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Role of Water in Electron-Initiated Processes and Radical Chemistry: Issues and Scientific Advances

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Contents

1. Introduction	356	2.2. Current Research Advances	364
1.1. Importance of Electron-Driven Processes in Aqueous Systems	356	2.2.1. Electronic Structure of Aqueous Phases	364
1.2. Challenge of Understanding Electron-Driven Processes in Aqueous Systems	357	2.2.2. Electron–Water Scattering Cross Sections	365
1.3. Current State of Understanding of Aqueous Systems Relevant to Aqueous Radiation Chemistry	359	2.2.3. Dynamics of Electronically Excited States	368
2. Initial Excitation and Relaxation Processes	362	2.2.4. Relaxation and Reaction Processes Occurring under Highly Nonequilibrium Conditions	369
2.1. Critical Research Issues	362	3. Reactions of Radicals and Ions in Aqueous Solutions	372
		3.1. Critical Research Issues	372
		3.1.1. Radical Diffusion	373
		3.1.2. Activated Radical Reactions with Stable Molecules	373
		3.1.3. Radical–Radical Combination Reactions	374
		3.1.4. Hydrated Electron-Scavenging Reactions	374
		3.1.5. Recombination of Hydrated Electrons	375
		3.1.6. More Complex Reactions	375
		3.2. Current Research Advances	376
		3.2.1. Structure and Energetics of Transient Radical and Ionic Species in Aqueous Environments	376
		3.2.2. Dynamics of Radical and Ionic Species and Coupling to Solvent Dynamics in Aqueous Systems	379
		3.2.3. Interfacial Processes	383
		4. Summary	384
		5. Acknowledgment	385
		6. Glossary of Acronyms and Terms	385
		7. References	386

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1. Introduction

An understanding of electron-initiated processes in aqueous systems and the subsequent radical chemistry these processes induce is significant in such diverse fields as waste remediation and environmental cleanup, radiation processing, nuclear reactors, and medical diagnosis and therapy. We review the state of the art in the physical chemistry and chemical physics of electron-initiated processes in aqueous systems and raise critical research issues and fundamental questions that remain unanswered.

1.1. Importance of Electron-Driven Processes in Aqueous Systems

The study of the radiolysis of water has been an active field for over 50 years¹ because of its importance in nuclear reactors, storage of transuranic and high-level mixed wastes, industrial applications, biology, and medicine. Research to develop an understanding of the consequences of electrons is at the core of many research programs, especially those sponsored by the U.S. Department of Energy, because the interactions of electrons strongly affect the feasibility and possibilities for the best use of present and future energy technologies.

The importance of electron-driven processes in aqueous systems is exemplified by radiolytic molecular hydrogen generation in some of the 177 waste tanks at the Hanford Site in Washington state, a Department of Energy nuclear weapons production facility.² It is known that some of the hydrogen gas is the product of hydrogen atom recombination reactions and reactions between organic radiolysis products. Some of the hydrogen also seems to be formed in fast processes following the primary energy depo-



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sition process, and these processes have not been fully explained.

Electron-driven chemistry is also important in water-cooled nuclear reactors, where radicals and ions that are created by ionizing radiation (e.g., hydroxyl radicals) lead to corrosion of the reactor infrastructure. An understanding of the reaction mechanisms for these radical and ionic species is needed to devise approaches to mitigate their corrosive effects. For example, hydrogen is injected into the reactor cooling system to inhibit the formation of H_2O_2 . However, the amount of hydrogen that must be added to effectively quench these reactions is much higher than that which has been calculated by currently available models.³ Recent evidence suggests that this discrepancy may arise from an insufficient knowledge of the chemical reaction rates at higher temperatures.⁴

Electron-driven processes in aqueous environments are also important because they generate radical and ionic species that interact with macromolecules. Knowledge in this area is important for the understanding of the impact of radiation exposure on biological systems as well as to advancing the fields of nuclear medicine and radiation therapy. Recent studies, which measured single- and double-strand breaks induced in DNA by electrons with energies well below molecular ionization thresholds, bring a different perspective to the source of damage in biologically important molecules.⁵ Water plays an obvious role in these reactions as it can lead to conformational changes in the macromolecules, for

example, A- to B-DNA. In addition, rapid relaxation processes in the solvent layers of DNA determine the electronic states leading to stable damage products, such as strand scission and oxidized bases.

Electron-driven chemistry at interfaces between aqueous solutions and solids is important in a number of areas. For example, an understanding of this type of interfacial chemistry is crucial to understanding corrosion, one of the major problems in the nuclear power industry. There is currently a lack of knowledge about the mechanisms for the transfer of energy, which is deposited by ionizing radiation into solids, to interfaces where it can create radicals and ions in solution. One example arises in the generation of H_2 in solid nuclear wastes such as those made from cement. It was found that the H_2 was formed in the water in the waste; however, it was clear that much of the energy that generated this hydrogen came from energy deposition in the solid.⁶ Utilization of these types of reactions may make it possible to generate hydrogen for the hydrogen economy using radiation from waste fuels. Also, it may be possible to make use of the energy deposited in particles, in so-called wide band-gap semiconductors, to efficiently decompose waste. This may be a particularly advantageous process, because charge separation can be enhanced.

There have been considerable efforts recently to develop new methods to destroy hazardous organic wastes. Techniques such as the irradiation of wastes or the use of supercritical water oxidation have been proposed.⁷ The possible enhancement of such destruction by interfacial chemistry was discussed above. In all destruction studies, one needs to understand the chemistry that occurs in these processes because one must verify that the destruction of one hazardous material does not lead to the formation of a product that is equally as or more toxic than its predecessor. For example, one must ensure that the destruction of polychlorinated biphenyls (PCBs) does not lead to the formation of phosgene. Simulations of supercritical water oxidation have assumed that reactions proceed similarly to the reactions in the gas phase.⁸ However, recent experimental data show that some of the fundamental reactions occur with greatly differing rates in the liquid phase (even in supercritical liquid) and in the gas phase.⁴

Many biological systems and waste treatment systems are biphasic, with micelles, colloidal particles, or liposomes encapsulating much of the important chemistry. It is critical to understand how these interactions occur. One example where electron-driven reactions are important is the potential use of TiO_2 for waste destruction. Irradiation of TiO_2 particles by light leads to the formation of holes and electrons in the semiconductor particles. Electron-transfer reactions then can occur at the interface between the particle and aqueous solution to react with solutes in aqueous solution. The goal is to apply this electron-driven reaction to destroy waste by using the TiO_2 particles as photocatalysts.

The one common thread that ties this research together is that all processes are controlled by the interactions of electrons with aqueous solutions and the chemistry and physics that evolve from these

processes. Some of the important research questions and technological challenges are as follows:

- How can we control the chemistry in nuclear reactors where reactions take place under extreme conditions, under high linear energy transfer (LET) radiolysis, and at interfaces?
- How is hydrogen gas generated in nuclear waste where radical reactions, interfacial chemistry, and primary radiolytic processes dominate?
- How can we perform hazardous waste destruction using supercritical water oxidation and radiolytic treatments in which radical, ionic, and interfacial chemistries are important?
- What is the impact of radicals produced in water radiolysis and interfacial chemistry on environmental monitoring and remediation?
- What are the biological effects of radiation to which radical and ion chemistries contribute significantly?
- What are the roles of radical and ion chemistries and interfacial processes in radiation therapy?
- What is the role of radical and ion chemistries in the processing of radioactive materials?
- What are the roles of radicals and ions in the deterioration of materials due to radiation damage?

The processes initiated by electrons can also be used as tools in tackling other complex chemical questions, including

- catalysis where interfacial chemistry induced by electron-driven processes can be used to understand reactive sites and
- energy conversion and storage, for example, the design of hydrogen storage materials for the hydrogen economy, where the well-controlled generation of ions can simplify the fundamental chemical studies.

1.2. Challenge of Understanding Electron-Driven Processes in Aqueous Systems

Radiolysis of water from natural and anthropogenic sources leads to the formation of aqueous electrons. Because of the complexity inherent in treating electron-driven processes in water, important questions regarding the primary chemical events remain even after decades of inquiry. The excitation, relaxation, and reaction processes driven by electrons in aqueous systems span a wide range of energies and time scales—from thermal energies up to tens of electronvolts and from femtoseconds to microseconds or longer.

Much of our current knowledge about the processes driven by electrons in aqueous systems comes from studies of the radiolysis of water. The general mechanism of the effects of high-energy radiation on liquid water was known by the early 1970s.^{9,10} Briefly, high-energy particles (such as 1 MeV electrons) create a sparse track of ionization events in liquid water (i.e., the track structure), which generate lower energy secondary electrons (i.e., a distribution of electron energies with mean below 100 eV). The secondary electrons have sufficient energy to cause additional ionization events, which create copious quantities of low-energy electrons with mean energy below 10 eV. The secondary events occur in close proximity to the

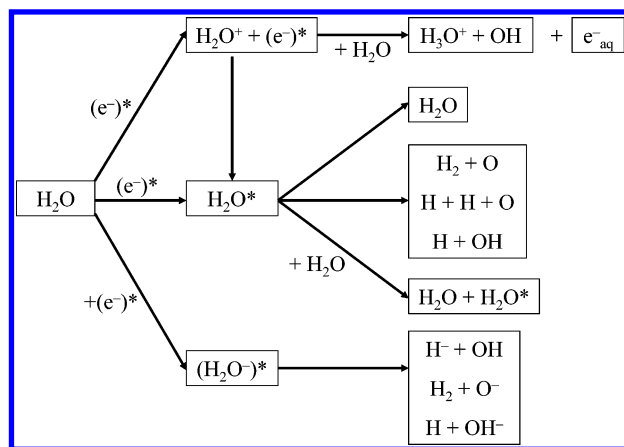


Figure 1. Initial processes in the decomposition of water by ionizing radiation.

primary event, resulting in nonhomogeneous distributions of ionizations and excitations called “spurs”. The electrons become hydrated, and H_2O^+ disproportionates to form H_3O^+ and OH on time scales faster than 1 ps. The thermalized radical and ionic species go on to react with water and other species in the solution to form a variety of species (e.g., H_2 , H_2O_2 , and OH^-). These results are summarized in Figure 1.

The difficulty in understanding electron-driven reactions in aqueous media (and in fact all reactions in aqueous media) begins with the media. Water is a highly polar, strongly hydrogen-bonding material, which means that one cannot easily treat the solvent as a continuum for some properties.¹¹ In fact, an understanding of the electronically excited states of a water molecule in liquid water is still very fragmentary. Understanding the dynamics of high-energy processes in water is complicated by the breakdown of linear response theory, so the solvent response to a perturbation cannot be approximated by the rate of solvent fluctuations—an approximation that does hold for many solvents. The importance of these problems was further highlighted with the efforts to calculate the structure and spectrum of the hydrated electron in liquid water. Early quantum calculations,¹² which used an electron, several water molecules, and a dielectric continuum, predicted that the spectrum was narrow and that the water molecules nearest the electron were aligned with the molecular dipoles toward the charge. This result was in conflict with results on similar hydrated electrons determined by electron spin resonance (ESR) measurements.¹³ The application of quantum path integral techniques showed that the consideration of the entire solvent led to bond–dipole alignment and suggested that the width of the absorption spectrum of the hydrated electron was due to multiple water structures around the electron.¹⁴ Finally, results from sophisticated, time-dependent quantum molecular dynamics calculations of the electron in water have been able to predict the spectrum and dynamics of the electron.¹⁵

The physical and chemical processes and their respective (approximate) time scales are shown in Figure 2. The ultrafast physical processes include the ionization and relaxation of the ions that are formed

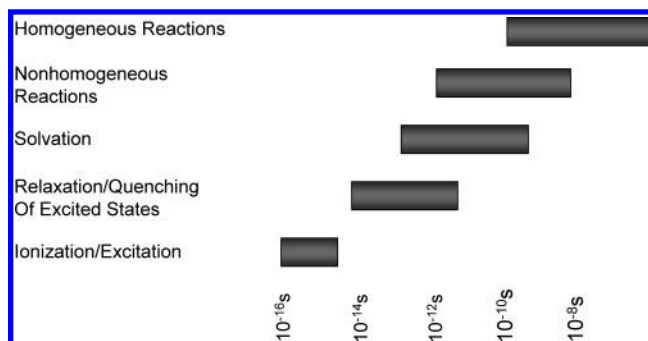


Figure 2. Approximate time scales of processes initiated by ionizing radiation.

by the ionization process. The physiochemical stage continues through the evolution of highly excited states and their interactions with the solvent (solvation). Reaction can overlap these relaxation processes. The chemical processes occur both when the ions and radicals are distributed nonhomogeneously in “clusters” of ionization and excitations (i.e., spurs) and homogeneously after the reactive species have diffused.¹⁰

Electrons with kinetic energies of the order of ≤ 100 eV play a pivotal role in the absorption of ionizing radiation by materials. The predominance of electrons in this energy range results from the long range of Coulomb interactions and the distribution of oscillator strengths of molecules. Even if the primary radiation is not charged (neutrons and photons, for example), high-velocity charged particles will be generated as the primary radiation penetrates the absorber. The swiftly moving ions transfer their kinetic energy to electronic excitations through Coulomb interactions with large impact parameters. In glancing collisions, the most loosely bound electrons of the stopping material receive an impulse that, through Fourier analysis, can be viewed as broad-spectrum photoexcitation. The oscillator strength of molecules peaks at ~ 20 – 30 eV and decreases to very low values of ~ 100 eV. Hence, for all radiation fields, the initial response of the stopping material is largely determined by the oscillator strength distribution of its valence electronic structure, which leads primarily to the formation of electrons with energies of < 100 eV.

The copious number of low-energy electrons generated in the slowing of high-energy charged particles makes them the focus of studies to understand the early stages of radiation chemistry. Electrons in the range of 30 – 100 eV will ionize more than one molecule so that there will be localized regions of high concentration of ionized species. For these reasons it is crucial to understand the scattering processes, both elastic and inelastic, that such electrons undergo. These processes will determine the spatial distribution of radicals and ions and thus determine the nonhomogeneous chemistry that will occur.

