kinetics of short-lived transients. Radiation chemical techniques are ideal for providing information about the nature, yields and reaction rates of the intermediate ions and radicals in typical supercritical fluids.

### III. A Model for Radiation Damage

The chemical effects of radiation are largely determined by the nature and detailed locations of the reactive species produced in the track of the radiation particle (H. G. Paretzke, "Radiation Track Structure Theory," in *Kinetics of Nonhomogeneous Processes. A Practical Introduction for Chemists, Biologists, Physicists, and Materials Scientists*, ed. G. R. Freeman, New York: Wiley-Interscience, 1987). To provide a framework for understanding the chemical consequences of the irradiation of matter, it is necessary to consistently combine all the available experimental and theoretical information into a model. This model has to be as simple as possible, but it must contain the complexity necessary for the accurate treatment of the various aspects of the problem under consideration:

- the basic physics of energy transfer from the primary particle to the target
- the subsequent physical (e.g., energy migration) and physico-chemical (e.g., ionization and dissociation) processes that take place within the first picosecond
- the fast diffusion-limited nonhomogeneous kinetics.

*Track Structure Simulation.* An important component of an acceptable understanding of radiation-induced chemistry is a detailed, accurate, reliable and predictive theoretical model for the track left behind in matter after irradiation. This track model must classify the different types of event and their immediate chemical consequences, and the spatial distributions of the highly reactive radicals and ions produced. Such a calculation necessitates detailed cross-sections for all the different possible types of collision event, including distributions of energy losses and scattering angles and the chemical nature of the reactive products.

*Liquid Phase Cross-Sections.* In the condensed phase very few cross-sections are available, consequently most of the cross-sections used in current models are either derived from gas phase data or have been calculated from the optical spectrum of the condensed phase. Good sets of experimental and theoretical cross-sections are available for gas-phase processes, but their

adoption in condensed phases produces systematic errors, particularly for low energy losses. Cross-sections derived from the optical spectrum are acceptable for electrons with incident energies above 200 eV, but are incorrect for low energy electrons. Low-energy electron collisions are not well characterized in condensed matter, and detailed experimental investigation is necessary (L. Sanche, *Radiat. Phys. Chem.* **34**, 487 (1989)). Addressing this need is particularly important because, as mentioned earlier, most of the energy of an incident radiation particle is degraded into large numbers of low-energy secondary electrons.

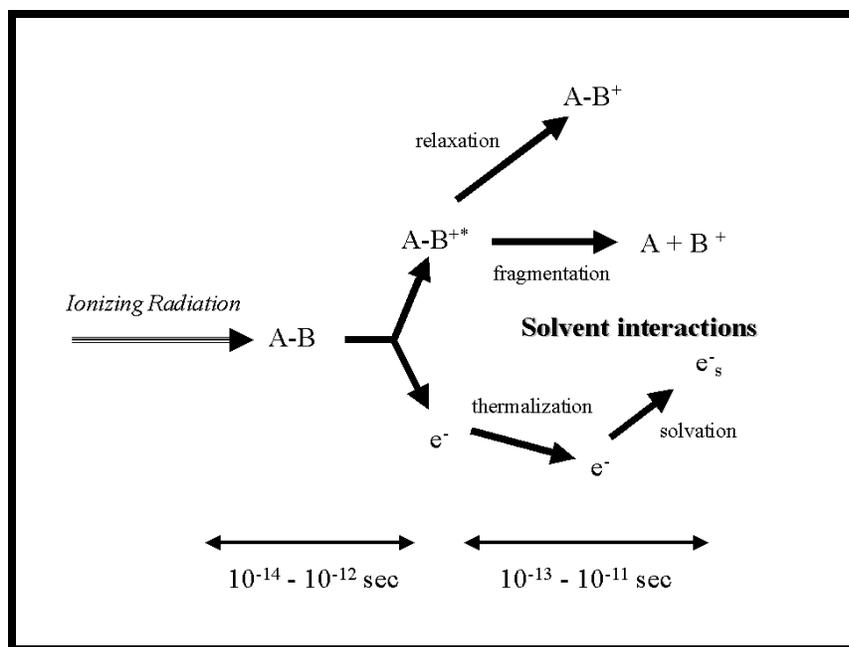
*Effects of Molecular Structure, Phase and Interfaces.* Current models of radiation tracks are based on a continuum model of the target structure which does not take into account the actual molecular structure. This treatment does not present problems for description of the large-scale track structure determined by the primary events. This is not the case for low-energy electrons which can have a very small mean free path in condensed matter. Track structure models should recognize the underlying molecular granularity of the target where necessary, and the possibility of collective excitations where appropriate. Models of this type are particularly important for applications to complex and heterogeneous targets, such as biologically active molecules and interfaces, and solid materials such as borosilicate glasses and ceramics.

*Tracks of High LET Radiations.* As discussed earlier, many medically and technologically important applications of radiation include high LET radiations, which can range from protons through  $\alpha$  particles to heavy recoil nuclei from  $\alpha$  decay or neutron irradiation (up to U). These types of radiation introduce the need to understand the chemical consequences of phenomena such as multiple ionization, Coulomb explosion, and ballistic recoil. Cross-sections for all these processes still need to be quantified, and the chemical physics resulting from the highly ionized and hot fragments must be properly characterized. The data situation here is much less complete than for electrons, which poses a major experimental and theoretical challenge for the development of a model for radiation damage.

#### **IV. Fundamental Processes Linking Physics to Chemistry**

Experimental and theoretical studies provide vital information on the discrete processes following energy deposition in radiolysis. With the development of picosecond pulse radiolysis and the application of highly sensitive detection techniques, it is now feasible to study a number of the fundamental problems at the border between chemistry and physics (C.D. Jonah, "Techniques for Studying Fast Reactions in Liquids" in *Chemical Reactivity in Liquids*, eds. Moreau, M. & Turq, P., Plenum, 1988). The time scales of these processes are given in Figure 4. There are a number of important problems where opportunities lie.

*Collective Energy Losses in Liquids.* The existence of exciton and plasmon transitions in liquids has been speculated upon, but there is no unequivocal evidence for their existence. The delocalization of such excitations is significant as it would have important consequences for the rates of dissociative decay and energy transfer. Liquid water and benzene have been considered as candidates for collective effects, but the searches have been inconclusive. It is now feasible to answer this question for liquids by using synchrotron facilities to determine the energy dependence of the optical constants (i.e., the real and imaginary parts of the refractive index) of liquids. In addition, nonlinear optical spectroscopies might be developed to probe the spatial extent of delocalized excitations. If successful in proving the existence of collective excitations,



**Figure 4.** Time scales of the fundamental processes in radiation chemistry.

these studies would lead to theoretical and experimental activity on their dynamics and decay channel branching ratios.

*The Nature of Ionization in Liquids.* A good understanding of the fates of the ions and excited states produced is vital to linking the physics to the chemistry of radiolysis, since many transformations take place before the thermal diffusion-limited chemistry starts. While radiation damage in liquids often begins with ionization, the nature of the ionization transition in liquids is poorly known. Fundamental questions that need to be addressed are:

- the role of direct and indirect transitions. What is the nature of the delay in indirect transitions and can real-time measurements probe this? What are the quantum yields for ejection vis-à-vis other non-radiative decays?
- the partitioning of the energy of the ionization between the cation and electron. Is the analogue of gas-phase photoionization spectroscopy feasible in the liquid?
- is the electron generated in the photoionization properly described as initially quasi-free? If this is the case then it should exhibit a “giant” polarizability which could be probed by femtosecond optical spectroscopy.

*Properties of Low-Energy Electrons.* In condensed matter, low energy electrons can induce optically forbidden excitations, anion resonances, and molecular dissociation to neutral and ionic fragments (L. Sanche, “Primary Interactions of Low Energy Electrons in Condensed Matter” in *Excess Electrons in Dielectric Media*, ed. C. Ferradini and J.-P. Jay-Gerrin, Boca Raton: CRC Press, 1991). The spatial distribution of the chemical products resulting from these interactions of low-energy electrons is a major determinant in the subsequent competition between track

reaction processes and chemical reactions with species in the bulk of a solution. Consequently, the elucidation of the properties and thermalization of low energy electrons is a major requirement for the understanding of short-time radiation chemical kinetics and is critical to creating predictive models. For instance, for ionization it is necessary to know:

- the radial probability density of geminate electron-cation distances
- the way that this distribution depends on the liquid and on excitation energy.

Recently, there have been significant advances in measuring low-energy electron cross-sections in amorphous ice, and these have enabled accurate models of the physics and chemistry of ice to be constructed. Unfortunately, these cross-sections do not seem to be transferable from the ice phase to the liquid phase despite the similarity in the structures of the two phases.

*Chemistry of Excited Chemical Species.* Radiation can produce highly excited chemical species not normally accessible thermally or photochemically. The competition between reaction and relaxation of these species can lead to drastically different chemistry from that expected under normal conditions. A number of experiments are now feasible to probe the relaxation processes including vibrational energy redistribution and dynamics of solvation and to understand the chemistry of the excited species.

A variety of chemical consequences has been ascribed to highly excited molecules in radiolysis. With the laser techniques, it is now possible to observe the relaxation of vibrationally excited states. This suggests experiments to determine, for example, how the competition between the relaxation of vibrational energy and the fragmentation of the highly excited cation modifies the products in radiolysis. Such studies expand the universe of chemical species that can be studied radiolytically.

*Solvation Dynamics.* Primary processes occurring in hazardous and mixed waste environments require a deep understanding of solvent fluctuations at extremes of temperature, pressure, and ionic strength. Solvation dynamics at interfaces can be restricted and slowed in certain environments (such as zeolites, cyclodextrins, and reverse micelles), and accelerated in others (such as the interface between water and the surface of metal-oxide semiconductor nanoparticles). To make accurate models of extreme environments such as the Hanford tanks, dynamical solvation studies need to be extended to include interfacial conditions. These include modeling the interface between concentrated acidic or basic aqueous salt solutions and solid interfaces (such as at carbonate salt cakes).

*Fundamental Studies.* All liquids respond to a change in local charge distribution by a dynamical rearrangement of the individual solvent molecules. This response is on time scales ranging from the most rapid intramolecular vibrations and librations down to the slower diffusive translational and reorientational motions. Development of femtosecond (far-)IR/Terahertz techniques will permit direct probing of the solvent molecules during solvation rather than relying on indirect information via fluorescent probes. In addition, generation of electrons, radicals, and ions in liquids by radiolysis considerably expands the number of species for which solvation experiments can be performed. Of particular significance is the study of lone ions in the absence of counterions, which is a unique aspect of radiation-induced ion solvation.

*Supercritical Fluids.* Supercritical water, carbon dioxide, and alkanes are of increasing significance in environmental remediation and in treatment of high-level hazardous wastes. The radiation chemistry of supercritical fluids is largely unexplored. Because of enormous changes in density and compressibility as a function of temperature and pressure of supercritical fluids, fundamental radiation and photochemical studies of the intermolecular fluctuations and solvation dynamics have the potential to provide copious information about low-energy primary processes.

## V. Interface Processes

Little is known about the fundamental processes that follow the absorption of energy by complex mixtures and heterogeneous systems. These processes can have important implications with respect to understanding radiation effects in radioactive waste storage, treatment and disposal, materials and device processing, planetary and space science, and biological systems. The presence of interfaces and interphases (i.e. mixed phases such as solids in contact with liquids and liquids containing small particles) introduces significant uncertainties in the dynamics and yields of radiation-induced reactions. Rates of interface processes can change dramatically due to catalytic effects, changes in the density of states at the phase boundary layers, and increased reactant densities. Depending upon the material, an exciton, free electron, or hole might be transferred to the liquid from the underlying substrate. It is unreasonable to expect G-values derived from bulk and homogeneous systems to be accurate or reliable for predicting yields of primary species at interfaces. At present, there are few experiments and no models that adequately describe radiolysis in mixed-phase systems.

*The Nature of Excitations at Surfaces and Interfaces.* Surface and interface excitations, which include negative ion resonances, excitons, surface states, and free charge carriers, can lead to ion-molecule reactions and reactive scattering of the neutral fragments. There are essentially no complete measurements of the absolute cross sections, product quantum-state distributions, or threshold energies for radiation-induced reactions at interfaces.

*The Mechanisms of Energy and Charge Transfer/Transport at Surfaces and Interfaces.* In structurally disordered materials the motion of the excitations cannot be described by Brownian diffusion. The motion of the excitations is affected by trapping and detrapping on defects and by transitions over barriers. In the case of a surface with relatively extensive disorder, the excitations will be localized and perform a hopping motion between different localization sites. When the structural disorder is small, the excitations will be partly delocalized and the transport properties will be intermediate between incoherent hopping and coherent band-like motion.

*Radiation-Induced Chemistry at Interfaces.* The local potential and bonding configurations at an interface can differ substantially from bulk configurations. The nature of the excited states at interfaces can be altered due to changes in Franck-Condon factors associated with bond elongation of chemisorbed species. Configuration mixing with the electron density of the underlying substrate will also occur. Thus, dissociation cross sections can be altered significantly by the changes in the electronic structure and the local environment introduced by the interface.

*Auger Processes and the Initiation of Reactions.* The destruction of full-valency wide-band-gap materials involves Auger-stimulated events. For example, damage of  $\text{ZrO}_2$  occurs via ionization of the zirconia 4p level followed by Auger decay from the oxygen 2p band. This results in reversal of the Madelung potential and expulsion of oxygen ions as well as Auger electrons. Both of these species are very reactive, so the importance of these processes in stimulating surface reactions needs to be established.

Femtosecond lasers and ultrafast pulsed radiolysis in conjunction with surface science and solid-state physics techniques offer a unique opportunity for understanding surface and interface effects. For instance:

- energy transfer mechanisms at the interface might be determined directly by time-resolved techniques
- surface defect type and density can be probed via temperature-programmed and photon/electron-stimulated desorption of probe molecules
- total cross sections and related mean free paths for the inelastic scattering of low-energy secondaries can be measured using high resolution electron energy loss spectroscopy and low-energy electron transmission studies of amorphous overlayers
- the solid-liquid interface can be studied by ultrafast radiolysis of particles suspended in solution
- quantum-state distributions of the products can be probed using sensitive laser detection schemes such as resonance-enhanced multiphoton ionization.

In addition, recent developments in the ability to produce liquid beams and liquid surfaces under high vacuum provide new opportunities to study electron and photon interactions at gas-liquid interfaces.

## **Panel B: Instrumentation**

### **CHAIR:**

Alexander D. Trifunac (Argonne National Laboratory)

### **PANELISTS:**

Jacqueline Belloni (University of Paris-Sud)

Andrew Cook (Argonne National Laboratory)

Robert Crowell (Argonne National Laboratory)

Richard W. Fessenden (Radiation Laboratory, University of Notre Dame)

Heinz Frei (Lawrence Berkeley National Laboratory)

John Miller (Argonne National Laboratory)

Robert H. Schuler (Radiation Laboratory, University of Notre Dame)

Seiichi Tagawa (Osaka University)

Gorakh Nath R. Tripathi, (Radiation Laboratory, University of Notre Dame)

James Wishart (Brookhaven National Laboratory)

## **I. Summary**

Novel experimental approaches are required to answer fundamental questions in chemical reactivity and in radiation chemistry. Current experimental facilities enable a broad range of research but are not adequate for studies that require cutting edge tools with faster time resolution, more sensitivity, and new detection capabilities. This is an opportune time to develop radically new concepts and devices for excitation and detection of chemical species produced by ionizing radiation. Radiation chemists have developed and utilized powerful tools for the study of both time-domain and steady-state chemical phenomena that result from the interaction of ionizing radiation with matter. Optical techniques, magnetic resonance and other analytic tools have been creatively applied to provide novel insights into chemical dynamics. Studies of transient intermediates and charge and energy transport transcend the focus of radiation chemistry and contribute to wider issues in chemistry. These studies have illustrated special capabilities and advantages of radiation chemistry to provide direct and decisive information on chemical processes involving charged species.

The study of radiation chemistry requires the use of intense sources of ionizing radiation with electron accelerators being the most widespread tools for radiolysis. In the United States special facilities for radiation chemistry are found at national laboratories. Current state-of-the-art in terms of time resolution and detection capabilities is limited to Argonne National Laboratory and Osaka and Tokyo Universities in Japan where routine picosecond radiolysis can be carried out. Nanosecond to microsecond pulse radiolysis capabilities are more widespread with facilities at Argonne, Brookhaven, the National Institute of Science and Technology, Notre Dame and other laboratories worldwide. This panel report focuses on the future. The coupling of lasers with electron accelerators will provide a breakthrough for the next generation of devices for radiolysis, which are based on laser driven photocathodes. Such devices have been developed for novel high energy physics accelerators. The new Brookhaven photocathode

accelerator is the first such device specifically built for radiation chemistry. Photocathode accelerators are being planned for radiation chemists in France and in Japan, as well.

The design of a novel subpicosecond electron accelerator is discussed below in some detail. The future is in developing an integrated laser-driven electron accelerator, which incorporates modern advances in laser detection and thus allows new opportunities for the study of ultrafast phenomena that are unique and complementary to laser photolysis. Such an ultrafast pulse radiolysis facility will define what is technically possible, will allow exploration of important new areas of study and will ultimately provide the testing ground for yet another generation of ultrafast devices and sources of ionizing radiation. Realization of this endeavor should make possible the development of cheaper, faster and thus more widely available tools for radiation chemistry.

## II. Present Status

Presently radiation chemistry in the U.S. is concentrated at the three national laboratories where specialized experimental facilities for radiolytic studies exist. Radiation chemistry and related studies are found worldwide.

The linear accelerator (linac) at Argonne is capable of operating in the picosecond time regime. The concept and practice of subharmonic bunching and pulse compression were developed at Argonne and were also installed at two accelerators in Japan. Synchronization of the picosecond electron pulse with a femtosecond laser pulse was realized at Osaka University in 1995. Other improvements on the system of Osaka University realized in 1997 were shortening of the electron pulse to 800 fs with 2 nC of charge, construction of a broadband femtosecond probe source (400-1600 nm), and development of a jitter compensation system. The time resolution of the system is 3 ps.

The new Brookhaven photocathode accelerator is the first such device specifically built for radiation chemistry with picosecond pulse capabilities. Physicists have built several photocathode linacs to test ideas on novel accelerator concepts, e.g., the Wakefield Accelerator in the High Energy Physics Division at Argonne. In 1998 the synchronization of a 5 MeV subpicosecond photocathode linac with a femtosecond laser will begin in the cooperation of Osaka University with the Femtosecond Technology Research Association.

The Notre Dame Radiation Laboratory operates a linac and two Van de Graaff accelerators providing nanosecond to millisecond pulses of electrons. Other highly developed Van de Graaffs are found in Delft, The Netherlands, in the Chemistry Division at Argonne, the Chemistry Department at Brookhaven, the National Institute of Standards and Technology, and many other locations worldwide. All these facilities are very old. The Van de Graaffs are more than 30 years old. The Argonne linac is of similar vintage with additions and developments (subharmonic bunching, pulse compression) occurring over the last two decades; the same is true for accelerators in Japan. The exceptions are the Notre Dame linac which is three years old and the new Brookhaven photocathode linac.

Over the years radiation chemists have developed and utilized powerful tools for the study of both time domain and steady state aspects of the chemical phenomena that result from the interaction of ionizing radiation with matter. The achievements of the past will not be summarized but will be used as an ample foundation for future challenges and opportunities where methodology of radiation chemistry can contribute to solving many relevant chemical and environmental issues.

### **III. New and Proposed Accelerators and Associated Detection Methods**

#### **A. Next Generation Linac**

The next generation linac facility will represent a significant advance in the methodology of pulse radiolysis. There are two general considerations why the construction of such facility is proposed:

- There are significant and broadly relevant fundamental chemical issues that can only be studied using a subpicosecond radiolysis facility. As discussed in the report of other panels of this workshop, there are exciting new experimental studies which will become feasible when ultrafast radiolysis methodology comes online.
- Recent developments of accelerator and laser technology make it feasible to conceive and construct a new state-of-the-art subpicosecond laser photocathode accelerator. Furthermore, there are exceptional experimental advantages of having the synchronized electron beam-laser pulse probe capability.

The rapid development in recent years of the technology in laser spectroscopy illustrates how whole new scientific vistas open when chemical processes and physical effects can be viewed at shorter and shorter times following their photoinitiation. For example, new insights have been gained into photosynthetic energy conversion, vibrational relaxation, and solvation dynamics.

Fundamental issues surrounding the primary events in radiation chemistry have yet to be resolved; for example, the answers to questions such as "What is the role of excess energy in chemical reactions of neutrals, ions, radicals, or in ion solvation?" and "What is the mechanism of charge transfer in the condensed phase?" These questions are relevant to areas as diverse as materials processing, device fabrication, catalysis, biological effects of radiation, and understanding radiation effects in radioactive waste.

#### **B. Subpicosecond Pulse Radiolysis**

Flash photolysis and pulse radiolysis explore two different yet complementary views of chemical reactivity. For example, the hydrated electron,  $e_{aq}^-$ , a species of tremendous theoretical and practical import, was discovered and its chemical properties were measured using pulse radiolysis techniques. On the other hand, flash photolytic studies have contributed considerably to an understanding of the formation dynamics of  $e_{aq}^-$ . The reverse situation was found when the chemistry relevant to solar conversion processes was explored; pulse radiolysis provided clearer and simpler demarcation of the intermediate chemical steps than was possible using optical formation in electron transfer studies and in research on colloidal systems.

The different selection rules governing energy absorption in photolysis and radiolysis continue to make the techniques complementary. Existing pulsed lasers provide photon energies less than approximately 6 eV. This is insufficient to ionize most dielectric solids and liquids. Recent advances in high-power lasers have broadened the applicability of flash photolytic techniques because of access to higher energy states via multiphoton excitation. Although multiphoton ionization can be used to access higher energy states in condensed matter, it is not capable of mimicking the effects of ionizing radiation. These issues are elaborated upon as follows.

Efficient multiphoton excitation requires resonant enhancement by lower excited states. With few exceptions, these lower states are formed more efficiently than the higher excited states that one wishes to study. Thus, one faces the daunting problem of discriminating against the lower states to focus on the states one wants to observe. One example occurs in the laser multiphoton ionization of alkanes where an equal number of ions and excited singlets are generated, whereas in radiolysis it has been shown that the excited states form primarily via ion recombination. This makes an accelerator more suitable for study of the chemistry of prethermalized charge carriers.

The spatial deposition of energy by relativistic electrons is different than that from UV or visible photons. In photolysis, the deposition creates isolated ions or excited states, whereas in radiolysis clusters of ions or excited states are formed in regions called spurs. This spatial inhomogeneity is often considered a complication - a subject that is of importance only to radiation chemists. However, this inhomogeneity provides unique opportunities to study ultrafast reactions between the short-lived intermediates. Achieving such high local concentrations using laser excitation is very difficult or impossible because of the large amount of energy that must be deposited. Auger recombination of free charges in semiconductors can be studied this way. Another class of processes that can be studied this way is "rare" recombination events in solids. These occur when the charges recombine near a defect and the heat released from the reaction transforms the defect. Such transformations are especially difficult to study using lasers, due to their rarity. However, such processes have practical impact because they are responsible for the slow degradation of photovoltaic materials.

Certain fundamental processes are specific to radiolysis and cannot be easily modeled using lasers. The subpicosecond linac offers exciting new possibilities. To study "direct effects", precursor reactions, and radiolysis in solids that are of importance to technological and environmental issues. Some of them lie at the heart of many Department of Energy interests, including development of durable high-level radioactive waste forms, managing radioactive waste solutions, and development of efficient particle detectors for high-energy physics.

Other advantages of the proposed linac derive from the fact that the laser that "drives" the photocathode is inherently synchronized with the electron pulse, with very little jitter in the synchronization (W. Gai *et al.*, *Proceedings of PAC89*, Chicago, IL, 612 (1989); P. G. O'Shea *et al.*, *Nucl. Instr. and Mth.* **A331**, 62-68 (1993); J. C. Bourdon *et al.*, *Proceedings of LINAC98*, Chicago, IL, 161 (1998)). This fact translates into considerable improvements in sensitivity and capabilities for detection schemes. Detection schemes can be based on laser-produced interrogating light pulses as opposed to the linac-produced light pulses (Cerenkov radiation) that

are presently used. Thus, the intensity and wavelength range will be available to develop new detection schemes for examination of transient species that are impossible to study at this time. This is discussed in some detail below.

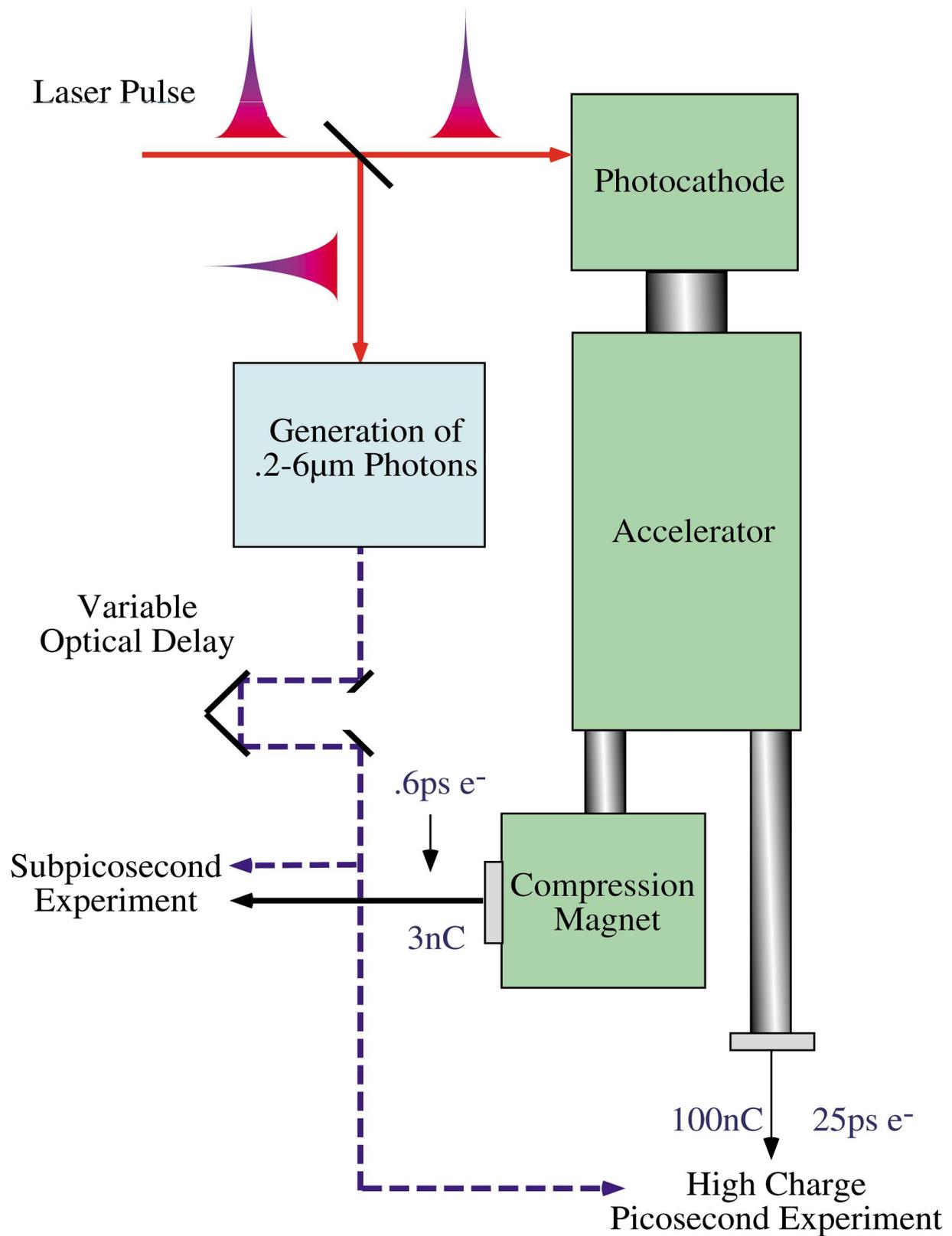
*Outline of the Laser-Driven Subpicosecond Pulse Radiolysis Facility.* When designing a subpicosecond accelerator one must consider the unique measurement problems that occur when the pump pulse is made up of ionizing particles rather than photons. Problems due to the much faster propagation in matter of an electron beam compared to a light beam, and space charge limitations must be considered. To carry out ultrafast pulse radiolysis one must be able to generate detectable concentrations of species and have a technique that can accurately measure the number and identity of these species with sufficient time resolution. The goal is to generate an adequate number of species so that optical absorption spectroscopy can be used as one of the probe techniques. Figure 5 shows a block diagram of the accelerator. Note that the diagram is highly schematic and does not attempt to display the detail necessary for either the electron-beam optics or the light optics. The timing of the electron pulse will be related to the time at which the light pulse strikes the photocathode. To first order, there is synchronization between the electron pulse and the optical probe pulse.

The size of the electron pulse is limited by space-charge considerations. If an electron pulse has a time profile of 0.6 ps, the physical length of that pulse is approximately 0.18 mm. Repulsion between electrons limits the number of electrons that can be put into such a volume. Simulations have suggested that 0.6 ps pulses of approximately 3 nC (approximately  $2 \times 10^{10}$  electrons) should be possible. To generate 0.6 ps electron pulses it is necessary to synchronize the laser to the linac to within a picosecond. For experiments that do not require such short pulses, much higher charges should be available. Simulations suggest that 45 ps pulses of 100 nC pulses should be possible.

Recent advances in accelerator technology are making it possible to generate subpicosecond electron pulses. Rapid development of tunable solid state lasers makes it feasible to generate subpicosecond pulses of light and utilize new detection schemes in the chemically important UV to infrared spectral region. A merging of these two technologies will provide an invaluable tool for radiation chemists. Assuming that subpicosecond synchronization is achieved between laser and linac, the next step will be to develop novel optical detection techniques.

#### **IV. Consequences of Laser Synchronization: Detection Schemes Leading to New Science**

*Time-Resolved Infrared Spectroscopy.* To determine the role of excess thermal energy and vibrational energy transfer in radiation chemistry, it is necessary to develop experimental methods to measure these directly. Advances in ultrafast mid-infrared laser techniques will make it possible to selectively probe vibrational energy transfer processes on the picosecond and even subpicosecond timescales (A. Tokmakoff, M. D. Fayer, *Accts. Chem. Res.* **28**, 439-445 (1995); G. Haran, W. Sun, K. Wynne, R. M. Hochstrasser, *Chem. Phys. Letts.* **274**, 365-371 (1997)). When coupled to an ultrafast linac it will become possible to study these fundamental processes for the radiolysis of pure liquids, solutions, and solids. Because of the lower



**Figure 5.** Block diagram of a pump-probe system of a photocathode linac with a compression magnet for ultrashort electron pulses.

absorption cross sections of vibrational versus electronic transitions, infrared spectroscopy is typically ~100 times less sensitive than UV/vis techniques. Therefore, the development of more sensitive detection schemes in the infrared region on the ultrafast timescale needed. This requires the development of broadly tunable (2.5 - 10  $\mu\text{m}$ ) subpicosecond infrared laser sources with sufficient pulse energy (10  $\mu\text{J}$ ) to generate measurable signals.

In addition to providing the means with which to directly measure vibrational dynamics, the structural specificity of infrared spectroscopy can be used to identify and follow the kinetics of transient species. Identification of short-lived chemical species is an important part of radiation chemistry, and transient detection techniques currently used in pulse radiolysis studies for this purpose are optical (fluorescence, UV/vis absorption) and magnetic resonance (pulsed Electron Paramagnetic Resonance (EPR), Fluorescence-Detected Magnetic Resonance (FDMR)) spectroscopies. Because of its inherent sensitivity to molecular structure, time-resolved vibrational spectroscopy and resonance Raman spectroscopy are more informative than UV/visible methods. Technological advances in the past several years in the area of step-scan Fourier-Transform Infrared (FTIR) spectrometry have made it possible to take advantage of the infrared selectivity to identify transient chemical species in the time-frame from nanoseconds to milliseconds across the entire infrared spectral region (5000 - 400  $\text{cm}^{-1}$ ). In contrast to the ultrafast laser techniques that probe primarily specific vibrational coordinates, step-scan FTIR is a broadband method that probes large spectral regions, which allows the simultaneous identification of multiple species.

Step-scan FTIR spectroscopy furnishes details on the geometrical structure (including regio, diastereochemistry) of intermediates, and is especially informative when the use is made of heavy isotopic labeling. For many materials and solvents of interest, e.g. acetonitrile, water, zeolites, hydrocarbon polymers, biological membranes, etc., the infrared spectrum is at least partly accessible, in some cases even over wide regions. While in some aspects complementary to the time-resolved resonance Raman method, transient FTIR spectroscopy has unique applications for molecules which have no chromophore for resonance enhancement, or when seeking structural information on parts of the molecule that are not enhanced by a chromophore. Nano- and microsecond FTIR spectroscopy of organic, inorganic, organometallic, and biological intermediates in solution, zeolites, polymers, and biological membranes has been demonstrated over the past two years. Application in pulse radiolysis may include spectroscopy of primary species produced upon absorption of radiation by the solvent. For example, one could identify  $\bullet\text{CH}_2\text{CN}$ ,  $\text{CH}_3\text{CN}^-$ ,  $(\text{CH}_3\text{CN})^{2-}$  in the case of acetonitrile and monitor the fate of each separately. UV/vis techniques are often unable to distinguish such species conclusively. The largest impact of IR methods is expected on mechanistic studies of chemical reactions initiated by the primary species (e.g. OH radicals, solvated electrons, or primary cations in non-polar solvents).