The determination of scattering cross sections with sub-100-eV electrons is difficult because the Born approximation, which relates the scattering cross section to the optical absorption, no longer holds at the lower energies.¹⁶ The use of different approximations for the scattering parameters leads to differ-

ences in simulations of track structure.¹⁷ Condensed-phase electron-scattering cross sections have been directly measured only for amorphous solid water films, although total and momentum-transfer cross sections are available for liquid water.^{18,19} In water vapor, the collision processes that remove energy from low-energy electrons have been studied by a variety of experimental techniques. These results, when translated to the liquid phase, provide qualitative agreement with experimental data (as discussed below). Femtosecond laser studies of electron localization, solvation, and reaction provide important insights into the fundamental processes of low-energy electrons.²⁰ However, the energy distribution of electrons from lasers is almost certainly not the same as from ionizing radiation. Consequently, a substantial gap exists in our understanding of the processes that initiate radiation chemistry in condensed matter.

Scattering data have been assembled to allow simulations that predict the yield and spatial distribution of species such as the hydrated electron (e^-_{aq}), the hydrated proton (H^+_{aq}), OH, H, and H_2 in pure liquid water.^{21,22} These simulations are based on a mapping of inelastic collisions to primary species without explicit consideration of relaxation processes and intermediate states. The accuracy of these models is judged primarily on their ability to lay the groundwork for understanding radiolysis experiments in the picosecond to microsecond time scales. These models can be expanded to radiation sources such as neutrons or α particles, where the primary ionization events (of ~ 100 eV) are within a nanometer of each other.²³ However, these models do not include many of the important fundamental processes, such as reactions of hydrated electron precursors and dynamics of excited states, that may well be more important when ionization density is higher.

Traditional experimental approaches to studying electron-driven processes in aqueous systems (e.g., electron-pulse radiolysis) have been instrumental in efforts to understand the initial processes in electron-driven reactions in liquid water.²⁴ However, these approaches do not provide a direct probe of many of the processes that occur on time scales of less than tens of picoseconds. Stochastic simulations have been useful for inferring more detailed information about this mechanism;^{21,22} however, these simulations require fundamental information about the physical and chemical processes, which is incomplete or completely lacking in some cases.

There are almost no data that directly probe the dynamical processes that occur with highly excited states. In addition to the primary steps in water radiolysis, including ionization and the production of highly excited states in water, it is clear that complex relaxation takes place. For example, in water radiolysis, the production of H^- and H_2 and the interference with the production of the hydrated electron, which has been seen in both photolytic and radiolytic formations of electrons, show that it is important to understand the dynamics of the relaxation of highly excited states.

Electron-driven reactions are important in systems other than pure water. In biological systems, proteins

and DNA are solvated by water molecules that appear to be differently structured (e.g., different hydrogen bonding patterns) from water in the bulk of the solution. For example, these solvation effects can affect the transfer of electrons in DNA, which can alter the denaturation of DNA. The structure could be similar to that found in thin amorphous water systems or similar to those in water–electron clusters.²⁵ These additional complexities can confound the understanding of how electron reactions occur in water.

Heterogeneous systems add to the complexity of understanding electron-driven reactions in water.²⁶ The presence of a surface will alter the structure of water near the surface. This change will occur for multiple reasons. For example, simply the existence of an interface provides a nonisotropic environment, orients water molecules, and will break up the structure of the water near the interface. In addition, strong interactions that can exist between the surface and water molecules will also change the water structure.

Finally, water has a wide range of properties depending on temperature and pressure. As has been previously mentioned, almost all electron-scattering measurements have been done in the gas phase or in amorphous solid water. Chemistry in water near room temperature is clearly important, particularly for biological systems, and increasing focus is being placed on chemistry at high temperatures and pressures of water, including supercritical water.²⁷ As is discussed later in section 3, radical chemistry changes at high temperature and in supercritical water. Clearly, even minor changes in water structure/internal energy can be important in defining chemical pathways.

To summarize, the challenges to understanding electron-driven processes in water include

- the complexities of the aqueous medium itself;
- the unknown structure of excited and ionized states in liquid water;
- the highly excited states and the relaxation of these states that can occur in water;
- the complexities that arise from the existence of large polymeric molecules, such as proteins and DNA, or heterogeneous materials, such as particles, catalysts, and surfaces; and
- the effect on reactions due to the change of water properties that can occur by changing temperature and pressure.

However, as discussed in sections 2 and 3, new theoretical and experimental techniques make it possible to attack these problems. New theoretical techniques provide frameworks for understanding processes in aqueous systems, and new experimental techniques make it possible to probe these frameworks in even more exacting fashion.

1.3. Current State of Understanding of Aqueous Systems Relevant to Aqueous Radiation Chemistry

Water can act in the reactions of interest both as a chemical participant and as a medium that modifies the chemical processes that occur due to its large

solvation effects. The influence of the solvent can be dramatic, modifying both the energetics and the dynamics of processes. In particular, because water is a highly polar substance, it can critically affect the energetics of charge rearrangement; with an ambient dielectric constant of nearly 80, electrostatic interactions are largely screened by the induced polarization of the solvent. Thus, the net interactions among charged species at equilibrium are brought into the same range as thermal energies ($k_B T \sim 0.6$ kcal/mol, k_B is Boltzmann's constant).

At the same time, the light mass of the protons and the nearly spherical geometric shape of water impart the possibility of very rapid large-amplitude reorientational dynamics and the corresponding ability to rapidly respond to the *changing* electrostatic fields characteristic of the charged components generated in electron-initiated events. The dynamical response times of water cover a very wide range—from those of ordinary nonpolar liquids, in the picosecond range, down to the few femtosecond range characteristic of water molecular stretch and bend vibrations. Of particular importance are the collective rocking motions of water (librations) operating in the tens of femtoseconds range; these can, for example, largely solvate a newly created charge on that characteristic time scale. Nearly half of the accommodation and development of solvation energy occurs in <50 fs, with the remainder typically requiring only a few hundred femtoseconds to equilibrate.^{28–30} In alcohols, for example, these times can extend to many picoseconds, because the alkyl tails limit ideal solvation structures and hinder the reorientation dynamics required to optimally interact with a solute.³¹

The hydration of ions also influences transport. Ionic mobilities in water are distinctly slower for small ions than for uncharged species of the same size. This decreased mobility is a result of the excess drag associated with the strong hydration of the ions and, thus, an effectively larger size.³⁰ However, the differences between charged and uncharged species already become rather small for molecular sizes. For hydrated excess electrons, of course, the compact size is wholly a result of the localization associated with solvent organization around the charge.

Many of the properties of water have their genesis in the strong intermolecular hydrogen bonds, each such bond having an average strength (potential energy) in the ambient liquid that is on the order of 5 times the available thermal energy. This network of hydrogen bonds carries with it the important ability to locally either supply or absorb relatively large amounts of energy to or from chemical reactants.^{32,33} At the same time, the tight coupling among solvent molecules also allows for rapid energy transport and energy dissipation. Model calculations,^{33,34} as well as sophisticated new experiments,³⁵ show clearly that energy resulting from chemical processes in water dissipates into the fluid on a remarkable picosecond time scale. Water was recently the subject of a special issue of *Chemical Reviews*, Vol. 102, No. 8, in 2002 with L. Pratt serving as the Guest Editor. Readers are referred to this issue for a number of important papers on the behavior of water, including

the summary of the recent work on the structure of water from scattering experiments and molecular simulations. High-quality X-ray and neutron-scattering experiments have enabled the extraction of reliable radial distribution functions against which simulations can be benchmarked. It is only recently that reliable radial distribution functions have been derived from experiment.³⁶

Many important electron-initiated processes occur at interfaces, and both solvation structure and solvent dynamics at interfaces can be significantly perturbed from the bulk. This perturbation can be due to specific interactions with the interface, which can, for example, induce orientational anisotropy, as well as simple geometric confinement of molecular motion. Here, we primarily want to emphasize that interfacial water should not be interpreted as limited only to macroscopic surfaces, such as a metal surface, but also includes the outer surface of solvent clusters and the hydration layer of macromolecular systems as important cases. In aqueous clusters, for example, there is growing theoretical and experimental evidence that various ions can preferentially locate at either interfacial locations or buried interior positions, depending on both the cluster size and the chemical identity of the ion.^{37,38} This inhomogeneous distribution can have dramatic effects on the chemical accessibility of the ion as well as its spectroscopic signature. One consequence is that such inhomogeneities need to be considered in experimental use of clusters as models of bulk materials. A particularly exciting advance is the rapid development of interface-specific spectroscopies that can be used to probe both the structure and the dynamics of the solvent and solutes.³⁹ In addition, theoretical work has indicated that the solvation structure and energetics at aqueous interfaces can be substantially different from those in bulk.^{40–42}

It is important to emphasize that water under physical conditions that are different from the most familiar ambient liquid conditions is also important. Supercritical water, which exists above ~ 650 K, can act in much the same way as the ambient liquid. Even at this elevated temperature, considerable intermolecular hydrogen bonding persists,⁴³ as would be expected on the basis of the energetics of solvent–solvent hydrogen bonding. As ion–water interactions are typically several times stronger than solvent–solvent interactions, it is not surprising that strong hydration of ions persists to even greater thermodynamic extremes than hydrogen bonding in the bulk fluid. Retention of nearly a full solvation shell of water persists to extremes of both high temperature and low solvent density (i.e., up to temperatures of ~ 900 K and down to solvent densities of 0.2 g/cm³). An important consequence is that even under supercritical conditions, ionic thermodynamics and electron solvation are far more similar to those at ambient conditions than might be naively anticipated. Furthermore, ionic transport coefficients are characterized by remarkably small changes with solvent density or ionic radius.^{44,45} In contrast to ambient conditions, small uncharged species exhibit mobilities that are typically an order of magnitude

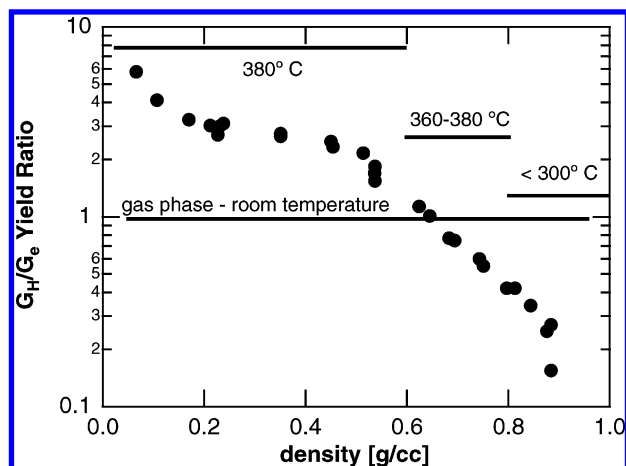
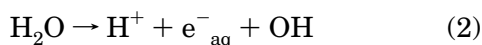


Figure 3. Ratio of the yield of H atoms to the yield of hydrated electrons as a function of water density.²⁷

or more greater than those of charged counterparts of similar bare geometric size.⁴⁴

Low-energy, electron-driven processes in supercritical water are important for both technological and scientific reasons. Supercritical-water-cooled reactors are a prime candidate for developing a new generation of reactors because of the increased thermal efficiency.⁴⁶ Supercritical water oxidation has also been proposed as a way of destroying toxic wastes.⁷ From a scientific perspective, supercritical water is an important medium for systematic studies because parameters that are important in radiolysis, such as the dielectric constant, the dissociation of water, and the solvent structure, can be altered continuously as a function of density without changing phase. As an example, consider the primary pathways for the decomposition of water by high-energy electrons or γ -rays:



The ratio of neutral dissociation to ionization (H/e) in the gas phase is approximately unity. However, in liquid water at room temperature, H/e is ~ 0.2 . As shown in Figure 3,²⁷ the ratio of the G values (see below for description) for the two pathways depends on the density of the system, and at densities of < 0.2 g/cm³, the dissociation pathway becomes 6 times larger than the ionization pathway. The fundamental decomposition processes depend strongly on water density and (presumably) structure.

G values are defined as the yield of radiochemical species per 100 eV of energy deposited in the absorber. Hence, G values are the source terms for models of radiation chemistry at times sufficiently removed from the initial deposition of energy that nonhomogeneous concentrations of radiochemical species have been dissipated by diffusion. Under the usual experimental conditions (room temperature and dilute aqueous solutions), the lifetimes of nonhomogeneous concentrations are on the order of microseconds. The nonhomogeneous radiation chemistry that occurs on the sub-microsecond time scale makes G values strongly dependent on the properties

of both the radiation field and the absorbing medium. The G values depend on linear energy transfer (LET), temperature, pressure, and scavenger concentrations. Primary G values are defined as the number of radiochemical species (per 100 eV of energy absorbed) at the end of the physicochemical stage of track development ($\sim 10^{-12}$ s after the initial energy absorption). Techniques for calculating primary yields have evolved from extensive research on track-structure simulation.⁴⁷ The main sources of uncertainty in these calculations are the branching ratios for the decay of highly excited and ionized water molecules into the radical and molecular species produced in aqueous radiation chemistry. The impact of these uncertainties has been greatly reduced by requiring that calculated primary yields be consistent with pulsed-radiolysis experiments.

At the other extreme of temperature from the system described above is amorphous solid water (ASW), which is a solid phase of water that is metastable with respect to the crystalline phase.⁴⁸ Amorphous solids, also known as glasses, are often described as structurally arrested or "frozen" liquids. Glassy phases of water ice can be formed via several methods.^{48,49} The water structure formed by vapor deposition on a cold (< 140 K) substrate is commonly referred to as amorphous solid water.⁴⁸ Recent experiments using nanoscale thin films of ASW⁵⁰ suggest that at the glass transition temperature (~ 136 K), the amorphous solid melts into a deeply supercooled metastable extension of normal liquid water prior to crystallizing near 160 K. The establishment of the relationship of ASW to supercooled and liquid water has indicated that ASW is a good model system for studying molecular processes in liquid water. One potential caveat is the fact that the transport and relaxation properties in ASW are many orders of magnitude slower ($> 10^7$) than in liquid water under ambient conditions. Nevertheless, this system should be useful in studying the early time dynamics of the inelastic and reactive electron-scattering processes.

Understanding the properties and processes in one phase may provide insight into related properties and processes in other phases. Thus, the progression vapor \rightarrow cluster \rightarrow liquid is often used as a paradigm for developing an understanding of liquid water. Likewise, properties of crystalline ice, such as the electronic band structure, can be used as a starting point for exploring amorphous solid water, and amorphous solid water is often used as a model for liquid water. The effects of the different phases of water on most aspects of electron-driven processes are poorly understood. Whereas the radiolysis of water is closely related to the nature of its electronically excited states, how those states and their dynamics change during phase transitions is largely unknown. Some processes that influence the outcome of radiolysis, such as the migration of excitations or electron solvation, are possible in some phases (e.g., ice or liquid) but not in others (e.g., gas phase). Likewise, "cage effects" are likely to have an important role in stimulated reactions in the condensed phases but not in the gas phase. Differences between condensed phases also have important consequences

for electron-driven processes. For example, vastly different time scales for molecular motion between amorphous solid water and liquid water will affect such critical processes as electron solvation and radical reactions. In general, almost every aspect of electron-driven processes in water is sensitive to the phase. Conversely, studies utilizing different phases provide a crucial opportunity for developing a comprehensive understanding.

Often, the simplest system to study both experimentally and theoretically is gas-phase water. Research on gas-phase water provides the basis for much of our thinking about the other phases. An example is the outstanding progress made in developing a theoretical understanding of the structure of small water clusters.^{41,51–56} Nonetheless, our current understanding of gas-phase water is often insufficient to allow predictions for the more complicated condensed-phase systems. For example, there have been very few calculations for electronically excited triplet states of isolated water molecules,⁵⁷ and there have been no calculations of full-potential energy surfaces, despite the fact that these excited states are believed to be critical in the nonthermal processes initiated by energetic particles in radiolysis.

Research on clusters is a critical bridge between the gas phase and the macroscopic condensed phases of water and is the place where a close coupling between theory and experiment is making tremendous progress. Rapidly emerging theoretical methods⁵⁸ for studying small clusters of water consisting of up to 100 molecules provide an unprecedented opportunity to isolate how specific arrangements of water molecules participate in these chemical processes. Clusters will play a vital role in understanding this chemistry by allowing us to isolate particular hydrogen-bonded morphologies and then to predict how these networked “supermolecules” adapt and rearrange when exposed to ionizing radiation. In fact, we are at the beginning of an era when everyday aqueous processes such as acid and salt dissolution can be followed in exquisite detail.⁵⁹ This approach provides a new way to strip away the averaging inherent in bulk measurements and to isolate key steps in a variety of fundamental processes. For example, the mechanism of electron transport through insulating media has recently emerged as a central issue in the explanation of vibrational structure in scanning tunneling microscopy (STM) images of single molecules, and progress on that problem is impeded by our lack of clear paradigms for vibrationally mediated electron transport.

One of the most important discoveries from the explosion of recent experimental research on water clusters^{41,51,52,55,60,61} is that even rather small water clusters, which can now be treated as a supermolecule at the cutting edge of *both* theory and experiment,^{53,54,62} display some of the complex behavior characteristic of the bulk. Several examples of the morphologies adopted by water clusters, as obtained by a collaboration of theory and experiment,^{52,55,56} are presented in Figure 4. Different cluster sizes present different, specific hydrogen-bonding morphologies according to the number of donor and acceptor

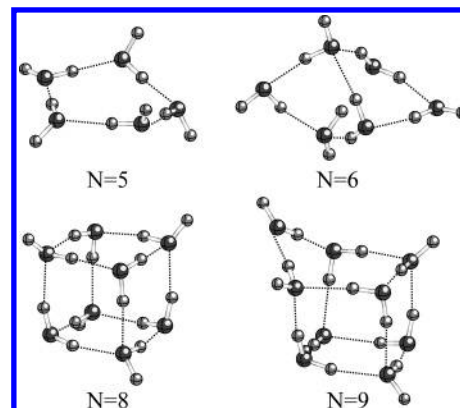


Figure 4. Lowest energy conformations identified experimentally^{52,56,61} for small neutral water clusters.

hydrogen bonds adopted by individual water molecules in the structure. The use of clusters to explore aqueous chemistry presents an avenue for research to establish how complex molecular networks deform at the molecular level when they accommodate free radicals, ions, and excess electrons. A critical goal of the research is to learn how to transfer these paradigms to larger systems, including the behavior of the hydrated electron. What are the rules governing the synergism between the state of the monomer and the supermolecular morphology? Such an effort will clearly challenge the state of the art in theoretical and experimental capabilities but will enable a microscopic understanding of how water molecules distort and change their role from solvent to participant in chemical reactions.

2. Initial Excitation and Relaxation Processes

2.1. Critical Research Issues

Figure 1 shows the range of initial processes induced by ionizing radiation in aqueous media. The molecular water cation and secondary electrons produced by the primary energy transfer initiate virtually all of the subsequent processes that govern the final outcome of the radiolysis process. For example, the secondary electrons can create electronically excited water molecules and transient negative ions, and they can cause subsequent ionizations. All of the species thus formed are chemically active.

Essentially all of the processes leading to water excitation in radiolysis are due to the interactions with low-energy electrons. The relative branching ratios for the decomposition of excited states are neither known nor understood in liquid water. In addition, the excited-state dynamics are expected to depend on the temperature, the phase of water, and the presence of solutes and interfaces. Branching ratios for the decomposition of gaseous excited water have been measured,⁶³ including ratios for dissociative attachment,^{64,65} and impressive advances have recently been made by examining low-energy electrons in ices.^{66–70} However, these measurements are still only a part of the larger puzzle.

Besides our qualitative understanding of the plausible scenarios regarding the primary and secondary

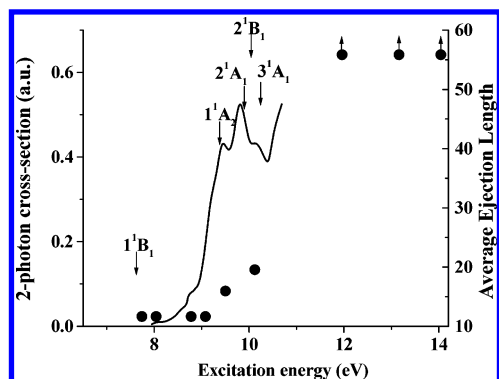
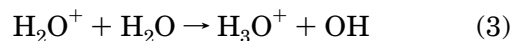


Figure 5. Two-photon absorption cross section for liquid water (left axis) with gas-phase transition assignments⁷⁷ and average ejection length of photoelectrons resulting from excitation of liquid water (●, right axis).⁷⁸

reactions of the radiation-induced cations and sub-excitation energy electrons, very little qualitative information exists about these processes. It is believed that proton transfer from the molecular cation of water to a water molecule occurs on the time scale of <100 fs and leads to the production of OH radicals and H_3O^+ ions, which subsequently hydrate, yielding the hydrated proton. Prior to thermalization, the dissociative recombination reaction of the secondary electron and the molecular water cation is believed to produce a singlet or a triplet excited state of water, which decays to a variety of radical and molecular species.⁷¹ Once its energy has been lost, trapping of the secondary electron gives the hydrated electron, e^-_{aq} .

The characteristics and mobility of electronically excited species (including cations, anions, neutrals, and subionization electrons) created during the radiolysis of water are often poorly understood. For example, the optical spectra of liquid water⁷² (see also Figure 5), crystalline ice,⁷³ and ASW⁷³ all have features characteristic of excitons. The excitons can be formed by direct excitation or via electron-ion recombination, but the importance of excitons in nonthermal reactions in condensed water is unclear, because track-structure simulations of radiolysis in liquid water can successfully reproduce many observations without the inclusion of mobile excitons. However, recent investigations of electron-stimulated reactions in thin ASW and crystalline ice films suggest that excitons can diffuse over distances as large as 40 nm prior to initiating reactions.⁷⁴ In particular, low-energy electrons can initiate dissociation of water molecules adsorbed at a water/Pt(111) interface even for very thick films ($\theta \sim 200$ ML and probably larger), where the energetic incident electrons are absorbed in the first ~ 20 ML of the water film. Similarly, it has also long been believed that hydronium ions readily diffuse in ice via a proton-hopping mechanism. However, recent work by Cowin and co-workers investigating the diffusion of hydronium ions deposited on thin water films has cast doubt on this model.⁷⁵ The relationship between exciton and hydronium mobility in ASW and crystalline ice versus liquid water is a topic for further research.

One of the daunting tasks in sorting out the relaxation pathways of electronically excited water is the fact that an excitation event in the 10–20 eV energy range results in a cascade of outcomes. Chemical rearrangements leading to free radical production begin on a time scale of tens of femtoseconds, depositing large amounts of thermal energy locally, which can, in turn, drive further chemical rearrangements in the surrounding water. To focus our attention on the essential features of the problem, consider the fate of an isolated ionized water molecule, H_2O^+ , embedded in relaxed water. It is expected that the proton-transfer reaction 3 occurs on



essentially the same ultrafast time scale (<100 fs) as the surrounding water responds to the introduction of an ion. What do we need to know about these primary processes? At a minimum, our goal should be to understand and predict how far, for instance, the OH free radical migrates from the H_3O^+ cation when both species are relaxed to the ambient temperature. Why do we not know this already? The process involves a combination of processes:

- dynamics of the intrinsic reaction,
- solvent perturbation of the reaction dynamics,
- vibrational energy transfer pathways,
- proton migration in unrelaxed water, and
- free radical relaxation in unrelaxed water.

Each of these processes has only recently been (or is in the process of being) unraveled and convincingly understood by direct observation in conjunction with theory and simulation. For example, the vibrational state distribution of the nascent OH radical in the gas-phase reaction is not presently known but should be accessible with the arsenal of state-to-state laser and molecular beam techniques presently at hand. Solvent relaxation dynamics around an ion are now also under control, with the fast, impulsive response of water being one of the triumphs of this field.^{28–30} The effect of the solvent on the dynamics of proton-transfer reactions is also a frontier area of chemical physics, and when the solvent is water, this process naturally couples to another active research area involving proton migration and mobility in water. Quantum mechanical effects on proton motion may be important because of the light mass of H, which further complicates the understanding of these processes.

Understanding of the properties and processes of energetic species in aqueous systems is further complicated by the presence of different local environments, such as those at interfaces. For example, electron-driven processes at interfaces can differ substantially from those occurring in the bulk liquid. In radiolysis, the interface may affect the primary and secondary radiation energy depositions, the spatial distributions of ionizations and excitations, and the energy transferred to water molecules near the surface. “Hot” electrons can be scattered or scavenged by the substrate, and solid surfaces can be sources of copious secondary electrons. In general, very little is known quantitatively about the trans-

port of energy across the solid/liquid interface. Low-energy electrons, holes, excitons, color centers, and other species formed by energy deposition in the solid may diffuse to, and drive reactions at, the surface.

Solute molecules can also affect the electron-driven processes. Despite the extensive literature on the radiation chemistry of solutes and their subsequent reactions in water,⁷⁶ there is little understanding of the fundamental charge-transfer and energy-transfer processes by which solute reactions are initiated. Furthermore, little is known about the effects of solute molecules and ions on the decay pathways of liquid water radiolysis. For example, the role of "hot" electrons and presolvated electrons on the efficiency of dissociative electron attachment (DEA) processes involving solutes in an aqueous environment is poorly understood.

The initial excitation and relaxation processes driven by low-energy electrons in aqueous systems span a wide range of energies and time scales. The complexity of the mechanism sketched in Figure 1 has made it difficult to deconvolute detailed information about individual steps in the overall process. Well-designed studies to gain fundamental information about the properties of energetic species in aqueous systems and the individual processes of this complex mechanism are essential.

2.2. Current Research Advances

Because of the complexity inherent in treating energetic processes in water, the primary chemical events remain mysterious even after decades of inquiry. Until very recently, one would have been tempted to conclude that the sheer complexity of the problem would preclude any attempts to establish realistic reaction pathways. On the other hand, the advancement of our understanding of chemical reaction dynamics in the gas phase, in clusters, and in condensed media has been so profound that the primary chemical events following energy deposition are now within reach. Thus, in the traditional scenario for treating chemical processes in water, we imagine an event that disrupts the molecular fabric of the local, molecular environment (or domain). This theoretical molecular domain is then interfaced with the extended medium and highly averaged to recover the bulk response. There are several recent developments that fundamentally change this picture. First, tremendous progress has been made in *ab initio* electronic structure methods, and soon they will be capable of handling sufficiently large systems, for example, up to 20 water molecules, with the accuracy required to characterize reliably the ground-state potential energy surface and address the complexity associated with the collective participation of water in a chemical reaction. Second, experimental methods have been developed to isolate the exact replica of the theoretical model system in the form of a cluster or cluster ion. This advancement allows us to rigorously establish the integrity of these methods by direct comparison with their measured properties in the absence of thermal averaging. Third, ultrafast laser diagnostics are now up to the severe challenges introduced by the extremely fast relaxation processes

in liquid water. Finally, the capability to create thin water films in a controlled manner has been developed. Such films provide low-temperature liquid media in which spatial control provides new opportunities to follow elementary transport of reactive species and the role of interfaces. Thus, *what has changed in the past decade is the maturity and refinement of physical science methods, particularly those that directly probe molecular properties and processes, to an extent that they can now handle the complexity inherent in treating the chemical rearrangements of the water itself.*

The following subsections present a description of the major challenges in electron-driven processes and the modern experimental and theoretical methods that can be and are being used to address them. This compilation is not intended as a complete list of relevant capabilities, but as examples of the recent advances that have been made, which now make it possible to address these complex problems.