The high signal-to-noise of very recent nanosecond FTIR experiments on electron transfer in transition metal complexes suggests that step-scan FTIR spectroscopy on the subnanosecond timescale will be feasible. Picosecond broadband IR probing would be very desirable because crucial elementary energy transfer, electron transfer, or fragmentation events occur on that time scale, and the band positions of transients can often not be predicted. The development of ultrafast mid-infrared photon detectors is currently underway.

*Time-Resolved Coherent Spectroscopy.* New information on energy levels, lifetimes of transient species, collisional processes, coupling strengths, and diffusion processes can be obtained through the use of transient coherent spectroscopy (e.g., Coherent Anti-Stokes Raman Spectroscopy (CARS), transient grating, photon echo, etc.). Although coherence spectroscopy has been used by solid state physicists for many years, such techniques have not yet been exploited in the radiation chemistry community. The main reason has been due to inability to synchronize the radiation source with a laser and obtain the required time resolution (1 ps). Because of the phase matching requirements of coherence techniques they offer the distinct advantage of zero background detection. However, because they have a nonlinear dependence on laser power, they require laser sources with high peak power (~ 100 kW). Additionally, optical dephasing rates are an ultrafast process at room temperature, typically <10 ps for vibrations and <100 fs for electronic transitions. This requires the use of ultrafast accelerators and lasers.

*Time-Resolved Resonance Raman Spectroscopy.* Like infrared spectroscopy this molecular spectroscopic technique provides a structure-sensitive method for studies of chemical reaction kinetics in liquids. The experiments provide information on structure, bonding, and chemical interactions in reactive intermediates. This has significant impact on other forefront areas of chemistry, e.g. solvation dynamics, cluster formation, photochemical electron transfer, coherence in chemical bond dissociation, and *ab initio* structure calculations.

Future developments of this technique involve (i) an apparatus based on an accelerator capable of delivering shorter pulses (<1ps), (ii) an appropriate probe laser system tunable in the range of 200 - 350 nm, (iii) resonance CARS/Coherent Stokes Raman Spectroscopy (CSRS), and (iv) a tunable UV-IR photolysis laser.

Our current understanding of intramolecular electron transfer and the subsequent bond dissociation in radicals is largely based on rate constants and product analysis, and debate continues on the nature of the electronic relaxation mechanism. The mechanistic questions can be settled, conclusively, by investigating the structural properties of such radicals in polar and non-polar solvents.

Thus far direct measurement of the spectroscopic properties of an excited solvated radical has not been feasible. Such studies will be performed with the new instrumentation which will provide a structural probe for the excited state chemistry of radicals. The chemical interactions involving coupling between the radical-solvent vibrations provide information on the solvation dynamics in the excited state on an extremely short time scale. The manifestations of the solvation dynamics in strongly hydrated radicals, such as  $O_2^-$ , on the bond dissociation energy can be examined.

The frequencies and anharmonicity constants for spontaneously created vibrational states should be different from the thermally relaxed states in solution, but this difference has not been observed in any molecule. In diatomic radicals such as dihalide anions undergoing thermal dissociation in solution, this physico-chemical effect is likely to be observed, providing a structural explanation for the thermochemical equilibrium  $X_2 \rightleftharpoons X\cdot + X\cdot$ .

*Linac-Pump, Laser-Pump, Laser-Probe.* This method will enable experiments with better than 100 fs time resolution without requiring tight linac-laser synchronization. New electron accelerators promise 1 ps time resolution, but it is possible to increase this by more than an additional order of magnitude using excited states of radical ions to drive interesting chemistry. This experiment will greatly benefit the study of electron transfer in systems with very short donor-acceptor linkages where the electronic coupling is very large. While still maintaining the special abilities of pulse radiolysis experiments to study electron transfer with accurately known energetics that are independent of distance, solvent polarity, and temperature, it will be possible to quantitatively examine new effects including adiabaticity, orbital symmetry, and solvent factors. The experiment can be accomplished by simply waiting as much as 50 ns following the electron pulse for electron capture and subsequent electron transfer to the low energy, “acceptor”, end of the molecule to occur. Photoexcitation with a sub-100 fs laser pulse will then allow us to study both electron transfer back to the original donor end of the molecule as well as the subsequent electron transfer to the acceptor. The dynamics can be probed with laser pulse width limited techniques like transient absorption, laser-induced fluorescence, and a variety of nonlinear optical methods commonly used by ultrafast spectroscopists.

*Single-Shot Ultrafast Detection.* Single-shot ultrafast detection schemes need to be developed as they will be critical for the study of scarce molecules such as those alluded to above, and to dramatically increase the rate at which dynamical data is recorded. Such methods have been demonstrated to provide pulse width limited time resolution over time windows of 1-100 ps depending on experimental configuration. This detection technique can be used either with the linac/laser pump/laser probe experiments described above, or, and with significant advantage, with new sub-picosecond linac experiments as a probe of the short time dynamics following the linac pulse. This is due to the good linac/laser synchronization available.

*Sensitivity Improvements in Pulse Radiolysis.* Currently, many important applications (reactions of radicals from amino acids, for example) are seriously limited by sensitivity because of weak absorption. Effort should be put into developing systems with tunable CW lasers for analysis. Gated diode-array detectors should be made available for recording complete spectra on faster time scales than are currently available.

## **V. Other Tools**

*High Field EPR.* The remarkable power of magnetic resonance spectroscopy has been amply demonstrated via real time and “slow” time studies of transient radicals and radical ions produced by pulse radiolysis. It is in the superior information content that magnetic resonance excels. In all fields of chemistry a drive to develop and apply higher and higher magnetic fields for Nuclear Magnetic Resonance (NMR) is obvious. EPR also benefits by applying higher magnetic fields utilizing superconducting magnets. Obvious advantages are, like in NMR, that g-shifts (like chemical shifts) allow separation of overlapping spectral lines. Furthermore high magnetic fields (95 GHz and higher) allow the study of paramagnetic systems which exhibit larger zero-field splittings. This is often encountered in inorganic solids. In the study of many photoexcited paramagnetic states in solids, selective photoexcitation of individual Zeeman components becomes feasible since the Zeeman splittings are often larger (at 95 GHz or higher) than the optical linewidth.

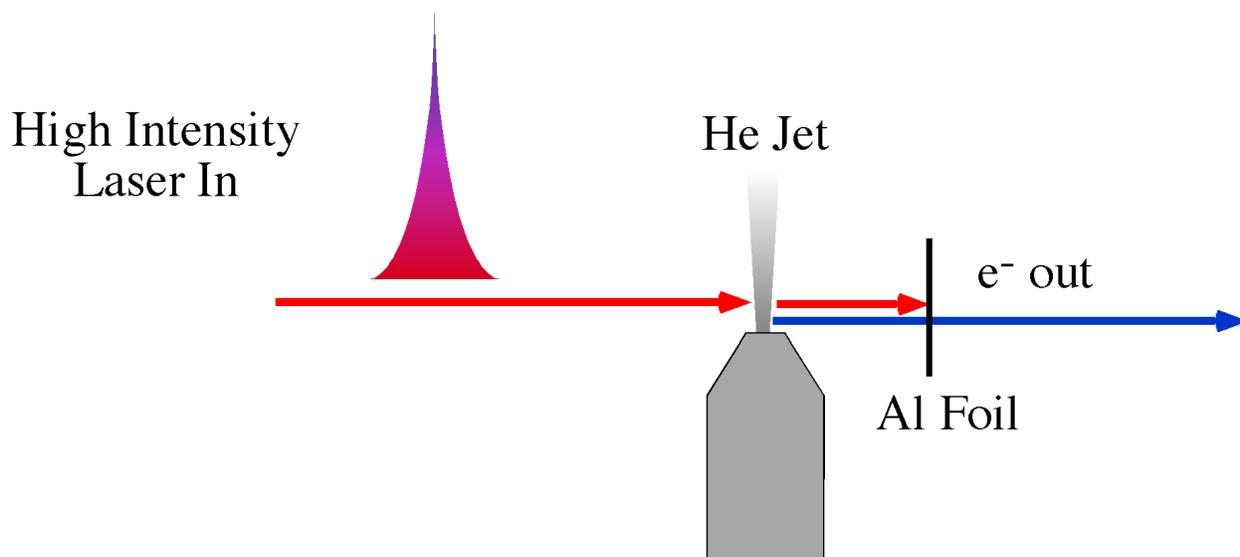
Much can be gained by using High Field EPR spectroscopy to examine radiation induced defects in frozen matrices, in zeolites, in solids, and in thin films. The sensitivity gain and the possibilities to probe the environment of paramagnetic species using now available pulsed High Field EPR methods make it a very useful technique for examining radiation induced defects.

*Novel Chromatography.* A new generation of chromatographic and electrophoretic analytical instrumentation based on diode array technology now makes it possible to examine overall radiation chemical processes at doses well below 1000 rads. As a result many interesting chemical problems that have not been previously accessible can be studied by radiation chemical methods. Specific recent examples include studies of the directing effect of phenyl substitution in the hydroxylation of aromatics, which have only micromolar levels of solubility, and selectivity in the internal electron transfer in the reduction of halogenated benzoates. Currently capillary electrophoretic methods are being developed which provide a complementary approach to the more conventional chromatographic methods. Mass spectrophotometric detectors are being developed for both chromatographic and electrophoretic approaches, which can provide positive identification of specific products. Very recently gel permeation chromatographic methods have been applied to studies of the radiolytic fragmentation of aliphatic hydrocarbons. Extension of these latter studies to other non-aqueous media is very promising. In general these various approaches complement the kinetic information obtained from time resolved experiments and provide very detailed pictures of the course of radiation chemical processes. It can be expected that their application in radiation chemical studies will rapidly increase in the near future.

*Future Laser-Based Pulse Radiolysis Technologies.* The ideas discussed above are within the realm of current technology. Their realization becomes a matter of orchestrating the combination of accelerator technology, solid state laser development, and novel detection schemes. Looking ahead, the next generation of time-resolved radiolysis will be accomplished *without* conventional accelerators. Questions relating to the possibility of designing 'table top' radiolysis tools capable of femtosecond time resolution and development of new detection schemes for the study of transient phenomena in radiolysis should be addressed.

Advances in laser devices are making it possible to generate subpicosecond electron bunches. Recently, it has been demonstrated that focusing a high power laser (25 TW,  $10^{18}\text{W/cm}^2$ ) (G. A. Mourou, C. P. J. Barty, M. D. Perry, *Physics Today* **51**, 22-28 (1998)) into a molecular beam produced by a helium gas jet yields a collimated beam of electrons. This is illustrated in Figure 6. The gas from the pulsed nozzle is tunnel ionized by the laser pulse and the peak electron density (on axis) approaches  $10^{19}\text{cm}^{-3}$ . The electrons produced by this method have a broad energy distribution that is  $<30$  MeV and a charge of  $\sim 1$  nC. These laser-based devices will be much smaller ('table top') than current accelerators and their lower cost will offer the advantage of wider use at university laboratories. Presently, these systems are not capable of producing high charges. Additionally, the electron energy is not monochromatic which limits the ability to transport the electron pulses from their point of generation. However, methods are being developed that will circumvent these problems in the not too distant future.

Technological developments in the design of high power lasers have generated novel ideas on how to use lasers to accelerate electrons and to create ultrashort electron and X-ray

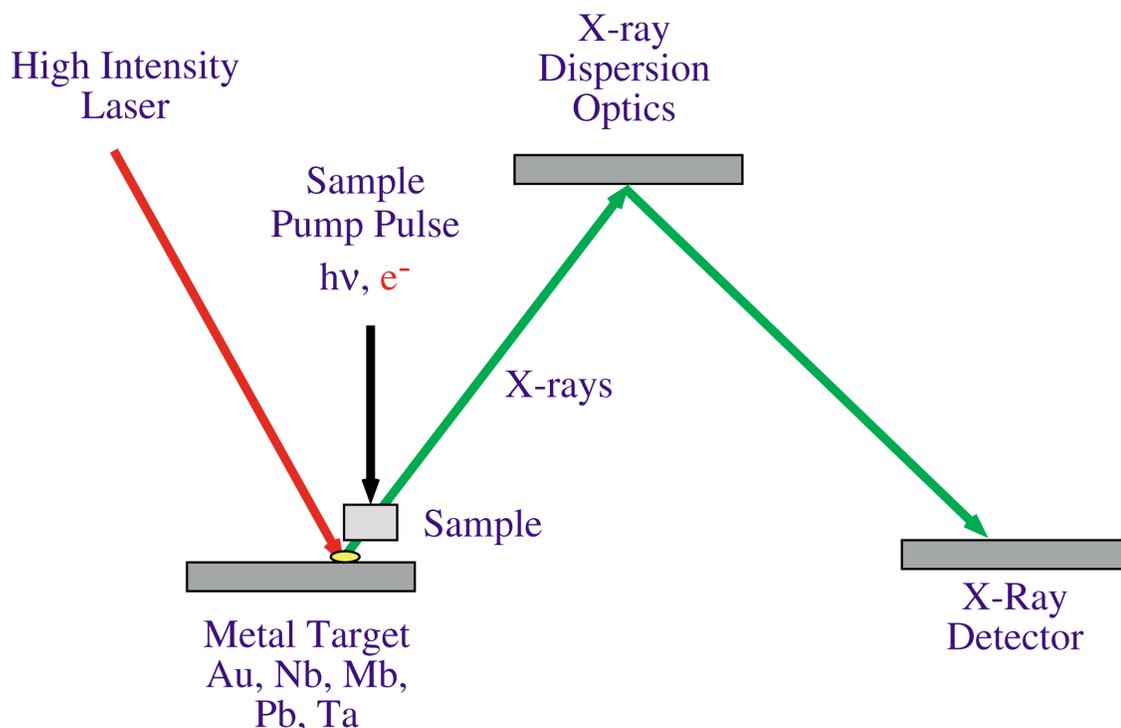


**Figure 6.** Generation of energetic electron pulses with a high-energy laser.

pulses. Ultrafast X-rays can, in principle, allow one to monitor chemical reactions in real time with atomic spatial resolution. The ultrafast X-ray technique can be used to study chemical reaction mechanisms by monitoring the structural changes of transient species. This method has been demonstrated through the observation of the photoinduced dissociation of gas phase SF<sub>6</sub> with 1.5-3 ps time resolution using X-rays near the sulfur K-edge at a photon energy of 2.48 KeV (T. Raki, K. Wilson, Z. Jiang, A. Ikhlef, S. Y. Cote, and J. C. Kieffer, *J. Chem. Phys.* **104**, 6066 (1996)). This is illustrated in Figure 7. Pushing this approach to the femtosecond time regime will make transient X-ray spectroscopy a powerful method of monitoring molecular dynamics in many radiation-induced processes. Significant improvements in laser technology, X-ray optics, and X-ray detection must be made to make this technique accessible to the radiation chemist.

A Coulomb explosion occurs when intense fields result in molecules that have multiple charges. The intense repulsion that results from multiple like-charges causes the molecule to immediately fly apart. Recent work of A. Castleman, Jr. at Pennsylvania State University (D. E. Folmer, E. S. Wisniewski, and A. W. Castleman, *Chem. Phys. Lett.* **287**, 1-7 (1998)) has used high energy femtosecond lasers to induce Coulomb explosions during the gas phase tautomerization of the 7-azaindole dimer. The explosion products were mass analyzed. Castleman used this technique to take snapshots of the reaction as it occurred and was able to show that the tautomerization reaction followed a stepwise mechanism on the subpicosecond timescale. Extension of this technique to the condensed phase would be a valuable tool for the radiation chemist.

High-energy femtosecond lasers are now capable of producing ultrahigh irradiances that are in excess of  $10^{20}$  W/cm<sup>2</sup>. At these high irradiance levels the field strength is on the order of a teravolt per centimeter which is larger than the binding Coulomb field for ground state electrons



**Figure 7.** Generation of ultrashort X-ray pulses with a high intensity subpicosecond laser.

in simple mono- to triatomic molecules in the gas phase. The interaction of the electric field component of the laser light pulse with molecules induces a dipole moment, which is dependent on both the molecular polarization and the magnitude of the applied field. If the light field is comparable to the Coulomb field, field induced dipoles can result in molecular spatial alignment and restricted rotational motion (pendular states).

An ultimate goal in radiation chemistry is not only to understand the fundamental physics that influence radiological events, but also to develop the ability to control them. Is it possible to preferentially induce charge transfer over dissociation during radiolysis? Can one accomplish necessary alignment in the condensed phase to achieve selectivity? Alignment of molecules in a strong electric field (i.e., high intensity laser) followed by irradiation by an ultrahigh intensity laser may make this possible. Future uses of synchrotron radiation and free-electron lasers should be considered by radiation chemists for both structural and time domain ( $\sim 50$  psec time resolution) studies.

## **Panel C: Nuclear Energy Production and Environmental Waste Management**

### **CHAIR:**

Gregory Choppin (Florida State University)

### **PANELISTS:**

Ned Bibler (Westinghouse Savannah River)

Don Camaioni (Pacific Northwest National Laboratory)

Ian Carmichael (Radiation Laboratory, University of Notre Dame)

Robert Cash (Duke Engineering)

Nada Dimitrijevic (Argonne National Laboratory)

David Griscom (Naval Research Laboratory)

Sergei Lyman (Brookhaven National Laboratory)

David McCracken (AECL-Chalk River Laboratories)

Dan Meisel (Argonne National Laboratory)

Stephen Mezyk (AECL-Chalk River Laboratories)

Shirley Rawson (Pacific Northwest National Laboratory)

Randy Scheele (Pacific Northwest National Laboratory)

Ilya Shkrob (Argonne National Laboratory)

Leon Stock (Duke Engineering)

William Weber (Pacific Northwest National Laboratory)

Francon Williams (University of Tennessee)

## **I. Summary**

Radiation is ubiquitous in nuclear reactors and in nuclear processing and storage facilities. It affects the chemistry of coolants, the integrity of materials of construction, and the stability and performance of processing chemicals in fuel cycle operations. Understanding the pervasive role of radiation chemistry in all aspects of the nuclear fuel cycle is essential to the safe and long-term operation of nuclear reactors and of fuel cycle facilities.

A common theme that appears in all of the subsections of the report of Panel C is the need to explore radiolytic processes that occur across two-phase interfaces, both solid-liquid and solid-gas. Solid-liquid interfaces abound in nuclear reactors, in high level radioactive wastes (HLW), and, indeed, in all nuclear waste forms. Colloidal particles participate in gas production processes, in gas retention, and in organic degradation of HLW. Their role and the role of radiation, at the molecular level, are not clear and the dynamic controls that they provide must be delineated. Surface chemistry can be activated and changed by radiolysis. Knowledge of such effects is important for the assessment of lifetimes of materials, as well as for safety assessments.

Chemical effects of simultaneous radiation recoils and electronic excitations pervade the materials and liquids used in nuclear reactors and the nuclear fuel cycle. A good understanding

is needed of these effects in order to ensure that the materials and processing chemicals perform as required for the proper operation of these systems. These studies should include the determination of the effect of changing the ratio of the dissipation of radiation energy via electronic and nuclear processes on microstructural and microchemical properties, and on the segregation, diffusion, and phase stability of materials such as fuel forms (oxides, nitrides, and carbides of uranium and plutonium), waste form glasses, and intermetallics.

## II. Nuclear Energy Production

To support current and future applications, many aspects of the effects of radiation chemistry in nuclear energy production require additional studies to achieve the necessary level of understanding to ensure safe and successful operation. To this end, this panel recommends the following areas of research.

*Water Radiolysis in Nuclear Energy Production.* Radiolysis of water in nuclear reactors and in fuel reprocessing systems is important for determining the lifetimes of component materials and in guaranteeing the safety and performance of critical components in and around the core of the reactor and in fuel cycle operations. Recommended studies include investigating the effects of temperature, pressure, solute concentrations, and Linear Energy Transfer (LET) on primary yields and kinetics of radiolytic aqueous species under reactor core and fuel cycle conditions. LET parameters should include alpha, beta, gamma, neutron, and heavy ion (such as oxygen, deuterium, helium, and proton) recoil interactions with water with an energy range up to 12 MeV. Studying isotopic effects will help elucidate the various mechanisms that may be present over a range of temperatures, solute concentrations, and fluid density conditions (from ambient conditions to supercritical water). Fundamental knowledge in this area is insufficient and few suitable experimental facilities exist. This increases the risk that this important area of research may be lost without proper support. This fundamental chemical information on the radiolysis of water at high temperatures and pressures under varying solution conditions, etc. can provide the basis for computer models to predict reactor core chemistry.

*Radiolysis at Interfaces, on Surfaces, and in Confined Spaces in Reactor and Fuel Cycle Facilities.* Radiolysis can affect the corrosion and hydriding of materials used in reactors and in fuel cycle facilities. Radiolytic effects at solid/gas, solid/liquid, and gas/liquid interfaces have not been characterized sufficiently to provide adequate information to ensure the probable lifetime and the safe use of various materials. Among the recommended parameters to be studied are the effects of different sized particles of fuels, silica, zeolites, colloids, ion exchange resins, etc. on the radiolytic processes. Surfaces can be chemically activated by radiation, and in addition, solution radiolysis may be different in confined spaces such as in oxide layers, pits, cracks, and grain boundaries compared to bulk solution.

*Mechanistic Studies of Organic Radiolysis under Reactor and Fuel Cycle Conditions.* Various classes of organic compounds in irradiated reactor systems and ancillaries have or will be used to recover fuel components and treat radioactive wastes. Radiolytic degradation of these organics can affect corrosion processes in reactor systems. This also is a safety issue because it can result in hydrogen production, and can affect the performance of solvents and ion exchange media used in fuel reprocessing. It is, therefore, essential to understand the complete mechanisms from

initial reactants to final products for the types of organics used. Factors to be studied include the effects of the classes of organics, as well as of oxygen, dose, dose rate, LET, and temperature.

*Fundamental Understanding of the Synergisms of Electron Excitations and Nuclear Collisions in Materials Used in Nuclear Reactors and the Fuel Cycle.* Understanding the chemical effects of simultaneous radiation recoils and electronic excitations that occur in materials used in nuclear reactors and the fuel cycle is needed to ensure that construction and waste form materials and processing chemicals perform as needed. Studies should include determining the effect of changing the ratio of electronic to nuclear stopping power on the evolution of microchemistry, microstructure, segregation, diffusion, and phase stability of materials such as fuel forms (UO<sub>2</sub>, PuO<sub>2</sub>, nitrides and carbides), glasses, and intermetallics.

*Radiation-Induced Redox Reactions of Metallic and Anionic Species in Solution under Nuclear Reactor and Fuel Cycle Conditions.* Studies of radiation-induced redox reactions of metallic and ionic species in solution under nuclear reactor (high [300 C] temperatures and pressures) and fuel cycle conditions are important to determine corrosion processes and radioactive species transport in nuclear reactors. They are also important to ensure long-term stability of process and waste storage vessels. These studies should include characterization of radiolytic-induced redox states of iron, nickel, chromium, and nitrogen compounds.

*Concurrent Theory and Model Development of the Above.* Concurrent development of models and theory as fundamental and experimental studies are performed is important to provide a basis to predict the behavior of complex multivariant systems in nuclear reactors and fuel cycle facilities. Such theoretical modeling should provide the basis for directed experimental investigations and for a better understanding of the fundamental chemical processes.

*Improve and Test Existing Chemical and Kinetic Radiation Chemistry Databases.* It is essential to improve and critically evaluate existing chemical databases to ensure the accuracy of theoretical predictions of radiolysis occurring in nuclear reactors and fuel cycle facilities. This information is needed to predict chemistry in nuclear reactors and fuel cycle facilities where measurements cannot be made. Accurate data on chemical reactions and mechanisms are needed to predict processes like corrosion and hydrogen evolution resulting from radiolysis of coolants (aqueous systems) in reactors. Comparison of theoretical predictions against well-characterized experimental results would ensure that the models can be used for all reactor conditions.

### **III. Stored and Processed Wastes**

The stored nuclear wastes in the United States, including those at Hanford, Savannah River, Idaho, etc., invariably contain highly concentrated aqueous solutions and solid suspensions. Five research needs for the continued safe and efficient storage of the waste are identified in this section.

*Initial Radiolytically-Generated Reactive Intermediates.* Radiation effects occur directly and indirectly with the solutes and solids and highly concentrated aqueous solutions and solid suspensions that constitute much of the stored wastes. Prolonged irradiation of systems with high solute concentrations affects the intraspur scavenging of the primary radiation products and

causes the buildup of reactive intermediates. Specifically, the accumulation and reactivity of the radiation-produced species can be expected to contribute significantly to the overall chemistry, and may complicate subsequent waste processing operations. Similarly, stored chemical energy in the form of solid state intermediates could contribute to the formation of 'hot spots' through episodic heat releases. Research needs in this area include:

- identification and characterization of new reactive intermediates;
- quantitative determination of radiation yields as a function of reaction parameters.

*Reaction Pathways.* The intermediates produced by radiolysis oxidize or reduce the organic and inorganic solutes to provide secondary reactive intermediates. The reaction cascade leads eventually to stable end products such as sodium oxalate and carbonate, together with reduced gaseous products. The reaction mechanisms of the original and modified organic constituents, as well as the coupled reactions responsible for the formation of gaseous products, need to be established to provide a fundamental understanding as a function of composition of the empirically observed differences in chemical behavior for storage systems, i.e.:

- the hydrogen to nitrogen, nitrous oxide, ammonia gas ratio produced in organic-, nitrate-, and nitrite-containing radioactive wastes;
- the synergistic relationships between the normally independent radiolytic, free radical, and ionic reactions;
- the influence of metal ion complexation on the reaction sequences.

The fundamental role of solids in the formation and the retention of gas needs to be addressed especially because solids absorb and retain the gaseous products. Such solids also cause interfacial processes which affect the radiation chemistry in these complex systems.

*Interfacial Processes.* Many of the systems encountered across the waste management complex are heterogeneous in nature. Interfacial processes and, in particular, the interfacial charge transfer processes are areas of growing interdisciplinary activity. The interfaces of interest to the technical community include:

- colloidal suspensions (particles of transition metal oxides, silica, alumina, etc.) that can provide high surface area for reactions and catalytic sites;
- actinide oxides (self-irradiated interfacial aqueous layers);
- organic interfaces (solid organic/liquid and liquid/liquid interfaces);
- radiolysis of water at the first few monolayers from the solid;
- interfaces within confined spaces such as in zeolites and ion exchange resins that may be used to partition or recover radionuclides for waste management or for medical or industrial uses.

In parallel with the accumulation of experimental information on these interfacial processes, a modeling effort to describe the interface and guide further experiments would be needed.

*Computational Modeling of Chemical Processes.* Theory and computational modeling of radiation effects and chemistry are needed to complement experimentally determined reaction mechanisms involving radiolytic products. Computational modeling is essential in extrapolating experimental results to temperatures and pressures other than those under which experiments were conducted. Additionally, several approaches to modeling will be needed to gain a comprehensive understanding of the heterogeneous systems of interest in waste management. Research needs in this area include:

- *ab initio* calculations of radiolytically and thermally activated transition states and associated intermediates;
- quantum mechanical molecular modeling which includes the relativistic thermochemistry of actinides;
- molecular dynamics simulations of the structural and electronic properties of solutes, solvents, and solid surfaces;
- mixed thermodynamic/kinetic modeling of complex systems that includes a mechanistic understanding of gas production, radiolytically induced organic aging, and electron transfer reactions associated with radiation-induced radicals and catalytic surfaces;
- reactive transport modeling of non-Newtonian fluids to address gas retention as a function of fluid rheological properties.

*High LET Processes.* Studies of radiolysis by high LET particles are of particular interest to the applied radiation chemistry community involved in DOE's environmental management mission. Technical difficulties in performing experiments with these radiation sources have led to a significant gap in the fundamental understanding of processes initiated by high LET radiation as compared to  $\beta$  and  $\gamma$  radiolysis. Because of the short penetration depth of this form of irradiation, high LET radiolysis at interfaces is of major importance.

#### **IV. Waste Forms**

Experimental studies of vitreous and alternative waste forms are needed as well as theoretical modeling of the fundamental processes to ensure satisfactory waste form performance for the tens of thousands of years that the form must confine the radioactive waste.

*Radiation Chemistry of Vitreous Waste Forms.* Complex borosilicate glasses are the current medium of choice for immobilization/disposal of high level radioactive wastes. Although basic and engineering studies of radiation effects in these glasses were performed prior to constructing the vitrification facilities, research of a more fundamental nature is necessary to make acceptable projections of the stabilities of these waste forms for thousands of years. Research opportunities include application of appropriate spectroscopic methods for the identification of point defects, valence changes of multivalent ions, clustering of alkali ions, and possible bubble formation in nuclear waste glasses after irradiation by  $\gamma$  rays, electron beams, and ion implanters. This research would build upon the large body of knowledge concerning point defects in amorphous silicon dioxide ( $\alpha$ -SiO<sub>2</sub>) derived from magnetic resonance and optical spectroscopies, as well as more limited EPR results for binary alkali borate and silicate glasses. For example, a potassium

silicate glass subjected to a  $\gamma$  ray dose of  $10^8$  rad has exhibited easily measured EPR spectra of superoxide ( $O_2^-$ ) and ozonide ( $O_3^-$ ) ions (which through disproportionation should lead to  $O_2$  molecules). The studies should include silicate and borosilicate glasses of greater complexity subjected to radiation doses up to terarads ( $10^{12}$  rads) since little is presently known about such systems. Since experiments are limited to very high dose rates over short times, the relation of such experiments to the low dose, long term effects in a repository is a major question.

Two important research opportunities which should be pursued are (i) the determination of the effects of dose rate, total dose, type of irradiation, and temperature on the production of defects in model nuclear waste glasses; and (ii) the assessment of the validity of extrapolating high dose-rate, short-term measurements to predict long-term effects under lower dose-rate conditions. Meeting these goals requires:

- developing an understanding of the mechanism of radiolytic damage from the atomic to microscopic scales (in these studies, the initial emphasis should be put on the reference systems: silica, alkali silicates, and alkali borosilicates);
- quantifying the effects of radiation and temperature on the generation, secondary reactions, migration and agglomeration of defects (e.g., coalescence of interstitial molecular oxygen into bubbles);
- linking of specific defects with any undesirable endpoints;
- studying the effects of glass composition and microstructure on the nature of radiolytic damage.

A wide range of spectroscopic techniques is needed to characterize the onset and evolution of radiolytic damage. Presently, the only way to obtain a terarad irradiated glass (within a realistic temperature regime) is to use tightly focused particle beams on microscopic samples. Consequently, many techniques that are currently used to characterize physical and chemical properties of bulk glass samples cannot be applied, and novel microanalytical tools, such as single-site EPR using atomic force probes and micro-Raman, should be employed to study the damage in such terarad glasses. An alternative approach is to detect the defects leading to undesirable endpoints at the onset of their formation, under low-dose conditions, by:

- using innovative time-resolved techniques for detection of short-lived reactive precursors of point defects (ps linacs, multiphoton pulse-probe laser techniques, time-resolved EPR and IR spectroscopies, etc.);
- developing or adapting yet unexplored approaches to structural characterization of identified point defects (e.g., high-field EPR, pulsed EPR, Mössbauer, solid-state NMR);
- developing or adapting techniques for noninvasive, selective detection of specific defects leading to microscopic damage (a recent example is the detection of interstitial oxygen through laser-induced near-IR emission).

Characterization of radiation-induced changes in the redox states of transition-metal ions, and formation of new solid phases, should include:

- reactions of metal cations and clusters with diffusing atoms, water, and gases;

- radiolytically induced secondary redox reactions of metal oxides (disproportionation);
- mechanisms of formation and growth of metal clusters and phase separation of oxides.

The resolution of questions concerning oxygen bubble formation can be pursued through:

- a better understanding of the mechanisms of formation and coalescence of interstitial gases and the reactions of oxygen atoms and molecules with primary charges, excitons, and metal cations;
- the identification of the reduced phases in materials exhibiting oxygen bubble formation.

An assessment of influences of high-dose irradiation on corrosion and fracture resistance of glass waste forms can be pursued by studying:

- radiolysis at the glass/water interface;
- effects of radiolysis on migration of metal cations to the interface and on migration of water inside the glass;
- reactions of metal ions in unusual oxidation states and radiolytically-generated metal clusters with water.

*Alternative Waste Forms.* Although borosilicate glass is the waste matrix of choice at present, other waste forms are being studied for use in disposition of high level wastes. These forms include ceramic, mineral, and metallic materials. An important need is to develop an adequate data base on radiation effects on these materials and the associated change in release rate of the stored radionuclides from the matrix. For example, amorphization has been observed following irradiation of these crystalline materials at high doses. Much more research is needed to obtain quantitative relationships between the dose and the degree of amorphization and any associated change in release rate. It is also necessary to develop appropriate methods for measuring the release rate following irradiation based on an adequate understanding of the mechanisms associated with the perturbed release rates. Such an understanding would be based on research on these radiation induced mechanisms which, in many cases, may be the result of secondary effects of the radiation.