2.2.1. Electronic Structure of Aqueous Phases

Research Issues. At the most basic level, information is needed about the electronic structure of aqueous phases, including electronically excited states. Poor understanding of the electronic spectrum of water in the liquid phase has hampered significant progress in understanding the primary steps that give rise to reactive species through dissociation or ionization processes. For instance, the delocalization lengths of initial excited states are not known, and the character of excited-state wave functions (Rydberg versus valence) is not well established in water. Experimental studies show that both radicals and ions are formed down to the lowest energies at which electronic excitation is observed; however, surprisingly little is known about the electronically excited states involved in these processes. The subsequent dynamics of electronically excited states are expected to vary dramatically with excitation energy. For example, the electron ejection length in the ionization channel increases monotonically as a function of excitation energy above 8.8 eV from ~ 8 to 50 \AA ⁷⁷ (see Figure 5). The extent of the initial wave function likely determines the electron spatial trapping distribution.⁷⁸ There have been relatively few attempts to theoretically describe the optical absorption spectrum of liquid water and ice, and this remains a significant challenge for electronic structure theory. In addition, ionization is assumed to occur by excitations from those water orbitals that dominate ionization in the gas phase. An understanding of how the ground-state electronic structure of a water molecule changes in a polarizable aqueous environment is needed to validate this simple picture. It is also important to characterize the different electronic states of the water cation and radical species that result from these ionization and excitation processes. Important questions that still have not been addressed are listed below:

- How is the electronic structure of an excited water molecule altered by the aqueous environment?
- Is information about electronically excited states of gas-phase water molecules a good guide to under-

standing the electronic spectra of condensed-phase aqueous systems?

- How does an aqueous environment alter the potential energy surface of excited electronic states of water, thereby affecting branching ratios (e.g., of radical dissociation products)?

- How are electronic excitations affected by the presence of an interface? How do changes in solvent structure near an interface affect the electronic structure of the water?

- How delocalized are electronically excited states in the condensed phase, and how does the delocalization change with increasing excitation energy?

Research Approaches. The capabilities of third-generation synchrotron radiation sources have created new opportunities for studying the electronic structure of materials. X-ray spectroscopy techniques are well suited to the study of all phases of water and their interfaces because X-ray-in/X-ray-out methods do not require a vacuum environment. It is now possible to make windows strong enough to withstand high pressures and thin enough to allow sufficient transmission of soft X-ray photons. X-ray absorption spectroscopy probes the unoccupied electronic states through core-level excitation processes.⁷⁹ Both valence and core levels can also be excited through inelastic scattering of hard X-rays.⁸⁰ The occupied orbitals in water can be studied using X-ray emission spectroscopy, where a valence electron decays into a core hole with the emission of an X-ray photon.⁸¹

Recently, several experiments have used X-ray spectroscopies to investigate the electronic structure of liquid water and crystalline ice utilizing core-level excitations.^{79–82} With X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy, a substantial number of water molecules in the liquid have been found to have fewer than four hydrogen bonds.^{79,81} Thus, these molecules have a free OH group, thereby resulting in a localized electronic state whose spectral intensity is directly related to the symmetry of the electronic orbitals and their rehybridization due to the local bonding environment.^{81–83} The structure of the liquid-like layer of ice near its melting point has also been studied using X-ray photoelectron spectroscopy (XPS) and XAS. The authors found that the thickness of the liquid-like layer is a sensitive function of the ice temperature and surface cleanliness.⁸⁴

Recent advances in electronic structure methods, as well as advances in computer technology, have also created new opportunities for detailed examination of the electronic structure of aqueous systems. Contrary to the abundance of results regarding the ground-state potential energy surfaces of water clusters^{53,85} and bulk water (see work by Sprik et al.⁸⁶ and Silvestrelli and Parrinello⁸⁷ and references cited therein), scant information currently exists about the nature and manifold of singly excited states,⁸⁸ and virtually no accurate studies of multiply excited states and their couplings from first-principles calculations have been reported. To this end, theoretical studies of the electronically excited states of small water clusters would be of great value for understanding the spectroscopy and ensuing dynamics of

electronically excited states of bulk water. Theoretical methods, such as multiconfiguration (e.g., complete active space) perturbation theory CASPT2⁸⁹ and generalized valence bond methods including configuration interaction (GVB-CI),⁹⁰ exist, and these methods should be useful for accurately characterizing electronically excited states for clusters as large as (H₂O)₆. Recent advances in time-dependent density functional theory (TD-DFT)⁹¹ offer hope of extending these calculations to larger clusters. These advances include improved exchange-correlation functionals with correct asymptotic behavior, which improve orbital energies, thereby improving the predicted excitation spectrum.⁹² Alternatively, hybrid methods that combine mixed quantum-classical models for the solute–solvent interactions together with classical molecular mechanics (MM) for the solvent–solvent interactions, denoted QM/MM methods,⁹³ offer an approach to extend the molecular orbital and density functional theory calculations of excited states to much larger clusters. Much useful information can be obtained from a hierarchy of such calculations, starting with the characterization of the low-lying excited states of small water clusters at the geometries of the low-energy local minima of the ground electronic states. These calculations can be readily extended to allow for finite temperature effects, by calculating the spectra for configurations sampled in Monte Carlo (MC) or molecular dynamics (MD) simulations⁹⁴ on the electronic ground state of the clusters. In addition, they can be carried out on cluster geometries obtained from simulations of bulk water. These calculations can provide excitation energies and transition moments. They also can provide valuable insight into the extent of localization of the various electronically excited states and also into the differences between the excited states of clusters and bulk water. The results of the *ab initio* calculations can furthermore provide input in the parametrization of semiempirical models that provide analytic representations of excited-state potential energy surfaces.⁹⁵ For this purpose, the new generation of flexible, polarizable interaction potentials for water that were parametrized from the results of *ab initio* calculations^{96,97} as well as extensions of the anisotropic site potentials⁹⁸ can be used as viable alternatives to the “direct” *ab initio* dynamics of low spin excited states.

2.2.2. Electron–Water Scattering Cross Sections

Research Issues. Detailed information about electron–water scattering cross sections is required to better understand radiation-induced phenomena in aqueous systems. Secondary electrons have a large amount of excess energy that must be dissipated before they are hydrated. The energy loss processes and associated kinematics (i.e., scattering) determine the path of secondary electrons and the distribution of the reactive species they create through electron-impact ionization, excitation, and dissociative attachment. Knowledge of the scattering cross sections of electrons in the liquid phase for energies <100 eV is vital for track–structure simulations of the nonhomogeneous distribution of reactive species that are localized within spurs. Current track–structure simu-

lations for liquid water model the electronically inelastic scattering cross sections either based on density-normalized, gas-phase cross sections or derived from the dipole oscillator strength distribution for liquid water.^{21,22} Ionization cross sections are modeled on the basis of the dominant gas-phase processes, excitations from the $1b_1$, $3a_1$, $1b_2$, and $2a_1$ orbitals of water.^{21,22} There is also evidence that the gas-phase cross sections can provide a reasonable guide for elastic and vibrational excitation cross sections in liquid water.^{21,22} Therefore, accurate cross sections for electron-water scattering in the gas phase are needed as a baseline for the processes in condensed phases. It is well established that the phase of water (e.g., liquid versus gas) can significantly alter the cross sections. Therefore, it is critical to understand the effects of the aqueous environment on the scattering processes, and knowledge of the electronic structure of the aqueous system including excited states, as discussed above, is vital to gain this understanding. Important questions that still remain unanswered include the following:

- Are gas-phase cross sections for electronic excitations and ionization a good guide for these processes in the condensed phase?
- How does the aqueous phase affect the scattering cross sections? What can we learn about these effects using solvation models (e.g., clusters and continuum dielectric models)?
- How good of an approximation is the use of the dipole oscillator strength distribution for electronic cross sections, particularly over the entire energy range relevant to the low-energy electron driven processes?

Research Approaches. Obtaining cross sections and branching ratios for electron-water scattering processes, even in the gas phase, poses significant difficulties.^{99,100} Dissociation studies pose key challenges to the experimentalist. Challenges include the detection of neutral ground-state fragments, particularly if the final state (electronic, vibrational, and rotational) is determined; the preparation of targets of unusual species for collision studies; and the exploration of the pathways and time scales of the dissociation of electron–molecule collision products with sufficient internal energy to dissociate (metastable dissociative decay). No calculations performed to date on polyatomic targets have attempted to provide detailed information about dissociation pathways or branching ratios. However, progress is being made on both experimental and theoretical fronts.

Reliable experiments focused on determining the gas-phase electron-impact cross sections (EICS) for the dissociation of a molecule into neutral ground-state fragments are now possible for a large number of molecules by combining electron-scattering techniques with optical techniques such as laser-induced fluorescence (LIF), resonant enhanced multiphoton ionization (REMPI), or absorption spectroscopy. Optical probing of the dissociation products provides a powerful and versatile tool for the quantitative detection of the final products of a dissociative electron collision process, in which the products neither have a charge nor carry any excess energy

that can be exploited for their detection. Moreover, optical techniques allow the final state-specific detection of the products (e.g., the selective detection of ground state and electronically excited atoms).¹⁰¹

In 2001, Zecca and co-workers¹⁰² published a critical review of experimentally determined EICS for selected polyatomic molecules in the gas phase for impact energies from ~ 0.01 to 1000 eV. Their review states, "...cross sections for electron scattering on H_2O , in spite of their crucial importance for understanding the biological effects of radiation and atmospheric processes, do not form a coherent set of data". For example, it was shown that the sum of cross sections for different channels did not yield the total cross section, and serious disagreements exist in the partial dissociative ionization cross sections (i.e., in the formation of OH^+ , O^+ , and H^+ fragment ions, measured by different groups using different experimental techniques). Furthermore, the set of H_2O cross sections included no experimental EICS for the neutral dissociation of H_2O into excited and/or ground-state fragments, even though the cross sections for dissociation to ground-state neutral fragments can be comparable in magnitude to ionization cross sections. In addition, no EICS for electronic excitation of H_2O can be found in the literature.

Recently, McConkey and co-workers¹⁰³ used a combination of electron-scattering and LIF techniques to measure the absolute cross section for dissociation of H_2O into a ground-state $OH(X)$ radical and an H atom. This cross section was found to have a maximum of $2.1 \times 10^{-16} \text{ cm}^2$ at ~ 60 eV. It is noteworthy that this partial neutral dissociation cross section is of the same magnitude as the total H_2O ionization cross section and has roughly the same energy dependence. Thus, electron-induced neutral dissociation and ionization of H_2O must be considered to be competing processes over the electron energy range from 10 to 100 eV with comparable cross sections in the gas phase.

Substantial investments have been made in the development of computational methods for studying the fixed-nuclei, electron–molecule scattering problem. The few successful methods¹⁰⁴ that have been developed, which are all variational in nature and make heavy use of the computational tools developed by quantum chemists to study bound-state problems, have all been shown to be capable of providing accurate cross sections for small target molecules and, in a few significant cases (such as Cl_2 , CF_4 , and CO_2), the calculated cross sections have been benchmarked against experimental measurements. Another exciting development is the adaptation of time-dependent methods, such as the multiconfiguration, time-dependent Hartree technique, to study "post-electronic" nuclear dynamics in electron–molecule scattering. First-principle studies of resonant vibrational excitation of a polyatomic have been carried out,¹⁰⁵ and the application of such techniques to dissociative processes now appears to be within the grasp of ab initio computational theory.

Despite rapid progress in the development of powerful theoretical methods for calculating electron-impact ionization cross sections of simple atoms from

first principles,¹⁰⁶ there continues to be a need for simpler, but reliable, methods for computing electron-impact ionization cross sections of complex targets. Fortunately, several such methods have been developed. The binary encounter dipole (BED) model of Kim and Rudd¹⁰⁷ provides single differential or energy-sharing ionization cross sections that can be used to predict the distribution of secondary electrons produced by electron-impact ionization. Unfortunately, the model requires target continuum oscillator strength distributions to several hundred electronvolts to cover a broad range of incident electron energies, and such information is available only for a limited number of species. For total ionization cross sections, the binary encounter Bethe (BEB) model¹⁰⁸ provides a simple analytical formula that requires only properties of the ground-state wave function. It has been successfully applied to compute total ionization cross sections for dozens of atomic and molecular targets.¹⁰⁹ Such methods could easily be used to provide cross-section data for modeling and would be a substantial improvement over the use of atomic stopping powers that are currently being employed in many tracking codes.

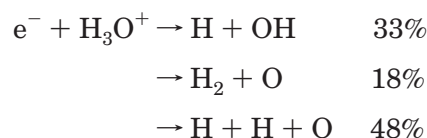
Recent first-principles theoretical calculations have provided valuable new insights into electron–H₂O collisions. Champion et al.¹¹⁰ used the distorted-wave Born approximation to obtain cross sections for electron-impact ionization from threshold levels to 10 keV. The total ionization cross sections were in good agreement with BEB model results¹⁰⁸ and experimental results; the singly differential (energy-sharing) cross sections displayed a significant improvement over the BED¹⁰⁷ results to provide reasonable agreement with available experimental results, and the calculation further provided triply differential cross sections. No account was taken of nuclear dynamics, so branching ratios into specific parent and/or fragment ion channels were not obtained. The first study to treat nuclear motion in a polyatomic target was the Gorfinkiel et al.⁵⁷ calculation of electron-impact dissociation cross sections for H₂O into neutral H + OH. Like the earlier coupled-state calculations of Gil et al.,¹¹¹ the results were sensitive to the number and detailed treatment of the low-lying electronically excited target states. The computed dissociation cross sections were similar in shape but larger in magnitude than the values measured by the McConkey group,¹⁰³ which were normalized to the 1972 dissociative attachment data of Melton.⁶⁴ Nuclear motion was treated only in one dimension using an adiabatic-nuclei approximation with fixed bond angle and OH distance. A more realistic multidimensional treatment would likely reduce the magnitude of the H + OH channel by allowing for flux into other dissociation paths.

Because the interaction of energetic charged particles with matter can be described by its complete optical spectra, it is of crucial importance to know the absolute photoabsorption cross section over a wide energy range. Very recent advances in inelastic X-ray scattering (IXS) spectroscopy have allowed direct measurement of the complete optical oscillator strength distribution of *liquid* water.¹⁹ IXS spectro-

scopy using hard X-rays is equivalent to optical spectroscopy as long as the momentum transfer is very close to zero. This inherently low signal-to-noise measurement is now possible using bright light sources such as the National Synchrotron Light Source at Brookhaven National Laboratory. The new measurements of the oscillator strengths in liquid water are rather different from those measured for the gas phase. This is an important finding because many simulations on the interaction of charged particles with liquid water have used scaled gas-phase values. This new IXS technique can now be used to probe the liquid-phase directly, and the information obtained should be helpful in improving the simulations. Although these measurements provide crucial information about total cross sections, they do not provide information about the final states produced in the scattering events, which are needed to more completely describe the trajectory of electrons and production of reactive species in the condensed phase.

The potential for advances in the theoretical understanding of electron-water scattering in the gas phase is significant; however, the value of this information in describing the condensed phases of water is limited at low electron energies. The potential for error in simple density extrapolation is large as the role of phase is expected to be considerable. For example, inelastic electron-scattering cross sections in gaseous, liquid, and ice water, calculated by employing dipole oscillator strength distributions and using the methodology developed by Ashley and by Green et al., are significantly different due to the effects of the condensed phase.¹¹² Experimental measurements of the oscillator strength of liquid water using the new X-ray light sources are very important. In addition, the development of techniques for calculating condensed phase scattering cross sections for electrons below 100 eV is needed. An accurate theoretical understanding of the effects of phase on electron scattering in condensed water is lacking, and this knowledge is central to a reliable description of the radiation-related problems of liquid and solid materials.

The influence of solvent water molecules on electron scattering and reaction processes is further demonstrated by the dissociative combination reaction of e[−] with the hydrated proton, H⁺(H₂O)_n. In the gas phase, the simple two-body reaction has three major dissociation channels¹¹³

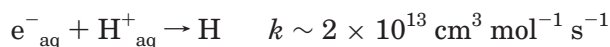


with the three-body channel dominating. In contrast, reaction of e[−] with the cluster H⁺(H₂O)₂ results

almost completely in the dissociation to H and water molecules:¹¹⁴



In the liquid phase, the reaction of the hydrated electron with the hydrated proton does not occur on a time scale shorter than the hydration of the presolvated electron to e_{aq}^- .¹¹⁵ At room temperature, the reaction of the hydrated electron with the hydrated proton (H_{aq}^+)



yields H atom at a rate that is fast, but slower than diffusion-controlled.¹¹⁶ The different outcomes for equivalent encounters in the three systems are obvious. Reliable methods for elucidating the role of solvent water in scattering and reactive encounter and for predicting outcomes of reactions in the different phases of water are a high priority.

2.2.3. Dynamics of Electronically Excited States

Research Issues. Detailed mechanistic information is needed about the dynamics of electronically excited states in aqueous media. In the gas phase, an isolated excited-state water molecule can undergo transitions to other electronic states by radiative or nonradiative (electronically nonadiabatic) processes and can dissociate by transition to an unbound state. The proximity of other molecules in condensed phases can lead to a variety of processes described below, which are induced by collisions of the excited-state water molecule with another molecule:

- additional pathways for quenching of the electronic excitation by nonadiabatic transitions to lower energy states, which will transform electronic energy to vibrational, rotational, and translational energy;
- excitation transfer to other molecules, which can include resonance energy transfer to another water molecule; and
- dissociation of the water into radical species or ionic species (e.g., by ejection of an electron).

In the condensed phase, these processes can result in local heating of the solvent and excitation migration. In liquid water, localized electronic excitations will experience a local environment that fluctuates in time, and the dynamics of the solvent fluctuations can greatly affect the processes. Important questions that should be addressed include the following:

- How does solvent reorganization around an electronic excitation affect the evolution of the electronic state?
- What is the mechanism for the migration of electrons, protons, and electronic excitations and what are the time scales? Can gas-phase collision processes help us understand these processes in condensed phases?
- What is the mechanism of quenching of an electronically excited state? How is the energy released by the quenching dissipated in the solvent, and what is the time scale?
- How are the dynamics of electronically excited states affected by the presence of an interface? How

do changes in solvent structure near an interface affect the dynamics?

Research Approaches. Ultrafast sources of high-energy radiation could be used to follow the short-time dynamics of energetic species created by electron-driven processes in aqueous systems. The Laser-Electron Accelerator Facility (LEAF)¹¹⁷ at Brookhaven National Laboratory and the Table-Top Terawatt Ultrafast High Field Facility (TUHFF)¹¹⁸ at Argonne National Laboratory, which is currently being developed, are two ultrafast sources of pulsed electrons that should be important for studies of nonhomogeneous processes in radiolysis. In the LEAF system, the electron pulse is produced by laser light impinging on a photocathode inside a resonant cavity. The emitted electrons are accelerated to 9.2 MeV by a pulse of radio frequency (RF) power, and the laser pulse is synchronized with the RF power to produce the electron pulse lengths as short as 5 ps. The TUHFF system makes use of wake-field acceleration to generate very short pulses of radiation. A femtosecond terawatt laser is focused into a pulsed supersonic gas jet to produce electron pulse widths that are expected to be ~ 1 ps. An analyzing optical pulse of 50 fs is also generated that is absolutely synchronized to the electron pulse.

New ultrafast X-ray sources with femtosecond resolution are currently being developed that could also be important for generating ionizing radiation for radiolysis studies. Both the SubPicosecond Photon Source (SPPS) and Linear Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center (SLAC) will deliver hard X-rays with a pulse width of 100 fs. The SPPS source began operation in 2003, providing 10^8 photons per pulse with a frequency of 30 Hz at a fixed energy of ~ 10 keV. The LCLS will be ready as the first hard X-ray free electron laser facility in 2007, providing an ultrabright source. It will deliver 10^{12} photons per pulse with a frequency of 120 Hz, and the energy will be tunable over the range of 1–10 keV.

All of these resources will be extremely useful for time-resolved radiolysis studies. The collective fluctuations of the hydrogen-bond network are expected to strongly influence the solvation of reactive intermediates in water. The solvation of charge displacements by electronic excitation of chromophores in the 1–2 eV range is dominated by the librational response of water, which occurs on the time scale of tens of femtoseconds, and additional contributions from the stretching and deformation of the hydrogen-bond network on sub-300 fs time scales. Longer time scales are associated with the breaking and reforming of hydrogen bonds, which play a crucial role in the transport processes, and with the reactions arising from the nonhomogeneous distributions of radicals and ions that are produced by ionizing radiation.

Core-level decays can be used to study ultrafast processes on a 0.1–10 fs time scale in aqueous systems using the O1s level in the water molecule. A hole created in the O1s level has a lifetime of ~ 1 fs, providing sensitivity to processes that take place on such a time scale. Using resonant photoemission,

where the direct photoemission process is resonantly enhanced at a core-level threshold due to coupling with the Auger decay process, the delocalization rate of excited states in ice has recently been studied by Nordlund et al. at Stanford.¹¹⁹ Upon excitation into the conduction band, there is no signature for resonant enhancement, indicating a delocalization process much faster than the lifetime of the O1s level. However, core excitation of states at the ice surface corresponding to the dangling OH bond results in a strong resonant enhancement in the photoemission cross section. This can be interpreted as a localized state on the OH group with no evidence of delocalization at the time scale of the O1s lifetime. It has recently been shown that the liquid state contains a large fraction of free OH bonds, so we can anticipate a behavior rather similar to that of the ice surface.⁷⁹ In X-ray emission spectroscopy (XES), a final state after the radiant decay process is obtained that is similar to that observed in valence photoelectron spectroscopy (PES). A comparison between PES and XES spectra from ice shows a shift of 1 eV in the spectral feature corresponding to the strong OH bonding orbital $1b_1$. A proton has been partly transferred to a neighboring water molecule during the lifetime of the core hole, ~ 3 fs. There is an isotope effect indicating different transfer rates depending on the mass of the hydrogen atom. Such techniques enable us to access ultrafast dissociation processes.

The scanning tunneling microscope (STM) provides a new possibility for injection of energetic electrons through a solution, to initiate electronic excitations in adsorbates bonded at specific atomic sites on a surface. By adjusting the tip-to-substrate distance, the injection energy can be controlled. Recent experiments demonstrate that shielded STM tips can work effectively in solution.¹²⁰

Detailed studies of desorption induced by electronic transitions (DIET) and photon-stimulated desorption (PSD) from nanoscale films of H_2O , from sub-monolayer to multilayer coverages, are providing insights into the initial electronic excitations and their evolution (with and without coadsorbed species) for a variety of substrates;^{67–69,74,121} however, much more work is needed. Ultrafast pulse radiolysis and photolysis experiments also need to be done on these complex systems. Theoretical calculations of the electronic structure of water–adsorbate systems, as well as the dynamics of energy transfer across the interface, are difficult, but will be critical to interpreting the experimental measurements and providing a picture of what is happening at the atomic/molecular level.

A longer range goal of theoretical studies of aqueous clusters is to consider the dynamics of the excited states. This is a very challenging problem; its complexity is illustrated by using the water dimer as an example. The lowest singlet excited state of the monomer ($1b_1 \rightarrow 4a_1$) gives rise to four electronically excited states in the dimer. Although these states may be energetically well separated at the geometry of the gas-phase dimer, this will certainly not be the case for the range of geometries important at finite temperature or even for following the time evolution

of the excited states formed by vertical excitation from the minimum of the ground state of the dimer. Thus, it will be necessary to include the complete manifold of states in simulations of the excited-state dynamics. It is now possible to achieve this by calculating the energies, forces, and nonadiabatic couplings “on the fly.”¹²² Such simulations would give energy distributions of the OH and H_3O^+ products as a function of the excitation wavelength. In extending the studies of the dynamics to larger clusters and to bulk water, it will be useful to adopt a QM/MM embedding scheme, with a small cluster, including two through five monomers, treated quantum mechanically, and the neighboring water molecules being treated via a force field that includes coupling with the molecules treated quantum mechanically. The geometry of the central cluster can be chosen to mimic that of condensed-phase environments (i.e., bulk water or ice), and the excited-state manifold can be obtained as a function of the surrounding environment. These simulations would allow for both radical and ionic dissociation channels. Further developments in the area of empirical or semiempirical force fields for water that incorporate the electronic degrees of freedom will enhance our understanding of these processes in clusters and in the bulk.

2.2.4. Relaxation and Reaction Processes Occurring under Highly Nonequilibrium Conditions

Research Issues. A molecular scale understanding of relaxation and reaction processes occurring under highly nonequilibrium conditions is needed. The initial reactions occurring at short times after deposition of energy from ionizing radiation will be affected by nonhomogeneous distributions of reactants. The effects of nonequilibrium energy distributions in the solvent and reactants on initial reactions, such as proton transfer from H_2O^+ to a water molecule, are not understood. In addition, the interaction of reactive species with each other must be considered, such as the recombination of H_2O^+ and an electron. Reactions involving solute molecules, as well as those with water molecules, must also be considered. Some of the pressing questions that should be addressed include the following:

- What are the threshold and branching ratios for the decomposition of the water and solute molecules?
- How energetic are the fragments (e.g., H^\cdot , OH), and what are their ranges in solution?¹²³
- How does the solvent affect the thresholds, cross sections, excitation processes, and potential surfaces?

The presence of interfaces and solute molecules adds more complications to the challenges already discussed for understanding electron-driven processes in aqueous systems. The structure of water near an interface is determined by the balance of hydrogen bonding between the water molecules and the local bonding to the surface. Because of the wide variety of geometric and electronic structures associated with different surfaces (e.g., metals, oxides, crystalline, amorphous), there are many different overlayer structures and species as a result of the adsorption process.^{121,124} Although the bonding of water molecules to the interface is relatively weak,

the interface greatly affects the solvent structure of the first few monolayers of water adsorbed at the interface. The change in solvent structure can greatly affect the electronic structure of excited states and their subsequent dynamics. In addition, coupling between electrons in the solvent and those in the solid can be very strong, thus altering the nature of the ground and excited electronic states and dramatically changing their dynamics (e.g., allowing ultrafast charge-transfer processes and opening unique channels for electron-driven processes). If the surface is a metal, electronic wave functions near the Fermi level extend into the solution and can significantly affect the behavior of the water and excitation processes, thereby affecting both the binding energy of molecules to the surface and any electronic excitation process. Therefore, understanding the structure of the first few layers of liquid water adsorbed on surfaces is critical. It is also important to understand how both the changes to solvent structure and the presence of a different material affect the electronic structure, dynamics of energetic electrons (i.e., electron scattering), dynamics of electronically excited states, and relaxation and reactions near the interfaces.

The presence of solutes in the liquid or adsorbed at an interface can also have a large effect on the observed electron-driven chemistry in aqueous systems. Solute species, particularly ions, can affect the solvent structure near the solutes. As in the case of interfaces, the effects of changes to solvent structure on electron-driven processes need to be understood. The scattering of electrons by solute species is an important area. For example, the role of "hot" electrons and presolvated electrons on the efficiency of DEA processes involving solutes in an aqueous environment is poorly understood. In addition, it is generally accepted that the hydrated electron is responsible for bond breaking to form halide ions in aliphatic compounds containing Cl, Br, or I. However, for fluorine-containing compounds, such as C_6F_6 , $\text{C}_6\text{H}_5\text{F}$, and CF_4 , where a few electronvolts of electronic excitation is needed for DEA, the hydrated electron is too low in energy to initiate dissociation, and the "hot" presolvated electrons may be implicated. In addition, giant enhancement effects are observed for electron-induced dissociation of chlorofluorocarbons (CFCs) coadsorbed with water, which are not understood and require further study.¹²⁵ The interaction of electrons with solute species in aqueous environments is relevant to issues facing planetary scientists¹²⁶ and radiation biologists. An important question is, "can charge and energy transfer¹²⁷ from transient negative ions (e.g., H_2O^{*-}) influence solute decomposition?"