*Theoretical Studies.* Development is needed in several key areas of theory and computer simulation to provide a molecular interpretation of experimental observations and to allow reliable predictions on the long term changes in waste forms. Such needs include detailed knowledge at the atomic level of the primary defect sites, the interplay between ionizing and ballistic effects of impinging radiation, and the dose rate effects, including limitations on predictions from accelerated radiation techniques. The probability of second-order kinetic processes should be dependent on dose rate such that the ultimate fate of waste forms may be completely different than that extrapolated from results of high dose rate studies. Therefore, models must explicitly include non-zero and non-first-order effects to obtain realistic estimates of dose effects.

Detailed *ab initio* descriptions of atomic scale structures and improved interatomic potentials are required, together with reliable theoretical models of short- and intermediate-range order in complex glasses, to predict confidently defect migration and energetics. The development of new simulation methodologies, which include the possibilities of electronic excitation, is essential to predict accurately both charge and energy transport patterns and to provide a reliable assessment of defect-defect interactions leading to redox chemistry.

Useful predictive models of long term nuclear waste form performance must combine this nanoscale description with a reliable treatment of defect accumulation and microstructure evolution.

## **Panel D: Solution Kinetics and Catalytic Processes**

### **CHAIR:**

Carol Creutz (Brookhaven National Laboratory)

### **PANELISTS:**

Chris Arumainayagam (Wellesley College)  
James Espenson (Ames Laboratory, Iowa State University)  
Etsuko Fujita (Brookhaven National Laboratory)  
Dirk Guldi (Radiation Laboratory, University of Notre Dame)  
Anthony Harriman (Ecole Europeenne des Haute Etudes, Strasbourg)  
Gregory Hartland (University of Notre Dame)  
Arnim Henglein (Hahn-Meitner Institut, Berlin)  
Joseph Hupp (Northwestern University)  
Kenneth Jordan (University of Pittsburgh)  
Larry Kevan (University of Houston)  
Keith Madden (Radiation Laboratory, University of Notre Dame)  
James Merz (Radiation Laboratory, University of Notre Dame)  
Olga Mičić (National Renewable Energy Laboratory)  
Pedatsur Neta (National Institute of Standards and Technology)  
Marshall Newton (Brookhaven National Laboratory)  
Piotr Piotrowiak (Rutgers University)  
Tijana Rajh (Argonne National Laboratory)  
S. Steenken (Max-Planck-Institut für Strahlenchemie, Muelheim)  
Susan Tucker (University of California, Davis)  
Bradford Wayland (University of Pennsylvania)  
David Werst (Argonne National Laboratory)

## **I. Summary**

Panel D envisages an ongoing important role for radiation chemistry in contributing to basic knowledge of solution kinetics and catalytic processes needed for the utilization and development of environmentally benign energy technologies.

In homogeneous systems, pulse radiolysis provides a sensitive and flexible probe of systems of emerging interest: novel, tailored, multifunctional, supramolecular structures; shape and size selective homogeneous catalysts; catalysts for reduction of carbon dioxide and for oxidation of water to oxygen; and for oxygen and hydrogen transfer. Radiation chemistry will be invaluable in preparing and characterizing new, electronically excited states and in the development of new synthetic organic strategies for free-radical and carbocation based organic synthesis. Critical needs are emphasized for radiation chemical data in a wider range of media (organic solvents, supercritical fluids); for development and maintenance of databases for kinetic

and thermodynamic data; and for enhanced opportunities for university utilization of National Laboratory based radiation chemical facilities.

The radiation chemistry of heterogeneous systems is complex and underdeveloped at a time when incisive and potentially fruitful studies are needed to underpin emerging technologies. Special opportunities identified are: microporous and mesoporous oxides in which radiation chemistry can be used to introduce and study metal ions in new valence states; organic radical intermediates; and chemical defect sites. Such studies are needed to optimize the catalytic properties of these channel- and cage-containing materials already of great significance in industrial heterogeneous catalysis. Additional opportunities include nanoparticles, which can be synthesized and studied by radiation chemistry methods to exploit large band gap semiconductors, and the preparation and development of films and ordered arrays of metals and semiconductors as catalysts.

Radiation chemistry studies, particularly with ultrafast synchronized accelerator/femtosecond laser sources, will contribute to a molecular level understanding of electron transfer in homogeneous and heterogeneous systems. Special opportunities identified include: very fast electron transfers to test theory for adiabatic reactions; electron transfer in supercritical fluids and other novel media at the extremes of temperature, pressure, and pH; electron transfer involving high energy intermediates, synthetic peptides, DNA and proteins; exploitation of the interplay of theory and experiment and the rapid advances in computational power to model electron and nuclear energetics and dynamics.

## II. Homogeneous Reactions

Radiation chemistry has been used to answer a wealth of mechanistic questions in homogeneous aqueous media near ambient temperature and pressure (“Thermodynamics and Kinetics of Carbon Dioxide Binding to Two Stereoisomers of a Cobalt(I) Macrocycle in Aqueous Solution,” C. Creutz, H. A. Schwarz, J. F. Wishart, E. Fujita and N. Sutin, *J. Am. Chem. Soc.* **113**, 3361-3371 (1991)). Questions addressed have ranged from the properties and reactivities of species intrinsic to irradiation of water, such as the hydrated electron,  $e_{aq}^-$ , OH and H, to other “simple” radical systems  $O_2^-$  (“Peroxyl Radicals”, Ed. Z. Alfassi, Wiley, NY, 1997; “Chemistry of Reactive Oxygen Species” R.E. Huie and P. Neta, *Reactive Oxygen Species in Biological Systems: An Interdisciplinary Approach* Eds. D.L. Gilbert and C.A. Colton, Plenum Press, to be published in 1998), the oxidants  $Br_2^-$ ,  $I_2^-$ ,  $CO_3^-$ ,  $SO_4^-$ , and the reducing radical  $CO_2^-$  to much more complex organic and inorganic molecules.

The short-lived primary radicals produced in radiolysis of water react with aliphatic compounds such as alcohols, acids, amines, ethers, halogen compounds, amino acids, etc., to produce secondary radicals which undergo further reactions of addition, oxidation, reduction, abstraction, etc. Rate constants have been compiled for 2,500 reactions of 350 aliphatic carbon-centered radicals with various solutes. (For information about rate constants and yields for the radicals mentioned here, see the Notre Dame Radiation Chemistry Data Center web site at <http://www.rcdc.nd.edu>.) Fundamental knowledge of such species enables design of conditions for study of molecularly more complex systems, e.g., aromatic compounds, select enzyme systems, and select water soluble porphyrin and metal complexes. Electron reactions have been

used to produce the desired reduced transients to determine rates of halide elimination from aromatic anions; the protonation of very strong bases (nitrogen, carbon, or metal centered); and to characterize redox equilibria with extremely unstable species such as Tl(II) and  $\text{CO}_2^-$ . Conditions can be chosen such that a single radical is produced. Kinetic discrimination by  $e_{\text{aq}}^-$ ,  $\text{CO}_2^-$ ,  $\text{CO}_3^-$ ,  $\text{N}_3$ , and other radicals has been used to produce non-equilibrium distributions of donor sites in multi-center redox molecules so that the rates of intramolecular electron transfer could be determined. Extension of such capabilities to other media will provide opportunities for new mechanistic and chemical breakthroughs.

The complementarity of flash photolysis and pulse radiolysis methods has been laid out elsewhere (*Photochemistry and Radiation Chemistry; Complementary Methods for Study of Electron Transfer*, Wishart, J. F. and Nocera, D. G., Eds.; *Adv. Chem. Ser.* **254**, American Chemical Society, 1998). Advantages of pulse radiolysis with UV-visible spectroscopic detection include: (i) High sensitivity for weakly absorbing species, especially ligand-field absorptions of first transition series metal ions; (ii) No (or at least less) inner filter. Functional photochemical systems of necessity contain species that strongly absorb light in some region of the spectrum. The sensitizer absorption makes it much more difficult to detect signal changes arising from chemical reactions not involving the sensitizer, especially when the desired signals are small; (iii) Synthetic control of the radicals produced as noted above; and (iv) Experimental flexibility through ready control of reagent concentrations through dose variations and through convenient changes of gases and pH.

*Novel Molecular Systems.* One promising opportunity for radiation chemistry lies in the recent availability of tailor-made molecules intended to address energy-related issues. Collaborations between synthetic chemists and radiation chemists can fruitfully explore multi-component molecules containing a series of functional units, including more elaborate systems based on molecular recognition principles. Radiation chemists must make these possibilities clear to those preparing large and complex molecular systems. Important on-going problems include the following: mapping of protein surfaces; long-range information transfer; electron tunneling across hydrogen bonds; atom-transfer and catalytic reactions; and chiral selectivity.

Supramolecular chemistry, whereby organized assemblies are formed by association of simpler molecular components, is a rapidly expanding area and can also benefit from the work of radiation chemists. Numerous supramolecular architectures (e.g., rotaxanes, helicates, knots) have been constructed. These systems usually contain several metal centers in close proximity or derive their structural integrity from multiple charge-transfer interactions between proximal aromatic units. The information stored in these structures can be switched by subtle modification of the binding energy that occurs upon changing the oxidation state of the metal or the electron affinity of the aromatic groups. Pulse radiolysis makes it possible to monitor the conformational changes that follow from injection of charge into the assembly. Important kinetic information can be obtained about how such intricate molecules unwind and re-arrange into new entities. This has obvious relevance to natural and modified enzymes, and is critical for a proper evaluation of future miniaturized electro-mechanical devices. Many such systems, like the double- and triple-stranded metallo-helicates, are now available in large quantities and have been studied by classical electrochemical methods. Evaluation of kinetic and mechanistic data

for the conformational changes that occur upon external stimulation will provide guidelines for energy-related projects.

*Kinetics and Mechanistic Studies of Chemical Reactions.* Pulse radiolysis is a unique technique that provides kinetic and mechanistic information on reactions of fundamental importance. The power of the technique is its ability to generate specific intermediates, such as radical cations, radical anions, or unstable oxidation states of metal complexes. Such species play prominent roles in catalysis and, in fact, radiation chemistry is invaluable for exploring catalytic mechanisms. Important opportunities remain. For example, the recent emergence of shape- and size-selective homogeneous catalysts is a field where radiation chemistry should be of special importance for unravelling reaction mechanisms. In particular, the reduction of carbon dioxide continues to be an attractive goal. Pulse radiolysis can contribute also to many other energy-related problems, including water reduction or oxidation, proton transfer, oxygen and hydrogen atom transfer, hydride transfer, and activation of hydrocarbons. Understanding the role of radicals in alkane monooxygenase oxidations can guide the design of new oxidation catalysts in the same way that understanding of photosynthesis has led to improved approaches to artificial photosynthesis.

Important future applications of radiation chemistry include redox-initiated bond formation or breaking, multi-electron reactions, and electron transfer in and through unusual media (e.g., membranes, reactive solvents, and molecular bridges). Specifically, transition metal complexes which activate small molecules can be addressed by the pulse radiolytic technique under conditions that allow key intermediate species to be identified and their reactivity to be monitored in real time. The technique is readily amenable to mechanistic studies under an unusually wide variety of operating conditions. Having established kinetic data for individual reactions, it becomes possible to extend the analysis to increasingly more complex and heterogeneous systems. In this way it becomes possible to model real world conditions under which competitive side reactions detract from the desired catalytic goal. The purpose of this work is to optimize important catalytic processes and to design more selective and efficient catalytic systems.

*Synthetic Strategies with Radiation Chemistry.* Radiation chemical methods can implement free-radical based methods for organic synthesis. This is a versatile method for generating radicals and other reactive species. It is applicable for real-world samples, including those which are transparent, turbid, or opaque. The identification of highly selective radical reactions, and recognition of the persistent radical effect, now open previously unrecognized synthetic opportunities. One technologically significant application is radiation-initiated living radical polymerization which provides new strategies for the design of block copolymeric materials. Significant use of radiation chemistry in synthesis requires detailed kinetic and thermodynamic characterization of non-aqueous solvent systems compatible with organic synthesis. Pulse radiolytic studies are necessary to provide information for the relevant reaction media. (Fossey, J., Lefort, D., Sorba, J. *Free Radicals in Organic Chemistry*, John Wiley and Sons: Chichester, 1995; Barton, D., *Sir Half a Century of Free Radical Chemistry*, Cambridge University Press: Cambridge, 1993; Curran, D. P., Porter, N. A., Giese, B. *Stereochemistry of Radical Reactions: Concepts, Guidelines, and Synthetic Applications*, John Wiley and Sons: New York, 1996; Georges, M. K., Veregin, R. P. N., Kazmaier, P. M., Hamer, G. K., "Narrow Molecular Weight Resins by a Free-Radical Polymerization Process," *Macromolecules*, **26**, 2987-2988 (1993); Use

of living free radical polymerization (using tempone as the capping group) from Michael Georges at Xerox in Ontario.)

*Media and Unusual Conditions.* To accommodate the widest possible range of substrates, solvents such as DMSO, DMF, acetonitrile, propylene carbonate, and THF should be studied by radiation-chemical methods in order to determine the primary processes and the primary product yields and to develop methods for manipulating reactive intermediates by adding suitable chemical scavengers.

The radiation chemistry of many compounds in aqueous solutions has been studied mostly under mild conditions. However, under extreme pH conditions the rates and mechanisms may be quite different. Since there is high “real world” interest in such extreme conditions, e.g. strongly acidic media in stratospheric aerosols and strongly alkaline media in radioactive waste tanks, the effects of such extreme pH's on the behavior of free radicals should be investigated.

Many technological and biochemical processes involve free radicals and other short-lived intermediates. Current examples include advanced oxidation technologies in various media, including supercritical fluids, and the biochemistry of NO and peroxyxynitrite. Radiation chemistry is a perfect tool for providing mechanistic and kinetic information on the intermediates involved in such processes. This can be done in the form of new measurements directed to specific processes.

*Chemical Reaction Databases.* It is crucial to critically review numerical properties and to compile them into electronic databases. These include, for example, reaction rate constants, transient spectra, reduction potentials, and radiolytic yields. This information aids in experimental design of all aspects of radiation chemical research, and enables one to optimize experimental conditions and avoid duplication of effort. Such databases are accessible to the casual user and aid in disseminating data to the greater chemical community. The Notre Dame Radiation Chemistry Data Center (web site at <http://www.rcdc.nd.edu>) currently fulfills this important role.

### **III. Heterogeneous Systems**

Radiation chemistry of heterogeneous systems is complex and underdeveloped at a time when incisive studies are needed to underpin emerging technologies involving heterogeneous systems. Indeed, many areas in chemistry are now successfully focusing more on complex systems. Heterogeneous systems involving constrained environments are of increasing importance in chemistry and present an opportunity for greater focus in radiation chemistry. Major topics include metal and semiconductor nanoparticles, microporous and mesoporous oxide materials, catalytic systems, polymers and polymer films, heterogeneous chemical sensors, microelectronic materials, reactions on surfaces, nanoscale lithography, nonlinear optical materials and high temperature superconductors. Reflectance optical techniques should be better developed and utilized for heterogeneous systems along with continued development of magnetic resonance techniques and newer single molecule spectroscopy methods such as confocal microscopy and near-field scanning optical microscopy.

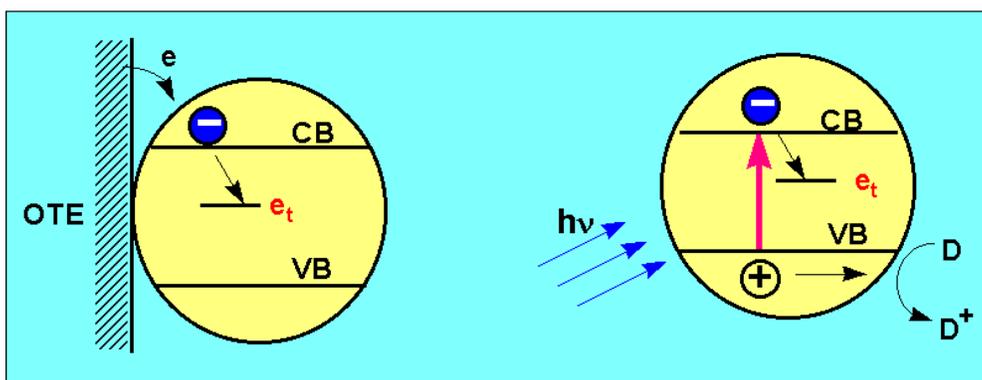
*Microporous and Mesoporous Oxides.* Microporous and mesoporous oxide materials, such as aluminosilicates (zeolites), aluminophosphates and silica materials, with channels and cages smaller and larger than about 20 Å respectively, are of dominant importance in industrial heterogeneous catalysis and of developing importance in microchemical sensors. Radiation chemistry has been used to create new valence states of metal ions, organic radical intermediates, and chemical defect sites which modify the catalytic properties of such oxide materials. Often these new chemical species can be stabilized in these oxide materials to create new catalytic potential which can be controlled and targeted towards specific catalytic objectives. (“Electron Spin Resonance and Electron Spin Echo Modulation Evidence for the Isomorphous Substitution of Ti in TAPO-5 Molecular Sieve”, A.M. Prakash, Vadim Kurshev and Larry Kevan, *J. Phys. Chem. B*, **101**, 9794 - 9799 (1997); “Spin Probes of Adsorption and Chemistry in Solids: Zeolites as Model Systems,” Werst, D. W. and Trifunac, A. D., *Mag. Reson. Rev.*, in press; “Radiation Induced Physical and Chemical Processes in Zeolite Materials,” Zhang, G. H., Liu, X. S., Thomas, J. K., *Radiat. Phys. Chem.*, **51**, 135-152 (1998); “From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis”, Corma, A., *Chem. Rev.* **97**, 2373-2419 (1997).)