Research Approaches. Addressing the challenging issues of electron-driven processes in aqueous systems will require new approaches that capitalize on recent advances to probe molecular scale properties and processes in complex systems. Tremendous advances have been made over the past several years in our understanding of the structure, energetics, and dynamics of aqueous systems. These advances put us in the position to be able to address some of the

difficult questions related to electron-driven processes in aqueous systems.

In radiolysis, more than one ion pair is created within a small volume (or within a spur). One of the critical factors that determines how much damage/product formation occurs from radiation is the competition between diffusion, combination, and reaction with other species in the solution. The spatial distribution of these ions is critical in determining the outcome of the competition events. Pulse radiolysis sources, with resolutions in the 10–30 ps range, can probe the details of these distributions. Photoexcitation experiments have the requisite time resolution, but cannot create the appropriate spatial distribution. A new class of radiation sources is now being commissioned such as the LEAF Facility at Brookhaven National Laboratory and the Elise Facility at the University of Orsay that make use of laser-driven accelerators to create pulses of ≤ 5 ps. The facility at the University of Osaka makes use of a chicane to shorten electron pulses to < 0.5 ps. A new technique, that of plasma wake-field acceleration in a gas jet using a terawatt laser, may make electron pulses of much less than a picosecond.¹¹⁸ The capabilities of these machines are sufficient to attack the question of the initial spatial distributions in spurs.

Due to the long mean free path of particles in an ultrahigh vacuum, it is possible to directly detect the primary radiolysis products from the irradiation of ASW and crystalline ice in ultrahigh vacuum. This fact has been exploited to develop an understanding of electron-driven processes in the solid phases of water.^{66–68,70,128,129} Due to the extremely short mean free path of particles in the vapor above the liquid ($\sim 10 \mu\text{m}$ at 4.6 Torr and 273 K), the direct detection of the primary radiolysis products is typically very problematic for liquid water. However, very thin (5–10 μm diameter) jets of liquid water can be introduced into high vacuum while keeping the background pressure at the level of 10^{-7} – 10^{-6} Torr.¹³⁰ Because of the rapid decrease in pressure with increasing distance from the jet, it is possible to have nearly collision-free detection of the primary ionic, atomic, and molecular products of water radiolysis using the techniques developed in the studies of ASW and crystalline ice.

There has been considerable interest in electron-, ion-, and photon-stimulated reactions in ASW and in crystalline ice. As described earlier, ASW is a model for liquid water. In addition, nonthermal processes in ASW are directly relevant in a number of astrophysical environments, such as comets and interstellar dust clouds, where ASW is prevalent. One major advantage of ASW is that, because of its low vapor pressure, it can be studied with the techniques of ultrahigh vacuum surface science. This approach enables detailed studies—such as the dissociation dynamics of excited states probed by low-energy electrons and REMPI spectroscopy—that are difficult or impossible in the liquid water.

Rowntree, Parenteau, and Sanche have carried out an extensive series of experiments on the role of transient negative ions and dissociative electron attachment in molecular solids in general and in

ASW¹²⁸ in particular. Their results suggest that the dissociative electron attachment resonances present in the gas-phase water survive in the condensed phase and are important in ASW. They have also investigated the role of pre-existing traps in ASW on the trapping of low-energy electrons and their capture from electronically excited adsorbates.⁶⁶ Michaud, Wen, and Sanche have used careful electron-scattering measurements to extract the scattering cross sections for various inelastic processes for electron energies of <100 eV.⁷⁰ These measurements are useful for modeling the distribution of events in the track structure of high-energy particles in water, for example, where previously gas-phase cross sections have been used.

The neutral (D , O , D_2 , O_2)^{67–69} and ionic (H^+ , H^-)¹²⁹ electron-stimulated desorption products from amorphous D_2O have been investigated by Orlando and co-workers. Using REMPI spectroscopy, they were able to map the internal (i.e., electronic, rotational, and vibrational) and translational energy of the neutral desorbing products. For the atomic products, they found that the yield was proportional to the number of ionizations induced by the incident electron, but that the dissociative state was the same, independent of the incident electron energy for energies from the threshold level (i.e., ~ 6 – 7 eV) up to 100 eV.⁶⁷ Looking at molecular hydrogen, Orlando and Kimmel found evidence for dissociative attachment resonances that are not seen in the negative ion channel.⁶⁸

Baragiola and co-workers have recently studied the radiolysis of cubic ice with 200 keV protons¹³¹ and the photolysis of ASW with Lyman- α photons ($E = 10.2$ eV).¹³² For energetic ions interacting with ice, it is known that the sputtering yield is proportional to the electronic stopping power of the ions (i.e., that the sputtering process is initiated by ionizations and electronic excitations). For the proton-irradiated ice, H_2O and O_2 were the primary sputtering products, with comparable yields. O_2 was also trapped in the ice during the irradiation. Lyman- α photons primarily resulted in desorption of water molecules, but the process was second order in the photon flux, which suggests that a two-photon mechanism is involved. The authors invoke the recombination of radicals as the mechanism driving desorption in the films. A two-electron process involving a long-lived precursor has also been invoked for the electron-stimulated production of O_2 from ASW.⁶⁹

Whereas a considerable amount is known about the nonthermal processes initiated in ASW and ice by photons, ions, and electrons, a unified picture is still elusive. For example, as mentioned above, the sputtering of ice by high-energy ions is a function of the electronic stopping power of the ice. However, there is currently no satisfactory model to relate this result to the processes that are initiated by low-energy electrons (typically $< \sim 100$ eV) even though those events are almost certainly responsible for the sputtering. Likewise, the relationship between the dissociation processes induced by, for example, a Lyman- α photon and an electron of the same energy is unknown. To address these and other issues, new

measurements are needed for energy and angular distributions of neutral fragments (including metastables). These will complement ongoing studies of yields and thresholds of neutrals and angular distribution of ions.

Multidimensional spectroscopic techniques [e.g., infrared (IR) and Raman] offer novel probes of the structure and dynamics of molecular systems.¹³³ They can be used to probe bulk water, interfaces, and transient species. Sequences of ~ 50 fs IR pulses allow creation and manipulation of coherences among localized vibrations. Furthermore, two-dimensional correlation plots of the signals provide femtosecond snapshots of molecular motions. Cross-peaks of selected vibrations (for instance, between a solute and local solvent modes) show their couplings, which can then be inverted to yield the underlying structures. State line broadening may be eliminated, thus allowing resolution of peaks that completely overlap in the IR spectra. By optically initiating a process, it is possible to follow the subsequent dynamics using local probes. These techniques will allow vibrational relaxation and energy transfer to be probed. Furthermore, pulse shaping allows control of many of the pulse parameters (such as pulse shapes, frequencies, delays, and phases), which can in turn be used for the design of pulse sequences to achieve a predetermined goal in analogy to nuclear magnetic resonance (NMR) spectroscopy. However, fundamental differences between NMR and optics, such as the relaxation time scales, require development of new strategies of pulse sequences. Finally, a mixture of many species with overlapping spectra can be separated by selectively enhancing the multidimensional spectrum of a desired species.

The techniques of coherent nonlinear and two-dimensional spectroscopy extended to the vacuum ultraviolet (VUV) with attosecond, high-harmonic sources offer approaches to revealing the time scales and mechanism of production and solvation of intermediates and the transport processes in water. Three-pulse photon echo peak shift measurements can be used to reveal the time scale of frequency fluctuations and the Stokes shift accompanying the solvation of reactive species. Such experiments on the hydrated electron should allow us to probe the local water structure. This requires very short pulses (~ 5 fs) to cover the bandwidth. Such preliminary experiments were recently reported by Wiersma's group.¹³⁴ Two-color peak shift measurements can be used to correlate the dynamics of two species, such as the correlation between the excitation of H_2O and the production of OH radical. When multiple overlapping resonances contribute to the absorption spectrum, such multi-resonant experiments can be extended to two-dimensional correlation spectroscopies to reveal the underlying structure and dynamic evolution of spectral components. Two-dimensional correlation methods offer an approach that can be used to follow the transport of excess particles. The infrared vibrational spectra of excess protons hydrated in different complexes are believed to show distinct spectral signatures in the mid-IR range. Two-dimensional correlation spectra between such spectral features

(i.e., "cross-peaks") can be used to understand the mechanism and time scale of proton transport through the breaking and re-forming of hydrogen bonds. Underlying all of these efforts is a need to systematically investigate the electronic and vibrational spectroscopy of intermediates, both experimentally and computationally.

Supercritical water will provide a convenient medium for altering solvent properties systematically. For example, the effects of solvent structure on the hydration of the electron can be investigated using supercritical fluids. The role of electron solvation has been investigated in methanol in both liquids¹³⁵ and supercritical liquids,¹³⁶ but to our knowledge, similar experiments have not been done using water because the starting system is hard to form.

High-resolution electron energy loss studies and Fourier transform infrared spectroscopy coupled with velocity, quantum-state, and angle-resolved DIET measurements can be major contributors to our understanding of hydration spheres surrounding ions, as well as ion pairs, in model aqueous systems such as ultrathin films of ASW, ice, flash frozen brines, and liquid beams.

Molecular beam techniques are ideally suited to synthesize nanoscale films because they allow for the precise control of many of the important growth parameters including the deposition flux, collision energy, incident angle, and growth temperature. It is known that thin films that are intentionally porous can be grown, with the extent of the porosity dependent on the impingement flux, substrate temperature, and the angle of incidence of the molecular beam.¹³⁷ Films with specific surface areas of $>1000 \text{ m}^2/\text{g}$ can be synthesized from a wide variety of materials using these techniques. These structurally tailored films provide novel platforms for studying electron-driven processes at interfaces and in confined geometries.

3. Reactions of Radicals and Ions in Aqueous Solutions

3.1. Critical Research Issues

The cascade of initial excitation processes, which are generally high-energy processes that occur over short times (e.g., less than tens of picoseconds), and subsequent relaxation processes leads to the production of reactive radical and ionic species. The primary reactive species produced by ionizing radiation of pure water are hydrogen atom (H), hydroxyl radical (OH), hydrated electron (e^-_{aq}), and hydrated proton (H^+_{aq}). Although thermally equilibrated and fully hydrated, they are not yet uniformly distributed throughout the solution. Any solutes present in concentrations higher than a few weight percent produce additional radicals from direct ionization and excitation, and the presence of solid interfaces can further affect what species are present at these early times. In this nonhomogeneous environment, recombination reactions, primarily of radical species, compete with diffusion to make the spatial distributions of the reactive species homogeneous, which takes several microseconds. The relative proportions of those radicals prevailing at this time can be adjusted

to provide a wide range of oxidizing to reducing environments by altering the pH and adding appropriate chemical scavengers. This opens up the possibility of many different secondary reactions of these radicals with each other and with dissolved substrates. The rate constants for a large number of such reactions have been measured under ambient conditions.⁷⁶ Immediate applications of such rate constant information abound in diverse areas, such as energy production and storage, nanoparticle synthesis, and remediation of high-level nuclear wastes. Furthermore, there is great interest and progress to be made in understanding the role of free radicals in biological systems, for example, in connection with radiation damage and therapy, oxidative stress, aging, normal cellular metabolism, and neural signaling. Advancing the understanding of radical reactions in water will have a strong impact on all of these topics. There have been many reviews of radical reactions, and our goal is not to try and cover all of these but simply to discuss the ones relevant to the radiation chemistry of aqueous systems.^{116,138–140}

It is well established that water intimately controls the chemical reactivity of dissolved species. Hydration alters the relative energetics of reactants, products, and transition states and physically mediates diffusion and caging; in some instances, individual water molecules may act as reactants and catalysts. Examples of strong hydration effects include alteration of acidity and basicity, facilitation of 1,2-hydrogen shifts, decomposition of certain oxoradicals (e.g., β -scission of alkoxyl radicals), and stabilization of ionic and zwitterionic structures. Although the effects of aqueous solvation on chemical reactions have been well established under ambient conditions, much less is known about these effects at other conditions, particularly the high temperatures and pressures characteristic of supercritical water. Whereas some useful correlations exist, predictive capability remains elusive, and it is not known how to extend the information available under ambient conditions to supercritical conditions. It is imperative to now address uncertainties of how the thermodynamics and kinetics of known chemical reactions, as well as new ones yet to be discovered, are affected by changes in temperature, pressure, pH, and ionic strength.

The reaction mechanism in radiolysis of pure water alone includes a long list of elementary reactions involving species such as H, O, OH, HO_2 , e^-_{aq} , H^- , OH^- , O^- , O_2^- , H_2O , H_2 , H^+_{aq} , H_2O_2 , and O_2 . Table 1 shows rate constants for reactions that have been used in models of pure water radiolysis in four studies^{141–144} between 1969 and 1991.¹⁴² The set of chemical reactions used by LaVerne and Pimblott¹⁴⁴ to investigate the consistency between radical-scavenger experiments and the sub-microsecond kinetics of water radiolysis is adequate for G value calculations. LaVerne and Pimblott¹⁴⁴ took these rate constants from the compilation by Buxton et al.¹¹⁶ In addition, the diffusion of these species is important, particularly at earlier times when their distributions are nonhomogeneous. A unique characteristic of many of these species is that they are open-shell radical systems (i.e., either neutral or ionic).