There seems to be great opportunity to significantly expand the use of radiation chemistry in this area along with the application and further development of optical, vibrational, and magnetic resonance characterization techniques commonly used in radiation chemistry. In particular, better development of transient methods applied to solid materials is needed. Incisive determinations of the local structural environment and its distortion around such radiation-induced species are needed since subtle distortions may have large effects on such stabilization. Controlled destabilization is another desirable goal. Custom stabilization of a whole host of catalytically active sites and intermediates is potentially possible. This should lead to better elucidation of the molecular details of catalytic processes on oxide surfaces which can lead to better catalytic control.

*Nanoparticles.* In colloid science, radiation chemical methods are contributing to the understanding of the electronic properties of semiconductor and metal nanoparticles. Such nanoparticles are important in chemical catalysis, photocatalysis (solar energy conversion), and electrocatalysis (Figure 8). As nanodevices are being developed in various laboratories, it is important to learn about the properties of the materials in the nanodimension. (A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **94**, 600 (1990); J. Michalik, “Silver Atoms and Clusters in Molecular Sieves and Clays”, *Appl. Magn. Reson.*, **10**, 507 (1996).) Radiation is a unique tool for the preparation of many nanoparticles and the study of their electronic properties. For example, excess electrons or excess holes can be deposited in a controlled manner on nanoparticles, and the chemical fate of the deposited charge carriers and the changes in the optical properties of the particles can be studied using pulse radiolysis. Opportunities for future research include the following topics:

- Large band gap semiconductors, such as metal oxides, can be further developed for radiation induced reactions. Radiation is able to excite such semiconductors whereas visible and UV light cannot do so. Because of the extremely strong reducing and oxidizing power of such particles, it is expected that strongly endothermic reactions can be initiated which are of interest for the synthesis of energy rich fuels.

- The radiation chemical preparation of nanocrystalline films of metals and semiconductors and ordered arrays of nanoparticles can be developed as novel catalysts in chemistry and photochemistry.
- Pulse radiolysis studies on the mechanism of nanoparticle formation should be further developed including the detection of “magic” clusters. Such studies complement molecular beam studies which are carried out on clusters in vacuum in various laboratories.
- Studies of the electrochemical behavior and electronic structure of subnano- and nanoparticles can be developed using radiation chemical techniques. This is important for a better understanding and improvement of certain technological processes such as metal deposition, corrosion, catalysis, and electrocatalysis.
- Pulse radiolysis can aid in the characterization of dyes adsorbed on nanocrystalline large band gap semiconductor surfaces. Selective charge injection into the dye and/or the semiconductor will provide information on the mechanism of charge separation processes in novel nanocrystalline dye sensitized photovoltaic cells.



**Figure 8.** Electron trapping in metal oxide nanoparticles by electrochemical and band gap excitation methods. Color changes observed as a result of charge trapping processes are reversible and have potential applications in display devices.

*Surface Chemistry.* The understanding of reactive species at surfaces is critical in such key areas as catalysis and the growth and processing of semiconductor structures. For example, an important application is the continuing effort to “shrink” semiconductor microelectronic circuits. (*Nanolithography: A Borderland Between STM, EB, IB and X-ray Lithographies*, Gentili, M., Dordrecht, Boston: Kluwer Academic Publishers, 1994.) This is essential for the next leap in miniaturization of electronics and for exploitation of novel quantum effects in new electronic and optical devices. However, the realization of nanometer resolution will only be achieved by employing a variety of techniques, such as self-organized assembly and the use of electron-beam lithographic and processing techniques, for which a molecular-level understanding of surface chemistry will be essential. Among the issues for the radiation chemist are the radiation chemical processes involved in the use of current and possible new resists, resist sensitivity, and energy transfer between resist molecules and the substrate. The subsequent transfer of patterns

from the resist into a semiconductor multilayer system, used for a final array of nanostructure devices, requires additional fundamental knowledge about the chemical nature of the etching process. Current processing technologies employ low-energy plasma or reactive-ion etching, for which the chemical processes are not well established. This is an area where radiation chemists can make considerable contributions with their ability to produce and determine the fate of reactive intermediates. These problems place the radiation chemist at the interface of several disciplines and promise exciting interactions.

Radiation chemistry can be used to produce and characterize surface intermediates important in the rational design of catalysts. For example, bond-specific electron-induced dissociation of adsorbates can be used to synthesize catalytically interesting surface intermediates in significant quantities, permitting characterization by an array of powerful surface science tools.

#### IV. Electron Transfer Processes

Electron transfer is the fundamental event underlying a range of critically important chemical and biological processes, both in homogeneous and heterogeneous systems. Understanding the appropriate mechanisms at a molecular level can be achieved by the use of radiation chemistry methods, in particular the emerging ultrafast synchronized accelerator/femtosecond laser sources.

An emerging theme in electron transfer chemistry is chemical complexity. Obvious drivers are multielectron catalysis (e.g. hydrogen evolution/removal in mixed waste environments, dioxygen generation from water), redox-induced bond breaking (e.g. remediation of haloalkane and dioxin contaminated sites), ion-coupled interfacial electron transfer (electrochemical photovoltaic energy conversion), and electron transfer in or through unusual media (e.g., bio-films, reactive solvents, and single-molecule bridges). Two or more of these themes can be combined, for example, exploiting long-range electron transfer to induce cleavage of a bond far from the initial capture site, i.e. "chemistry at a distance." ("Contemporary Issues in Electron Transfer Research," P. F. Barbara, T. J. Meyer, and M. A. Ratner, *J. Phys. Chem.* **100**, 13148-13168 (1996); "Electron Transfer Reactions," *Chem. Rev.* **92**, (365-490, (1992); M.D. Newton, *Chem. Rev.*, **91**, 767-792 (1991); C. C. Moser, J. M. Keske, K. Warncke, R. S. Farid, P. L. Dutton, *Nature*, **355**, 596-802 (1992); G. L. Closs, J. R. Miller, *Science*, **240**, 440-447 (1988); *Photochemistry and Radiation Chemistry: Complementary Methods for the Study of Electron Transfer*, Wishart, J. F., Nocera, D. G., Eds.; *Adv. Chem. Ser.* **254**, American Chemical Society: Washington, DC, (1998); "Highly Mobile Electrons and Holes in Isolated Chains of the Semiconductor Polymer Poly(phenylenevinylene)," *Nature*, **54** 392 (1998).)

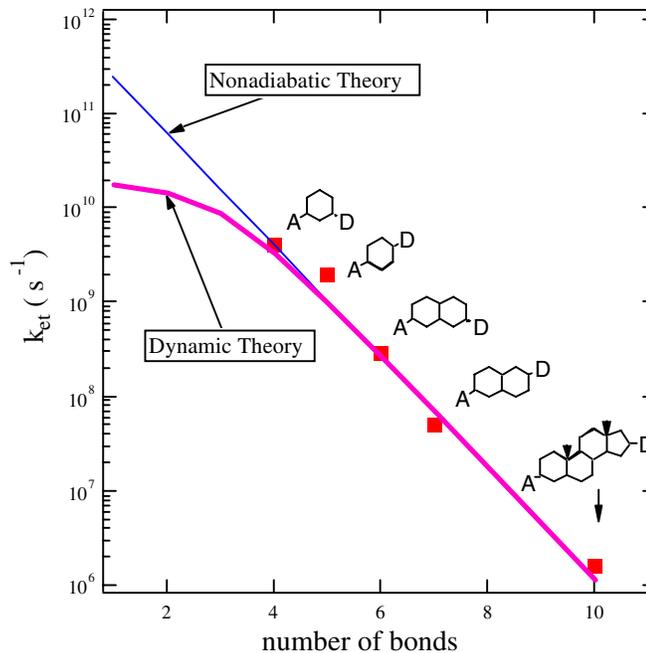
Supercritical fluids constitute a new exciting medium with highly practical applications. Well characterized electron transfer systems should be utilized as probes of the solvation energetics and dynamics in these solvents. In addition, studies of electron transfer related processes should be extended to extreme pressure, temperature, and pH conditions. ("The Measurement of an Electron Transfer Reaction in a Non-Polar Supercritical Fluid," K. Takahashi, C. D. Jonah. *Chem. Phys. Lett.*, **264**, 297 (1997); "Electron Attachment to NO in

Supercritical Ethane," M. Nishikawa, R. Holroyd, and K. Itoh. *J. Phys. Chem. B* in press, (1998).)

Another major scientific and intellectual challenge is the independent creation of potent intermediate species that are by their very nature highly unstable with respect to further chemical reaction. Access to these would offer unprecedented opportunities for rapid production and subsequent mechanistic examination of high-energy one-electron intermediates. In many cases these species are inaccessible via conventional photochemical methods (e.g., precursors may be non-light absorbing) or electrochemical methods (indiscriminate delivery of multiple electrons can sometimes occur). Radiation methods, in contrast, are often uniquely well suited to high-energy chemical intermediate creation. Relevant examples include: unusual oxidation states of transition metal systems; intermediates in multielectron transfer catalysis, naked metal atoms, and nanoscale metal particle dispersions (colloids); preparation of conduction band or trapped electrons in semiconductors without creation of holes (or conversely, creating holes without electrons); and creation of organometallic radicals that can be used to launch complex inner-sphere reactions, e.g. net atom transfer reactions. Many contemporary heterogeneous catalysis problems in condensed phases in fact are interfacial electron transfer problems.

Electron transfer in biological systems (proteins, DNA, and synthetic peptides) poses a particularly worthwhile challenge to radiation chemistry. Most of these electron transfer processes proceed on ground-state potential energy surfaces, making pulse radiolysis a truly unique tool for these studies. The potential payoff of these investigations is enormous, with its scope ranging from fundamental science to radiation protection. ("DNA: A Molecular Wire?" J. M. Warman, M. P. de Haas and A. Rupprecht, *Chem. Phys. Lett.* **249** 319-322 (1996); S. Steenken, *Chem. Rev.* **89**, 503 (1989).)

Pulse radiolysis is particularly valuable for critical tests of the predictions of electron transfer theories because it enables experiments in which the energetics do not depend on distance or solvent polarity. Fast, laser-coupled accelerators will enable new experiments, such as this proposed test of "dynamic control" of electron transfer rates at short distances. The plot in Figure 9 compares existing rates with two theoretical ideas: 1) nonadiabatic theoretical predictions that rates will continue to increase as electronic coupling increases, and 2)



**Figure 9.** In "dynamic control," intramolecular electron transfer rates at short distances would be limited by rates of solvent motions.

dynamical theoretical predictions that rates will be limited by solvent motions, but not by the electronic coupling between donor (D) and acceptor (A) groups. Laser-coupled accelerators make possible measurement of rates in the region in which the theories differ.

*Electronically Excited States.* Historically, pulse radiolysis has been used to produce reactive species in their *ground* electronic states. However, the availability of the strongly reducing solvated electron as a reagent in pulse radiolysis opens the door to producing electronically excited states. Such states are most likely to be formed when the reaction to produce the ground electronic states is extremely exergonic and lies in the Marcus inverted region. Excited states of organic radical ions or metal complexes are hypothesized to be products of many highly exergonic electron transfer reactions and may be very useful in schemes to measure very fast electron transfer. But little is known about those excited states, which have rarely been characterized. Experiments with new accelerators can answer critical questions: Are excited states produced by capture of solvated electrons or solvated holes? Can radiation chemistry techniques, particularly with newer, fast accelerators, be a powerful method for determining their excited-state spectra, lifetimes, energies, and reactions?

The advent of fast (5 ps) accelerators opens a new domain in which cooling of the highly energetic intermediates can compete with electron transfer processes. Similarly, formation of vibrationally hot acceptor states can occur. These effects will require use of time resolved Raman and IR spectroscopy. The necessary capabilities should be added to the state-of-the-art accelerators.

Interaction between theory and experiment will play an increasingly important role in resolving these issues, both in the design and the analysis of novel experimental schemes. Here the rapid advances in computational power and the ability to realistically model the complex systems, including the capabilities for self-consistent treatment of electron and nuclear energetics and dynamics, are major developments.

It is to be emphasized that in resolving the crucial issues in electron transfer highlighted above, the complementary capabilities of radiation chemistry and laser spectroscopy should be fully exploited. To make the most of these opportunities, it is essential to maintain the strongest possible links between the National Laboratory facilities and the universities, and to ensure that the evolution of these facilities keeps pace with the emerging scientific problems.

## **Panel E: Environmental Remediation**

### **CHAIR:**

Prashant V. Kamat (Radiation Laboratory, University of Notre Dame)

### **PANELISTS:**

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David Bartels (Argonne National Laboratory)

Joan Brennecke (University of Notre Dame)

Diane Cabelli (Brookhaven National Laboratory)

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## **I. Summary**

Environmental remediation using radiation chemistry is one of the most promising Advanced Oxidation Processes (AOP), but we currently lack the ability to predict and control the radiation chemical processes in complex environmental systems. This panel has identified four major topics in the basic research areas of (i) heterogeneous radiolysis, (ii) reaction mechanism and kinetics in homogeneous solutions, (iii) incorporation of emerging methodologies such as supercritical fluids, and (iv) theoretical and kinetic modeling of systems relevant to environmental remediation problems.

A more fundamental understanding of radiolytic reactions in heterogeneous systems is necessary in order to establish the resultant chemistry and predict the ways with which we can control chemical transformation in complex environmental systems such as those found in natural and synthetic environments. It is imperative that we understand how the radiation source, intensity, and energy determine reaction rates, mechanisms, and product distribution in heterogeneous systems and address the issue of radiation catalytic effects induced by metal oxide supports.

Understanding the basic mechanisms of advanced oxidation processes will allow optimization of the technological processes, with respect to versatility and commercial

competitiveness. The issues involved here are (i) establishing the mechanisms of free radical reactions such as those applicable to remediation processes, and (ii) improving the overall efficiency of remediation by controlling the reactivity and the generation of free radicals. It is also necessary to elucidate the roles of secondary radicals generated in competition with the primary oxidation of target contaminants.

There is a need for studies which characterize supercritical fluid solvent environments and correlate this characterization with observed reaction dynamics and transport of solute species. Radiation chemistry has an important role to play as a unique tool in the study of such supercritical fluid solvent effects in electron transfer, redox, and free radical reactions.

Theoretical and kinetic modeling efforts should be directed towards (i) providing a means to predict critical quantities not readily measured, (ii) offering a protocol for prioritizing future experiments, and (iii) providing a microscopic picture of a system of interest where reactivity is not well understood.

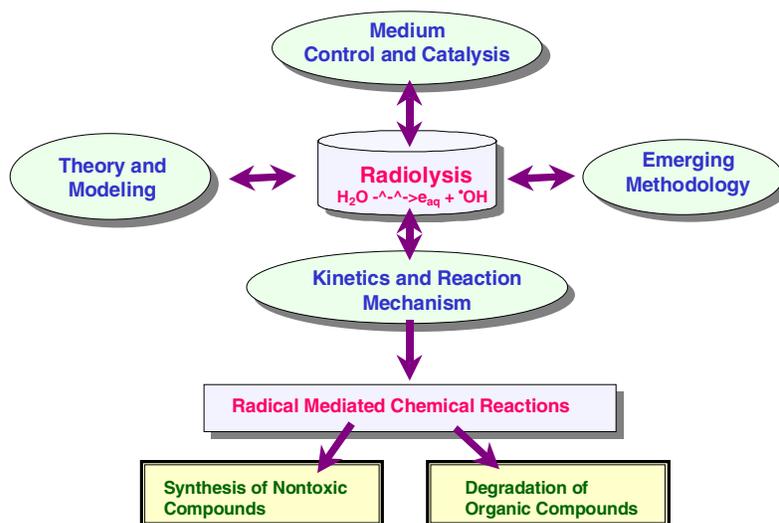
## II. Status and Issues

The purification of water and air resources is a challenging issue for the 21<sup>st</sup> century. While society enjoys the comforts and benefits that chemistry provides, from drugs to dyes, from composites to computer chips, the task of treating wastes generated during manufacturing and processing of the commodities, and the appropriate disposal of various products and byproducts is becoming a major concern. Consider for example, the problems encountered with halogenated organic compounds. The ubiquitous nature of halogenated organics, from trichloroethylene to the wood preservative pentachlorophenol, has spawned considerable discussion about the impact of such halogenated organics in the environment. Chlorophenols are a serious health concern in drinking water treatment as they can be present in the source water or be formed as a byproduct of chlorine-based disinfection methods. The chemistry of chlorophenol is representative of the chemistry of a class of much more toxic pollutants such as chlorinated dioxins, chlorinated dibenzofurans, and polychlorinated biphenyls (PCBs). Another class of compounds that has emerged as a focus of attention, *vis-a-vis* their impact on the environment, is dyes and pigments which are the single largest group of industrial chemicals produced (Tincher, W. C., *Textile Chemist and Colorist*, 1989, 21, 33; Kamat, P. V. and Vinodgoopal K., in *Organic and Inorganic Photochemistry*, Ramamurthy, V. and Schanze, K. eds. Marcel Dekker, 1998, vol.2, 307).

Environmental remediation using radiation chemistry is one of the most promising Advanced Oxidation Processes (AOP). UV-peroxide, ozonation, the photo-Fenton process, photocatalysis, and sonolysis are some of the other popular methods employed to oxidize the organic compounds (See for example, Ollis *et al.* *Environ. Sci. Technol.* 1991, 25, 1523; O. Legrini *et al.*, *Chem. Rev.* 1993, 93, 671-698). These methods are based on one distinguishing feature, the generation and use of hydroxyl radicals as the primary oxidant for the degradation of organic pollutants. Mineralization may not be a necessary avenue for remediation in all cases. Conversion of a pollutant into a useful nontoxic product (e.g., fuel or polymer) may be an alternative desirable goal.

Free radicals are formed when water is irradiated with ionizing radiation such as  $\gamma$  rays or a high energy electron beam. These radiolytically generated radicals are very effective in degrading organic compounds (See for example, Getoff, N. and Solar, S. *Radiat. Phys. Chem.* 1986, 28, 443; Hilarides, R. J. *et al. Environ. Sci. Technol.* 1994, 28, 2249; Stafford, U. *et al. J. Phys. Chem.* 1994, 98, 6343; Cooper, W.J., Curry, R.D., and O'Shea, K.E., eds, *Environmental Applications of Ionizing Radiation*, Wiley-Interscience, New York, 1998). The strengths of radiation chemistry are its capability to selectively generate radicals with desirable properties and to provide a procedure for investigating ionic species and one-electron redox processes (Von Sonntag, C. and Schuchmann, H.-P., *Angew Chem. Intl. Ed.* 1998, 30, 1229; Mao Y. *et al. J. Phys. Chem.*, 1991, 95, 10080). In homogeneous solutions, a technique that has been of particular value for the evaluation of the elementary steps and the identification and characterization of the transients is time-resolved pulse radiolysis. This is a particularly powerful tool when used in complement with time-resolved laser photolysis to study excited states and radicals generated from homolytic bond rupture.

Radiation processing is extensively used in industry to produce a wide range of products. In the environmental area there have been many successful demonstrations of radiolytic destruction of pollutants in liquid and gas phases, as well as some reports of its effective use in mixed and solid phases. Since environmental systems, such as soils, are composed of complex mixtures of minerals, metals, humic substances, ions, microorganisms, and inorganic and organic contaminants, it is necessary to understand radiolytic reactions in multicomponent and multiphase systems. Use of radiolysis in the environmental remediation of wastewater and contaminated soil and sediment is a promising treatment technology, but the ability to predict and control resulting chemistry is lacking. Along with the removal of target chemical contaminant, one should also address the issues concerning the elimination of a series of intermediates of progressively higher oxygen-to-carbon ratios that are involved in the conversion of an organic molecule to  $\text{CO}_2$ . Therefore, it is essential to improve substantially our basic understanding of the radiation chemistry (reactions, pathways, and rates) in various systems, especially those made up of mixed inorganic and organic phases. This is outlined in Figure 10.



**Figure 10.** Radiation chemistry strategies for environmental remediation.

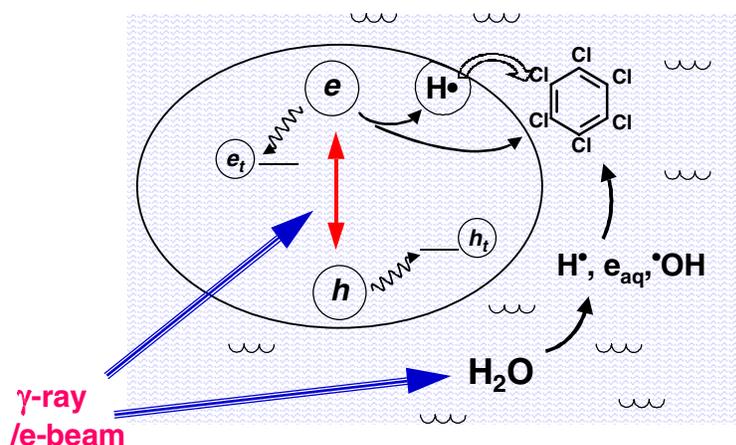
A comprehensive compendium of experimental results on the reactions of reactive species with a wide variety of compounds currently exists at the Notre Dame Radiation Chemistry Data Center. This database and bibliography is widely used and considered essential for all groups involved in remediation studies, from the most basic to the most applied. Maintenance of this database and expansion of it into more extensive compilation of metal reactions, heterogeneous systems, and other reactive radicals is essential.

### III. Heterogeneous Radiolysis

A fundamental understanding of radiolytic reactions in heterogeneous systems is necessary in order to establish the reaction mechanisms and control chemical transformation in complex environmental systems, such as those found in natural and synthetic environments.

*Fundamental Radiation Chemical Processes Occurring in Complex, Heterogeneous Matrices.* In order to understand heterogeneous radiolysis in complex media, it is necessary to study pollutant interactions at simple inorganic and organic surfaces. The goal of these studies is to understand energy deposition in environmental solids and the transfer of this energy to material sorbed at the interface, and to elucidate reaction mechanisms and kinetics at interfaces (illustrated in Figure 11). This would also allow the rational design of remediation strategies.

It is important that the studies on the single component model systems be complemented with parallel studies on real systems. This will provide a sensitivity analysis to identify rapidly the most important factors. Those features anticipated to be particularly important in the inorganic phase(s) are the radiation-induced catalysis on oxides and the role of metal centers on oxide surfaces.



**Figure 11.** Surface mediated versus solution mediated charge-transfer processes: radiolytic dechlorination of hexachlorobenzene in oxide slurries.

There is a substantial need for the development of theory to predict the reactivities of metal oxides because of the variety of their properties. In the organic phase(s) the impact of Natural Organic Material (NOM) and the role of synthetic surfactants are clearly of importance (Hilarides, R. J. *et al.*, *Environ. Sci. Technol.* 1994, 28, 2249), but are poorly, if at all, understood in environmental systems and little insight is provided by previous studies using aqueous-phase radiolysis. Furthermore, there are potentially many opportunities to promote reaction specificity

and to tailor chemistry using surface modification (with redox active groups, metal, silanization). Structure/reactivity relationships for various classes of pollutants are also considered to be a research priority.

Electron and hole trapping, triplet excitons, and surface-promoted chemical reactions dominate when oxides and zeolites are subjected to high energy radiation (Zhang, G. *et al.*, *Radiat. Phys. Chem.* 1998, 51, 135; Shkrob, I.A. and Trifunac, A.D., *J. Chem Phys.* 1997, 107, 2374). There is a need to understand the catalytic properties of different oxides for promoting degradation of adsorbed organic compounds. Since environmental systems are complex and consist of mixed phases of inorganic and organic components, it is necessary to determine the ways in which the radiation chemistry at simple interfaces predicts interactions in the actual systems. First, an understanding of the micro- and mesostructure of the environmental system is required and subsequently the nature of multiphase radiolytic interactions needs to be elucidated. This description must also include partitioning of the pollutants amongst the various organic domains, sorption and orientation at interfaces, reactive interactions with interfaces to which the pollutant is sorbed, and free radical diffusion in systems less dense than soils.

The complexity of the systems and the number of potentially important factors require the identification of the important controlling reactions and reactants. Strong coupling between model and real systems is necessary to assure that the most important reactions and reactants have been identified and that the interactions between the various components of the system are correctly interpreted.

*Influence of Radiation Source (Type and Energy) on the Chemistry Occurring in Heterogeneous Systems.* The radiation chemistry of solutions is somewhat understood. This is not the case, however, in solid systems where dose rate and interfacial effects promote differences in the reaction kinetics and efficiencies produced by gamma irradiation and high energy electron beams. Therefore, it is imperative that we understand how the radiation source, intensity, and energy determine reaction rates, mechanisms, and product distribution in heterogeneous systems. It is also important to consider the effect of pulsed versus steady-state radiation on the resultant radiation chemistry. There is a critical need to establish a procedure to determine absorbed dose and distribution of absorbed dose in solid systems or heterogeneous slurries. Such methods are particularly essential in order to experimentally verify mathematical predictions (Monte Carlo simulations) of dose distributions in heterogeneous cross-sections.

*Extending Fundamental Understanding to Solve Challenging Problems in Environmental Remediation.* Depending on the specific features of the environmental remediation problem, there are a variety of ways in which radiolysis may be employed. While it may prove to be highly effective as a single-step treatment process, it is more likely that knowledge of the factors that influence reaction specificity may provide the means to control degradation reactions and target pollutant transformations. These reactions may result in enhanced solubility (enhanced bioavailability) and diminished toxicity (enhanced biodegradability), leading to successful integration of heterogeneous radiolysis with other treatment strategies, such as bioremediation.

Radiolysis of pollutants in organic matrices may also result in cross-linking of the pollutant into the natural organic matrix, thereby immobilizing it in a nontoxic and/or nonbioavailable form. Since the scale of the soil and sediment contamination is so large, in situ

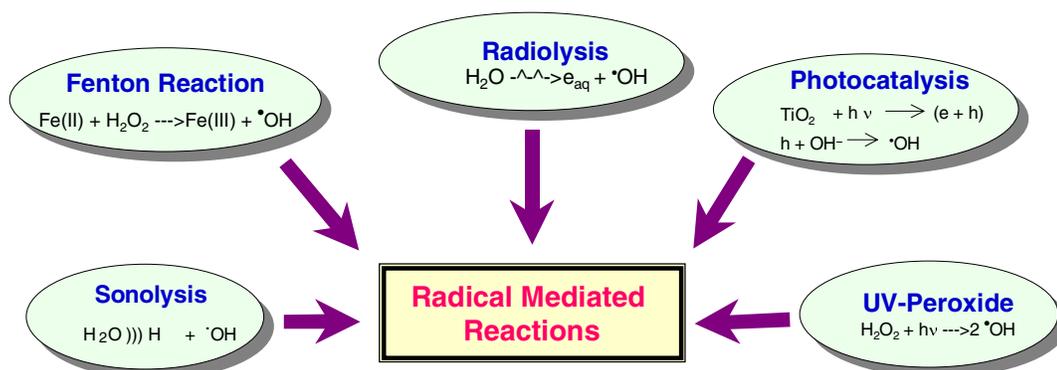
remediation processes are often considered the only economic means of treatment. Complete knowledge of the catalytic properties of natural or synthetic oxides and clays would offer pollution control strategies other than degradative pathways, and promote synthetic pathways and methods to recover and/or recycle resources. Finally, enhanced understanding of radiation chemistry in heterogeneous systems will also serve as a useful tool to characterize environmental systems and give additional insights into other (nonenvironmental) heterogeneous systems.

Addressing all inherent aspects of the chemical problems outlined above requires new techniques and updating of established methods. Of particular interest is the necessity to monitor transient behavior in heterogeneous systems. Time-resolved detection techniques such as conductivity, microwave absorption, resonance Raman, near IR, and pulsed multifrequency EPR should be extended to meet the new experimental needs.

#### IV. Kinetics and Mechanisms of Radical Reactions in Homogeneous Solution

Degradation of environmentally hazardous chemicals is often initiated via short-lived radical intermediates. In order to predict and understand the fate of contaminants in waste streams and evaluate new strategies for environmental remediation it is essential to establish the underlying chemistry at a fundamental level. Rate constants of free radical reactions, equilibrium constants, and redox potentials of short-lived transients obtained using pulse radiolysis would be valuable in designing radiolytic degradation of organic compounds.

*Radiolysis in Relation to Advanced Oxidation Processes.* Understanding the basic mechanisms of AOP (e.g., UV-peroxide, ozonation, the photo-Fenton process, photocatalysis, sonolysis, and gamma radiolysis; profiled in Figure 12) will allow optimization of conditions and provide desired versatility and commercial competitiveness. It is particularly important to establish the mechanisms of the free radical reactions in the remediation processes, and to improve the overall efficiency of remediation by controlling the reactivity and generation of free radicals.



**Figure 12.** Advanced oxidation processes induce chemical degradation via oxidative radical (e.g. •OH) generation.

Potential systems for the purification of ground water involve the use of metals in high oxidation states. These can be studied effectively using radiation chemistry techniques which enable selective oxidation and reduction of metal centers. In aqueous solution, pulse radiolysis is a unique tool for the generation and study of  $\bullet\text{OH}$  radicals and other powerful oxidants. This allows for elegant mechanistic model studies that can lead to a better understanding of the advanced oxidation processes in complex environmental systems.

Environmentally relevant systems are multicomponent and understanding the interactions of these components is critical. In particular, this may involve the study of  $\bullet\text{OH}$  or other radical reactions with a substrate in the presence of a metal or other electron donor/acceptor. This may, again, lead to product selectivity within these advanced oxidation processes. Challenges also exist in the area of ozonation processes to understand the role of  $\text{O}_3\bullet$  and  $\text{O}\bullet$  in the oxidation of organic compounds using time-resolved mechanistic studies.

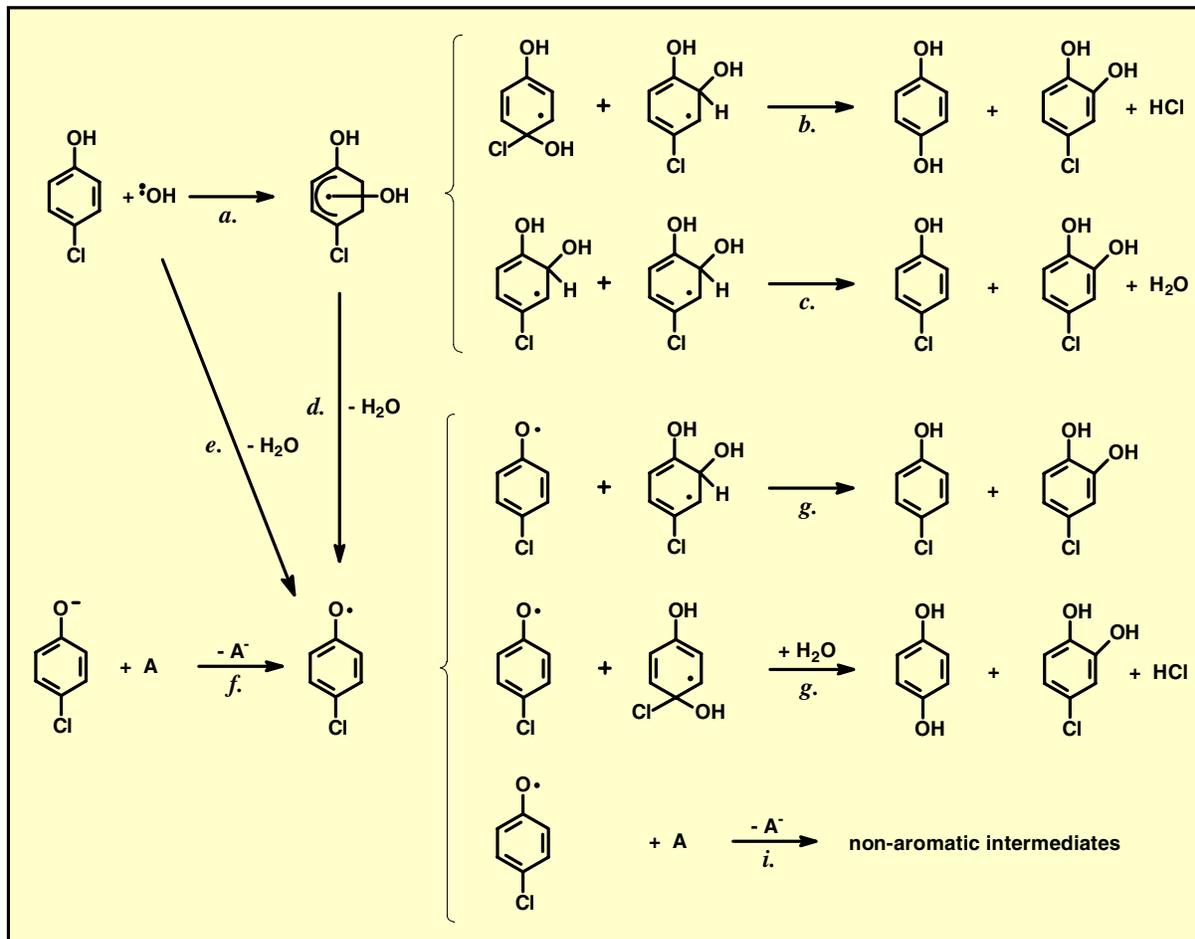
Biomimetic models of enzymatic systems which are the active components of bioremediation are attractive as they can function in water (an environmentally benign solvent), are simpler, more specific, and also more resistant to extremes of reaction conditions (temperature, pressure, pH) than the enzyme. The enzymes often function as redox catalysts, with active sites that are metal-centered, and such one electron oxidation and reduction processes can be conveniently probed using pulse radiolysis studies.