Table 1. Rate Constants for Reactions Used in Models of Pure-Water Radiolysis in Four Studies between 1969 and 1991

reaction ^{a,b}	<i>k</i> (M ⁻¹ s ⁻¹) ^{a,b} at 25 °C			
	WBRM ^c	BM ^d	CMD ^e	LP ^f
e ⁻ _{aq} + e ⁻ _{aq} → H ₂ + 2OH ⁻	4.5 × 10 ⁹	5.1 × 10 ⁹	6.0 × 10 ⁹	5.5 × 10 ⁹
e ⁻ _{aq} + H ⁺ _{aq} → H	2.2 × 10 ¹⁰	2.4 × 10 ¹⁰	2.3 × 10 ¹⁰	2.3 × 10 ¹⁰
e ⁻ _{aq} + H → H ₂ + OH ⁻	2.5 × 10 ¹⁰	2.5 × 10 ¹⁰	2.5 × 10 ¹⁰	2.5 × 10 ¹⁰
e ⁻ _{aq} + OH → OH ⁻	3.0 × 10 ¹⁰	3.0 × 10 ¹⁰	3.0 × 10 ¹⁰	3.0 × 10 ¹⁰
e ⁻ _{aq} + H ₂ O ₂ → OH + OH ⁻	1.2 × 10 ¹⁰	1.3 × 10 ¹⁰	1.2 × 10 ¹⁰	1.1 × 10 ¹⁰
e ⁻ _{aq} + O ₂ → O ₂ ⁻	2.0 × 10 ¹⁰	1.9 × 10 ¹⁰	1.9 × 10 ¹⁰	1.9 × 10 ¹⁰
e ⁻ _{aq} + O ₂ ⁻ → HO ₂ ⁻ + OH ⁻	2.0 × 10 ¹⁰	3.3 × 10 ⁶		
e ⁻ _{aq} + HO ₂ → HO ₂ ⁻	2.0 × 10 ¹⁰	2.0 × 10 ¹⁰		
e ⁻ _{aq} + HO ₂ ⁻ → OH + 2OH ⁻		3.5 × 10 ⁹		
e ⁻ _{aq} → H + OH ^{-b}	8.3 × 10 ²	8.3 × 10 ²		
H + OH ⁻ → e ⁻ _{aq}	2.0 × 10 ⁷	2.0 × 10 ⁷		
H ⁺ _{aq} + OH ⁻ → H ₂ O	1.4 × 10 ¹¹	1.4 × 10 ¹¹	3.0 × 10 ¹⁰	1.4 × 10 ¹¹
H ₂ O → OH ⁻ + H ⁺ _{aq} ^b		2.6 × 10 ⁻⁵	5.5 × 10 ⁻⁶	
H ⁺ _{aq} + O ₂ ⁻ → HO ₂	5.0 × 10 ¹⁰	5.0 × 10 ¹⁰	3.0 × 10 ¹⁰	3.8 × 10 ¹⁰
HO ₂ → O ₂ ⁻ + H ⁺ _{aq} ^b	2.5 × 10 ⁶	8.0 × 10 ⁵	1.0 × 10 ⁶	
H + H → H ₂	1.0 × 10 ¹⁰	1.0 × 10 ¹⁰	1.0 × 10 ¹⁰	7.8 × 10 ⁹
H + OH → H ₂ O	2.5 × 10 ¹⁰	2.0 × 10 ¹⁰	2.4 × 10 ¹⁰	2.0 × 10 ¹⁰
H + O ₂ → HO ₂	2.0 × 10 ¹⁰	1.9 × 10 ¹⁰	1.0 × 10 ¹⁰	2.1 × 10 ¹⁰
H + O ₂ ⁻ → HO ₂ ⁻	2.0 × 10 ¹⁰	2.0 × 10 ¹⁰		
H + HO ₂ → H ₂ O ₂	2.0 × 10 ¹⁰	2.0 × 10 ¹⁰	1.0 × 10 ¹⁰	
H + H ₂ O ₂ → OH	4.0 × 10 ⁷	9.0 × 10 ⁷	1.0 × 10 ⁸	9.0 × 10 ⁷
OH + OH → H ₂ O ₂	5.0 × 10 ⁹	4.5 × 10 ⁹	4.0 × 10 ⁹	5.5 × 10 ⁹
OH + HO ₂ → O ₂	1.2 × 10 ¹⁰	1.2 × 10 ¹⁰	1.0 × 10 ¹⁰	
OH + O ₂ ⁻ → O ₂ + OH ⁻	1.5 × 10 ¹⁰	1.2 × 10 ¹⁰		
OH + H ₂ O ₂ → HO ₂	4.5 × 10 ⁷	4.5 × 10 ⁷	5.0 × 10 ⁷	
OH + H ₂ → H	4.5 × 10 ⁷	4.5 × 10 ⁷	6.0 × 10 ⁷	
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2.7 × 10 ⁷	2.7 × 10 ⁶	2.0 × 10 ⁶	
HO ₂ + O ₂ ⁻ → O ₂ + HO ₂ ⁻	1.5 × 10 ⁷	1.5 × 10 ⁷		
HO ₂ ⁻ → H ₂ O ₂ + OH ^{-b}		1.0 × 10 ⁴		
H ₂ O ₂ + OH ⁻ → HO ₂ ⁻		1.0 × 10 ⁸		
2O ₂ ⁻ → O ₂ + H ₂ O ₂ + 2OH ⁻	1.7 × 10 ⁷	5.6 × 10 ³		

^a Except when it is a sole reactant or product, water is omitted. ^b Unimolecular decay rates have units of s⁻¹. ^c Willis et al.¹⁴¹ ^d Burns and Moore.¹⁴² ^e Chatterjee et al.¹⁴³ ^f LaVerne and Pimblott.¹⁴⁴

Computer codes are available for stochastic simulations of electron radiolysis of water (see Pimblott and LaVerne²² for a review). Miller¹⁴⁵ discussed the intrinsic uncertainty in these methods due to our limited knowledge of dielectric relaxation in water and proposed an alternative approach based on well-established aspects of track-structure simulation in water. Stochastic simulations of radiolysis that follow the history of individual molecules usually invoke the approximation of independent reaction times¹⁴⁶ rather than actually simulating Brownian motion. This method has been applied most often to low-LET radiation, where large fluctuations occur in the number of radicals produced in spatially isolated energy deposition events.

Although the reactions of radical species have been studied over wide temperature ranges for gas-phase systems, the data for aqueous-phase systems is more limited. As illustrations, we focus the discussion on several relevant examples for which aqueous solvation changes the nature of an important kinetic process and the fundamental nature of the process is not well understood over a wide range of physical conditions.^{4,27,147–153}

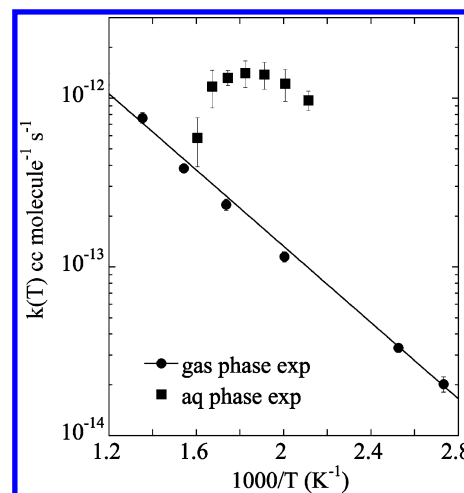


Figure 6. Thermal rate constants for the reaction of OH with H₂ in aqueous solution (■)⁴ and in the gas phase (●).¹⁵⁷ The solid curve is an Arrhenius fit for the gas-phase rate constants over the temperature range of 350–800 K.

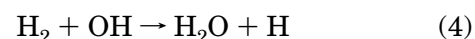
3.1.1. Radical Diffusion

Many reactions of radicals, particularly radical recombination reactions, have small activation energies and are limited by the rate of diffusion of the radical species. In addition, competition between reactions and diffusion of species, such as e⁻_{aq}, H, OH, and HO₂, is important in the early stages of the electron-driven process when these species are thermalized but not homogeneously distributed. As an example, consider the diffusion of the OH radical. Direct measurements of the diffusion coefficient of transient neutral species are difficult, and the actual data on OH radical diffusion are limited.¹⁴⁷ The temperature dependence of the OH diffusion coefficient has only been estimated, using Stokes law or assuming the same temperature dependence as water self-diffusion.

Diffusion of radical species is controlled by the solvation structure and energetics around them, as well as the dynamics of the solvent molecules. Recent studies have shown evidence of the importance of solute-solvent interactions,^{154,155} however, the relative importance of short-range solvent-solute interactions versus more collective effects of the solvent (e.g., friction) on the diffusion coefficients is still in question.¹⁵⁵ Also, recent studies of ion diffusion in supercritical water indicate that local interactions of solvent with the ions are the source of the anomalous behavior of the diffusion coefficient with respect to density under supercritical conditions.¹⁵⁶

3.1.2. Activated Radical Reactions with Stable Molecules

Reactions of radical species with stable (closed-shell) molecules involve bond breaking and bond making, which generally lead to an activation barrier. As an example, consider the reaction



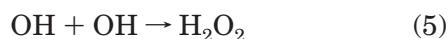
which is important in water-cooled nuclear reactor pipes in which hydrogen is added to the coolant water as a scavenger of hydroxyl radicals to prevent corrosion. As shown in Figure 6, this “simple” reaction

has been found⁴ to unexpectedly slow above 275 °C ($1000/T = 1.82 \text{ K}^{-1}$ for $T = 275 \text{ °C}$). The gas-phase rate constant increases monotonically with temperatures from 300 to 1000 K, and the activation energy for this reaction is $\sim 5.0 \text{ kcal/mol}$ for the temperature range of 125–325 °C.¹⁵⁷ The activation energy in water is $\sim 3.5 \text{ kcal}$ for temperatures between 200 and 250 °C, and the rate constant is enhanced by a factor of ~ 10 over the gas-phase value at 200 °C. The aqueous-phase rate constant drops off precipitously at temperatures $> 275 \text{ °C}$, and at 350 °C, the rate constant is only a factor of ~ 1.6 larger than the gas-phase value. The temperature dependence of the aqueous-phase rate constant is not understood at this time. Furthermore, researchers attempting to model supercritical water oxidation have used gas-phase combustion literature reaction rates, modified for bulk solvent effects.⁸ To extrapolate from the gas phase, the effects of solvation on reactants, transition states, and products need to be understood and predictable. Not only are the models quite complex, but it is also not certain that they properly describe the chemistry; further study of these processes is needed. Therefore, it seems to be very important to directly measure a number of representative OH radical reactions in high temperature and supercritical water, to see whether simple corrections to the gas-phase rate constants can be trusted. Other benchmark reactions that ought to be measured include the H abstraction reaction from methanol and the addition of OH to benzene or phenol.

The rate constants for these types of activated reactions are significantly influenced by the change in energy along the reaction path, which in turn is modified by the change in solvation structure and energetics around the reacting species along the reaction path. Clearly, an understanding of the solvation and how it changes with temperature and pressure is essential to understanding these reactions in aqueous environments. This information is needed for the reactant species and for the transition states as well. In addition, the role the solvent plays in the reaction dynamics needs to be considered.

3.1.3. Radical–Radical Combination Reactions

The reaction of two radical species, such as e^-_{aq} , H, and OH, can lead to the production of a stable molecule or anion. As an example, consider the recombination of OH radicals



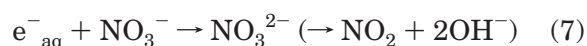
which is an important termination reaction for the OH radical. This reaction, as well as the reaction of OH with H atoms and with e^-_{aq} , is diffusion-limited at room temperature. However, the activation energies for all of these reactions are well below the activation energy for diffusion, when measured at up to $\sim 200 \text{ °C}$. This behavior has not been explained, except for the postulation of a small activation barrier of a couple of kilocalories per mole of unknown origin that begins to limit reaction once the diffusional barrier is overcome at higher temperature.¹⁴⁸ Understanding this reaction also emphasizes the need for

measurements of the OH radical diffusion coefficient, and especially for the free energy of hydration of OH over the entire water phase diagram.

Although knowledge of the factors controlling radical diffusion, as discussed above under section 3.1.1, is necessary to understanding this radical recombination reaction, it is clearly not sufficient to explain the experimental findings. Information is also needed about the reaction energetics as the two radicals approach each other, which will be influenced by the solvation structure around the radicals and how the solvation spheres around these radicals interact with each other. The interactions of small radicals such as H and OH with H_2O in terms of the free energy of solvation are weak in contrast to that of ions, so that the energetic effects on reaction rates can be subtle and accurate calculations will be required.¹³² A further complication is that the two open-shell systems can interact on multiple potential energy surfaces. The interaction of two doublet OH radicals will give rise to an attractive singlet state that leads to H_2O_2 and three triplet states that give rise to the possibility of disproportionation to triplet O and water. Production of triplet O has been observed in photolysis of H_2O_2 in solution and matrices. The yield is very small in neutral or acidic solutions and increases with pH. The spin–orbit operator couples the singlet and triplet states. The effect of spin statistics on the reaction rate is generally included by a simple temperature-independent multiplicative factor, such as $1/4$, when the spin–orbit coupling is small. Small spin–orbit couplings may be found for molecules containing first-row atoms and hydrogen but can be substantial when heavier atoms such as transition metals are involved. In solution, the caging of the radicals in close proximity can lead to multiple encounters giving multiple opportunities for transition from the triplet to singlet states. The dynamics of this process are not understood, and the temperature dependence of these effects has not been considered.

3.1.4. Hydrated Electron-Scavenging Reactions

The hydrated electron can react with a variety of species present in irradiated water, including water itself, as well as with solutes in aqueous solutions. As examples, consider the scavenging of hydrated electrons by nitrate and nitrite



which are well studied processes in radiolysis experiments. Figure 7 shows the temperature and pressure dependence of the rate constants for these reactions as measured by Elliot et al.,¹⁴⁸ Buxton and Mackenzie,¹⁴⁹ and Takahashi et al.¹⁵³ The rate constants for these reactions are too small to be diffusion controlled, and the large increase in the reaction with NO_3^- for $T > 375 \text{ °C}$ ($1000/T = 1.54$ for $T = 375 \text{ °C}$) is unexpected and not understood. In addition, the pressure dependence of these reactions shows unex-

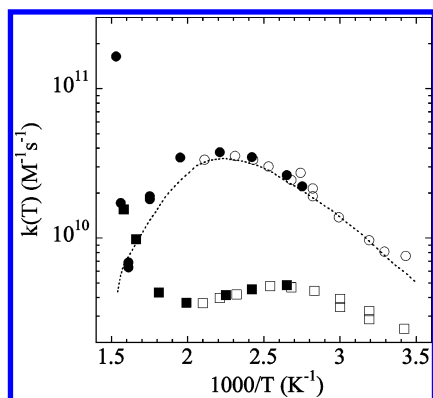


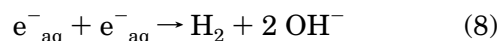
Figure 7. Reaction rate constant for the electron with NO_3^- (circles and dashed line) and NO_2^- (squares) as a function of temperature at 257 bar. Open symbols are experimental results of Elliot et al.,¹⁴⁸ solid symbols are from Takahashi et al.,¹⁵³ and the dashed line is from Buxton and Mackenzie.¹⁴⁹

pected behavior that is not understood.¹⁵³ The few studies of activation energies that have been extended to higher temperature^{149,153} have often found unexpected behavior where the rate constants decrease at elevated temperature. To understand electron-transfer reactions, high-temperature measurements of the electron free energy of formation¹⁵⁸ will be essential. Also needed are conductivity measurements of the hydrated electron mobility¹⁵¹ over a much broader temperature range.