*Reactivity Enhancement and Inhibition of Counterproductive Free Radical Processes.* A variety of “natural” chemicals react with  $\bullet\text{OH}$  forming secondary radicals. The reactions of these species with pollutants are largely unknown. The need exists for further investigations on the chemical fate of functionalized (e.g., halogenated) peroxy radicals, oxygen addition to heteroatom-centered radicals, reversibility of oxygen addition, rearrangement and fragmentation in oxygen-centered radicals, and of radicals originating from inorganic substrates, such as phosphate and carbonate (See, for example Figure 13.). Secondary radicals are frequently more selective although often at the expense of reduced reactivity.

The roles of unusual oxidation states of free and complexed metal ions in degradation processes in pollutant transformation need to be addressed. The effect of metal contaminants on the reactions of reactive intermediates is an important issue that may provide opportunities for metal decontamination based on radiolysis.

Zero-valent metals, for example, provide possible solutions to groundwater problems. Another general approach is metal ion chelation, allowing for the stabilization of unusual oxidation states. With respect to metal-ligand chelates, oxidation may take place both at the metal center and within the ligand adding to the complexity of the mechanism. Furthermore, a change in metal oxidation state may be accompanied by ligand exchange, and change in ligand coordination and redox properties.

*Understanding Pollutants in Natural Waters.* Radiation chemistry has a major role to play in understanding the fate of pollutants in seawater, freshwater, and cloud droplets. The importance of clouds, and thus aqueous phase chemistry, is increasingly clear in atmospheric processes. The reactivity of small inorganic radicals deriving from  $\text{SO}_x$  and  $\text{NO}_x$  can be measured using pulse



**Figure 13.** A complex reaction mechanism illustrating radiolytic oxidation of 4-chlorophenol in aqueous solution.

radiolysis and these rate constants are essential for modeling atmospheric mechanisms. In addition, no effective method exists for sampling  $\text{HO}_2$  in the atmosphere. The chemistry behind the luminol-type scavengers of  $\text{HO}_2$  is not well established and pulse radiolysis is an ideal tool for studying these systems.

## V. Emerging Methodologies: Supercritical Fluids

A key feature of supercritical fluids that makes them attractive for applications is the ability to tune the solvent strength by adjusting the density with small changes in temperature and/or pressure. Supercritical fluids have already been exploited for environmental remediation purposes, and the potential for other such applications is large (Brennecke, J. F., *Chemistry and Industry* 1996, 831). Real and potential applications include both extraction and reaction processes. The following opportunities for radiation chemistry in supercritical fluids are noted.

*The Combination of Supercritical Fluid Extraction/Processing with Radiation for the Purpose of Hazardous Waste Remediation.* It is possible that radiation chemistry could be used to enhance,

optimize, or control some of the supercritical fluid processes mentioned above. For example, hydroxyl radicals have been identified as important oxidizing species in supercritical water oxidation; thus, this process might be enhanced by radiolysis or photocatalysis.

Opportunities also exist for the application of CO<sub>2</sub> radiolysis as an advanced oxidation solvent. There are reports in the literature of gas and liquid phase radiolysis of CO<sub>2</sub> and CO<sub>2</sub>/co-reactant mixtures. Interestingly, these reports demonstrate that radiolysis of CO<sub>2</sub> is a convenient source of oxygen atoms (Karasawa, H. *et al. Bull. Chem. Soc. Jpn.*, 1979, 52, 902; Takamuku, S. *et al. J. Am. Chem. Soc.* 1980, 102, 1441), as demonstrated by the generation of oxidation products of alkanes and alkenes, and the hydroxylation products of aromatic compounds. Therefore, it would appear that there is significant potential for the use of CO<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub>O mixtures as oxidative systems. If this proves feasible, the much lower critical temperature and pressure of CO<sub>2</sub> may make the overall process much less expensive than supercritical water oxidation.

*The Use of Supercritical Fluid Processing in Combination with Radiolysis for Environmentally Benign Synthesis and Separations.* Radiation chemistry in supercritical CO<sub>2</sub> might prove to be a very useful synthetic tool as modern emphasis on “green” chemistry intends to replace organic solvent based industrial processes. Supercritical CO<sub>2</sub> has been shown to be a very promising solvent for industrial-scale polymerization, with both free-radical and cationic chain propagation (Canelas, D. A. and DeSimone, J. M. *Adv. Polym. Sci.* 1997, 133, 103). Fixation of CO<sub>2</sub> under supercritical fluid conditions is also an important area of opportunity for the use of radiation chemistry to advance benign synthesis and production of useful chemicals and fuels (Jessop, P. G. *et al., Chem. Rev.* 1995, 95, 259). This will include the use of heterogeneous and homogeneous catalysis for the development of supercritical CO<sub>2</sub> itself as a C<sub>1</sub> feedstock.

Another area of potential importance in environmental remediation involves the use of reverse micelles in supercritical fluids. Of particular interest is the formation of reverse micelles in supercritical CO<sub>2</sub>, whose polar cores can be used as a microreactor environment to carry out water soluble reactions in a benign solvent. Some very useful redox chemistry might be easily carried out if positive and negative charges can be transported to the irradiated micelles.

*Basic Experimental and Theoretical Research in Kinetics and Reaction Mechanisms in Supercritical Fluid Solvents.* The promise of supercritical fluids lies in the broad range of solvating environments which can be accessed in these fluids by altering thermodynamic conditions. The feasibility of controlling chemical processes in supercritical fluids will rely on ability to predict the effect of the changing solvent environment on solute dynamics and reactions. Thus, there is a need for studies which characterize supercritical fluid solvent environments and correlate this characterization with observed reactivity dynamics and transport of solute species. Radiation chemistry has an important role to play as a unique tool in the study of such supercritical fluid solvent effects in electron transfer, redox, and free radical reactions. The fate of free electrons is largely unknown in supercritical fluid environments. Theory and simulation will play a vital role in the characterization of supercritical fluid solvent effects, as these tools will provide fundamental microscopic understanding of these effects and, eventually, predictive capabilities.

Basic research on ionic and free radical reactivity in supercritical water is currently an active field (Savage, P. E. *et al. AIChE J.* 1995, 41, 1723), but detailed mechanistic studies of radiation-induced chemistry, including electron transfer and oxidation/reduction reactions, are needed. These investigations will also further our understanding of Supercritical Water Oxidation (SCWO) processes, which typically are able to completely mineralize organic material.

Radiation chemistry in supercritical CO<sub>2</sub> is virtually unexplored. Fundamental radiation processes include production of CO<sub>2</sub><sup>+</sup>, CO<sup>+</sup>, and O<sup>+</sup> cations which cluster with neutral CO<sub>2</sub>. Neutral dissociation to produce CO and O(<sup>3</sup>P) is a major channel. Electrons are not captured by CO<sub>2</sub> in the gas phase, but evidence suggests they are captured in more dense fluid. Major unanswered questions involve the transport and reactivity of the radiolytically produced cations, the fate of the radiolytically produced electrons, the reactivity of O(<sup>3</sup>P) in the supercritical environment, and the radiolytic yields of all these species as a function of temperature, pressure, and density. Addition of water and/or H<sub>2</sub> to the supercritical CO<sub>2</sub> should result in production of H• and •OH radicals whose chemistry can be further exploited, but this possibility is unexplored.

## VI. Theory and Modeling for Environmental Remediation

Theory makes significant contributions by (i) providing a means to predict critical quantities not readily measured, (ii) offering a protocol for prioritizing future experiments, (iii) providing a microscopic picture of a system of interest where reactivity is not well understood. In addition, theory can prove useful in providing spectral and property predictions that facilitate experimental identification of transient intermediates.

*Applying Gas-Phase Models to Solution-Phase Problems.* Since the fundamental chemistry of interest in remediation processes involves the making and breaking of chemical bonds, any modeling protocol must accurately describe this process in order to be useful. Although quantum mechanical methods can suffer from critical flaws in describing open-shell molecules in some instances, these deficiencies are sufficiently well understood that they can be overcome either by resort to sophisticated correlated methods or density functional theory. A more fundamental challenge is the extension of well tested gas-phase techniques to include homogenous medium effects, both equilibrium and nonequilibrium (Tapia, O. and Bertram, J., eds., *Solvent Effects and Chemical Reactivity*, Kulwer, Dordrecht, 1996). These extensions may take the form of continuum or atomistic models, although in the latter instance this may require resort to combined quantum mechanical/molecular mechanical models.

*Modeling of Heterogeneous and Mesoscopic Systems.* Radical reactions taking place either at a solid surface or involving catalysts or reactants attached to a solid support introduce new complications for modeling. Such systems include macroscopic dimensions for the solid, and this can make quantum mechanical methods difficult to employ. Possible modeling approaches deserving of additional study include (i) treatment of the solid as a simple dielectric continuum characterized by a dielectric constant different from that of the solution (useful for supports, as opposed to reactive surfaces); (ii) treatment of the solid using slab-Hartree-Fock approaches (typically involving periodic plane wave basis sets)—such methods are complicated by the aperiodicity introduced by reacting species on the surface, but are still potentially tractable; and

(iii) further development of quantum mechanical/molecular mechanical methodologies to model the majority of the solid using molecular mechanics but critical regions using quantum mechanics—such an approach could be folded inside a continuum solvent model for maximum physicality. In addition to reactions occurring on surfaces, chemistry taking place within the adjacent layers of solvent are expected to be different from that occurring in the bulk solution. Theory provides a versatile tool for examining such effects, and potentially providing information that will facilitate experimental confirmation of such processes.

A key challenge in modeling solid phases under irradiation conditions is the accurate description of charge localization resulting from electronic motion, e.g., from deposition of ionizing radiation, spurs, etc. In a first-order model, experimental observations may allow such effects to be approximated by point charges in quantum mechanical calculations. A worthwhile area for future research is the *ab initio* prediction of these charge localization processes.

*Extension of Kinetic Databases.* Over the past several decades, a vast amount of data has been acquired for reaction rates of radiolytically produced species in aqueous solution. These data have been assembled into a kinetic database (<http://www.rcdc.nd.edu>) that continues to serve researchers in many fields as a crucial resource. Future extensions of the database can take advantage of synergies between theory and experiment with respect to identifying and characterizing the most important gaps in the current coverage.

At the most fundamental level, models that predict the effect of dose rate on rates of primary radical formation are needed. Such models will need to address differences between pure liquid water, homogeneous aqueous solutions, and heterogeneous mixtures.

*Ab initio* prediction of rate constants not currently available in the database will provide information on the relative importance of uni- and bimolecular reactions that may merit experimental study. It should be emphasized that theoretical predictions are not expected to supplant experimental measurement, but rather to complement and prioritize experimental efforts in an economical fashion. For example, the carbonate radical anion would be expected to be found in most environmental systems, but the chemistry of this radical remains relatively uncharacterized. Computational prediction of its potential role in new systems provides a particularly efficient means to evaluate whether experiments are warranted.

Finally, a key advantage of theoretical models is that they provide enhanced microscopic details for bimolecular reactions. Thus, they are ideal for extending the current database to include creation rates for secondary, tertiary, etc. radicals, partitioning of solutes between phases, differentiating between rates occurring in different phases, and in general making the kinetic model more versatile and microscopically accurate.



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## **Appendix II: Program**

### **Research Needs and Opportunities in Radiation Chemistry**

April 19-22, 1998

Indian Oaks Conference Center  
Chesterton, Indiana

#### **PROGRAM**

##### Sunday, April 19

- 5:00 - 9:00 p.m. Registration, Waterbird Lobby
- 6:30 - 8:00 p.m. Buffet Dinner, Kingfisher Room
- 8:00 - 9:30 p.m. Welcoming Reception, Kingfisher Room

##### Monday, April 20

- 7:00 - 8:30 a.m. Breakfast, Kingfisher Room
- 8:00 - 8:30 a.m. Registration

#### **PLENARY SESSION** Sandpiper/Egret Room

8:30 a.m. Introductory Remarks  
Robert S. Marianelli, Division of Chemical Sciences, DOE

8:45 a.m. Workshop Overview  
Paul Barbara, University of Minnesota

Plenary Lectures  
Paul Barbara, Presiding

9:00 a.m. Fundamental Aspects of Radiation Research: Current Status, Future Objectives and  
New Applications  
Herwig G. Paretzke, Institut für Strahlenschutz, GSF

9:30 a.m. Energy Transfer, Fragmentation and Ion-Molecule Reactions Occurring within the  
Femtosecond Time Scale  
Léon Sanche, Université de Sherbrooke

- 10:00 a.m. Coffee Break
- 10:15 a.m. Subpicosecond Pulse Radiolysis Coupled with Laser Detection  
John R. Miller, Argonne National Laboratory
- 10:45 a.m. Basic Research: What Role Can It Play in the DOE Weapons Complex Cleanup  
Shirley Rawson, Pacific Northwest National Laboratory
- 11:15 a.m. Radiation and Chemistry in Nuclear Waste: Colloids, Interfaces and Radicals  
Dan Meisel, Argonne National Laboratory
- 11:45 a.m. Effects of Radiation on Solid Nuclear Waste Forms  
William J. Weber, Pacific Northwest National Laboratory
- 12:30 p.m. Lunch, Kingfisher Room
- 1:45 p.m. Thermodynamic Control of Reaction Rates in Supercritical Fluid Solvents  
Susan C. Tucker, University of California, Davis
- 2:15 p.m. Kinetics of Free Radical Reactions  
James H. Espenson, Ames Laboratory, Iowa State University
- 2:45 p.m. Break
- 3:00 p.m. The Use of Radiation in Nanoparticle Research  
Arnim Henglein, Hahn-Meitner Institut
- 3:30 p.m. Studies of Radiation Chemistry with Surface Science Techniques  
Chris R. Arumainayagam, Wellesley College
- 4:00 p.m. Break
- 4:15 p.m. The Role of Radiation Chemistry in Supercritical Fluids for Environmental Remediation  
Joan F. Brennecke, University of Notre Dame
- 4:45 p.m. Linkages between Basic Research and Applications: A Kinetic Modeling Approach  
William J. Cooper, University of North Carolina at Wilmington
- 5:15 p.m. Radiolysis in Heterogeneous Systems: Reductive Dechlorination on Environmental Surfaces  
Kimberly Gray, Northwestern University
- 6:30 p.m. Dinner, Kingfisher Room

## PANEL DISCUSSION SESSIONS

8:00 - 9:30 p.m. Panel Discussions

Panel 1 Egret Room  
    Panel 1A Egret Room  
    Panel 1B Kingfisher Room  
Panel 2 Sandpiper Room  
Panel 3 Sea Gull Room  
Panel 4 Blue Heron Room  
    Panel 4A Blue Heron Room  
    Panel 4B Mallard Room  
    Panel 4C Board Room  
Panel 5 Palomar Room

### Tuesday, April 21

7:00 a.m. Breakfast, Kingfisher Room  
8:30 a.m. Panel Discussions  
12:00 a.m. Lunch, Kingfisher Room  
    (Panel Chairs meet for lunch in Egret Room)  
1:00 p.m. Panel Discussions  
6:30 p.m. Dinner, Kingfisher Room  
8:00 p.m. Panel Discussions

### Wednesday, April 22

7:00 a.m. Breakfast, Kingfisher Room

### **PLENARY SESSION** Sandpiper/Egret Room

Paul Barbara, Presiding

8:30 a.m. Summary Reports from Panel Chairs  
11:30 a.m. Concluding Remarks  
12:00 a.m. Lunch, Kingfisher Room