The reaction of the hydrated electron with a scavenger can be viewed as an electron-transfer process from a solvent cavity onto the scavenger. This process is influenced by solvation energetics and dynamics as well as electronic energies and transition rates. The solvation effects include solvation structure and energetics for creating the cavities around the electron and the scavenger molecule and the energy needed to reorganize the solvent in passing from products to reactants. Finally, for the reaction of the hydrated electron (an open-shell radical) with an open-shell scavenger, multiple spin states are accessible during the processes, and a proper accounting of the spin statistics is required as is a proper treatment of spin-orbit coupling. All of these issues combine to make these processes a challenge to understand at a fundamental level.

3.1.5. Recombination of Hydrated Electrons

Hydrated electrons formed in water radiolysis produce potentially explosive hydrogen via disproportionation.



At room temperature, the activation energy for this reaction¹⁵⁰ is equivalent to the activation energy for e^-_{aq} diffusion to within the error bars.¹⁵¹ The reaction is diffusion-limited up to $\sim 150^\circ\text{C}$, but at higher temperatures, the rate constant drops off sharply. Recent measurements have revealed an unusual dependence of reaction rates on water density in the near-critical region.^{27,152} The proposed mechanism is the formation of a singlet dielectron $(\text{e}^-_{\text{aq}})_2$, which

reacts with the surrounding water, although this process is not understood.

Many of the considerations of the electron-scavenging reactions discussed above under section 3.1.4 apply to this reaction. Solvation structure and energetics of the separated electrons as well as the solvent reorganization required for the process to occur are clearly important factors influencing the reaction. Simulations have been performed for the dielectron in water in which the two electrons are treated quantum mechanically using density functional theory¹⁵⁹ and configuration interaction calculations.¹⁶⁰ In these calculations, empirical potentials are used for the water-water interactions, and pseudo-potentials are used for the electron-water interactions. These studies indicate that the dielectron is stable relative to two separated hydrated electrons and provide other properties such as the average geometry of the electronic distributions. The nature of the reaction pathways for the dielectron is a subject for future research.

3.1.6. More Complex Reactions

It is important to understand the selectivities of radical attack on more complex inorganic and organic solutes, in particular with respect to biologically important molecules. Working out the mode(s) of attack and selectivities for common functional groups is a necessary first step, and global rate constants have been determined for reactions of many simple carbon-, oxygen-, and nitrogen-containing compounds and of inorganic and transition metal ions. Compilations of these evaluated rates are widely available.¹⁴⁰ We note, however, that such information is often insufficient to predict the course of radical attack on more complex compounds due to the new possibilities arising from cooperative interactions between two or more neighboring functional groups. As an example, reaction of OH with glycine, which has three functional groups, is exceedingly complex.¹⁶¹ In addition to determining the selectivities of attack, examination of the unique effects of the aqueous medium on the course of reaction of hydroxyl and other radicals is needed. For example, the hydroxyl radical may react predominately with O-H functionality, followed by solvent-catalyzed conversion of alkoxy radicals to carbon-centered radicals.¹⁶² Further examples of radical mechanisms needing clarification include the reactions of hydroxyl and hydroperoxyl radicals with efficient hydrogen donors such as phenols and hydroperoxides. Here the key information required is the role of intermediate hydrogen bond formation prior to hydrogen atom transfer and the role of the solvent structure in affecting hydrogen atom transfer. Theoretical, kinetic, and product studies are essential for understanding nontraditional mechanisms of hydrogen atom transfer.¹⁶³

By chemical intervention and manipulation of conditions, it is possible to control the absolute yields and branching ratios of various products formed in chemical reactions, thereby selectively minimizing the formation of dangerous products in favor of desirable or benign ones. Success is dependent on a knowledge of the reaction mechanisms, as well as

how new mechanistic pathways might be opened by various additives. This requires identification of the transient species involved and accurate characterization of the energetics and dynamics of the pathways by which they may be formed, interconverted, and destroyed. A significant scientific challenge in this area is the development of predictive capability to attain full knowledge of the mechanisms of all relevant chemical reactions at all temperatures and densities that may be of interest in irradiated aqueous systems. This ambitious goal can be accomplished only through a synergistic combination of experimental, theoretical, and computational approaches. It will be necessary to select a few of the most important reactions, perhaps including but not limited to those noted above, for intense experimental scrutiny over a full range of reaction conditions. Furthermore, it must be recognized that many transient species are present only in low concentrations and, thus, cannot be readily observed experimentally. Full understanding therefore requires that theoretical and computational approaches deriving from first principles of classical and quantum mechanics must be advanced to achieve accurate predictive capabilities.

As discussed above, the reactions of radicals and ions created by low-energy electrons in aqueous systems provide challenges for experimental and computational studies. The mechanisms of reactions in irradiated aqueous systems are complex, and many of the elementary reactions are not fully understood, particularly over the wide range of conditions that are important in these systems. It will be necessary to improve our understanding of many fundamental scientific issues to successfully meet the broad challenge of developing a truly predictive capability. A great deal of progress has been made in understanding the factors controlling reactions in condensed phases, but significant fundamental challenges still remain for reactions of radical species created by low-energy electrons. In particular, the complexity introduced by open-shell reactants has not been adequately addressed.

All of these processes, from diffusion to radical reactions, can be dramatically affected by solid interfaces, which are of enormous technological importance in essentially all practical applications of ionizing radiation. For example, a number of unresolved issues regarding radiation-induced redox processes in heterogeneous systems hinder the efficient use and environmental acceptance of nuclear power and complicate remediation efforts of high-level radioactive waste.

3.2. Current Research Advances

Although there has been a great deal of progress made in understanding the factors controlling reactions in condensed phase, new experiments continue to reveal our lack of fundamental knowledge about these processes. For instance, section 3.1 provides examples of reactions with temperature dependences of the rate constants that are not understood and one case—recombination of two hydrated electrons—in which the fundamental mechanism is not even known. Predictive capability for rate constants over

wide ranges of conditions, such as temperature, pressure, and ionic strength, requires knowledge of the processes at a molecular scale, including how solvation structure, energetics, and dynamics change with different aqueous environments. During the past several years, significant progress has been made in the development of both experimental and theoretical methods that allow molecular processes to be probed directly, as well as methods that allow accurate values of benchmark equilibrium and dynamical properties to be obtained. These advances now make it possible to gain the fundamental information needed to predict rate constants from ambient to supercritical conditions. The following subsections present modern experimental and theoretical methods that can be used to address the major challenges in understanding reactions of radicals and ions in aqueous systems and also provide examples of recent accomplishments in these areas. This compilation is not intended as a complete list of relevant capabilities but as examples of the recent advances that have been made and that now make it possible to address these complex problems.

3.2.1. Structure and Energetics of Transient Radical and Ionic Species in Aqueous Environments

Research Issues. The starting point for understanding the reactive behavior of radical and ionic species is knowledge of the structure and energetics of isolated reactive species in aqueous environments. To characterize the mechanism of any given reaction of interest, it is first necessary to unambiguously identify the transient intermediates, including their structure and energetics in the hydrated environment. In heterogeneous systems, the influences of interfaces must also be considered. Much of the current research is limited to ambient temperatures, atmospheric pressures, and solutions of low ionic strength. Technological interest in processes that occur at high temperatures, high pressure, and high ionic strength now makes it desirable to know the free energies of formation and of hydration for all relevant species as a function of temperature, pressure, pH, ionic strength, and other reaction conditions. Thermodynamic properties, such as solvation energies or standard free energies of formation, of ions and radicals in aqueous solutions are critically important to gain a fundamental understanding of the reactive processes of these species. Experimental determinations of these properties are often difficult even for stable species. The aqueous free energy of formation is presently available for many inorganic (both neutral and ionic) compounds and for a small number of simple organic compounds. However, this information is not nearly sufficient for covering the wide and expanding range of the reactions of interest. The thermochemical properties of transient species and free radicals are even more difficult, often impossible, to determine experimentally. At the same time, the free energies of formation provide the only means for evaluating aqueous solubilities of many neutral radicals, a parameter of great importance in atmospheric and environmental chemistries. At present, these energies are known with sufficient accuracy for only a small number of radicals such as

NO, O_2^- , SO_2^- , N_3 , NO_2 , ClO_2 , and OH. Accurate experimental data for many more species are needed as is the information on the radical thermochemical properties outside the standard conditions, preferably over the full phase diagram of water. The latter is particularly important for the hydrated electron, H atom, and OH radical, which are key species in the high-temperature water radiolysis. With all of the difficulties of experimental determinations and with the variety of species of interest and medium conditions, computational approaches hold a great promise for aqueous thermochemistry. However, to fully realize their potential, a significant improvement in reliability and accuracy of these approaches must be made to bring them on par with experimental methods.

The solvation structure around open-shell radical species under a variety of different solvent environments is also of particular importance. Although there has been a significant effort to understand the effects of temperature and density on ion solvation and ion pairing, these effects for neutral radical species such as OH are unknown. Calculations performed to date¹⁶⁴ on OH interactions with water have not systematically studied the effects of the open-shell nature of the radical on the solvation structure. It has also been postulated that the polarizability of these species may be enhanced, which results in larger many-body effects. Much can be learned about solvent interactions with radical species from studies of small clusters, but the importance of long-range collective contribution will require studies of bulk-phase systems. For closed-shell ionic systems, the solvent structure can be probed directly by neutron^{165,166} and X-ray scattering.¹⁶⁷ These types of studies have provided the first view of how the solvation structure changes to give increasing ion pairing as the density of the aqueous system decreases.¹⁶⁸ This type of detailed information is currently lacking for solvation of neutral radical species. Furthermore, the change in the relative importance of different solvation effects with conditions (e.g., solvent density and temperature) still needs exploration. Important questions that should be addressed include the following:

- How are solvent–solute interactions altered by the open-shell nature of radical species? How is solvent structure affected by an open-shell solute?
- What is the relative importance of short-range and long-range interactions in determining solvent structure and energetics around radical species, and how does this change with temperature, pressure, and ionic strength?
- What approaches are appropriate for prediction solvation free energies for transient species?

Research Approaches. Knowledge of the structures and relative energies of all participating species, that is, thermodynamics, is fundamental to the understanding of any chemical transformation. From information on such static properties it is often possible to infer the direction and feasibility of chemical reactions and, in some instances, to estimate the rate constants as well. Although such information is usually available for the stable reac-

tants and products, identities and properties of the transient free radical intermediates and of the relevant activated complexes are elusive. Free energies and enthalpies of formation for radicals and ions in aqueous solution are of particular significance in this context. Reliable values obtained from experiment are also of great importance because they provide benchmarks for advancing theory-based computational methods for predicting solution properties of radicals and ions. Although less informative than free energies of formation, one-electron reduction potentials are also useful in predicting driving forces of radical reactions in solution and, through the Marcus free energy relationship, reaction rates. Two important reviews of the available data were published by Wardman¹³⁹ and Stanbury¹⁶⁹ in 1989. These reviews are somewhat dated now, and a significant amount of new and corrected data has appeared since their publication (some dramatic revisions and new developments are given elsewhere¹⁷⁰). Thus, a comprehensive critical revision of the reduction potentials for radicals and other transients is also needed.

Due to the instability of radicals in solution, fast kinetic techniques have widespread application in the measurement of radical solution thermochemistry. Pulse radiolysis has been and, no doubt, will remain a premiere tool for obtaining thermochemical data for radicals. The most useful detection technique has been ultraviolet–visible (UV–vis) transient absorption spectroscopy, but both time-resolved electron paramagnetic resonance (EPR) and conductivity have made extremely valuable contributions. The three pulse radiolysis centers in the United States (Argonne National Laboratory, Brookhaven National Laboratory, and the University of Notre Dame) have the expertise and instrumentation for these measurements. This capability has provided a wealth of information about electron-driven processes and holds great promise to continue making important contributions in the future.

Conventional electrochemical techniques have been of limited utility for measuring reduction potentials involving radicals because reversible electrode conditions are difficult to attain in water. However, advanced methods using microelectrodes and rapid scan techniques, coupled with analytical models that include the effects of follow-up reactions, may now enable experimentalists to make advancements on aqueous systems. In particular, laser photoelectron emission polarography,¹⁷¹ which can take advantage of radiolytic methods of preparing transient radicals for electrochemical analysis, have promise, although further validation of this technique by comparison with more established methods is needed.

Photoacoustic calorimetry (PAC) and photothermal methods¹⁷² also hold promise for measurements of aqueous thermochemistry. Although often used to obtain C–H bond dissociation energies in nonaqueous media, the use of pulsed-PAC for aqueous bond dissociation energies is relatively unexplored. Recent advances in pulsed laser techniques and cell designs, together with improved understanding of how to derive reaction enthalpy from a photoacoustic signal, now make PAC particularly suitable for measure-

ments of solution. An important but less recognized feature is that the free energy of reaction is also determinable by relating the reaction volume to the reaction entropy.¹⁷³ Applications to high-pressure systems have been demonstrated,¹⁷⁴ although application to high-temperature supercritical water systems may require development of high-temperature piezoelectric materials or cell designs that make use of thermally insulating sound-conducting materials to acoustically couple high-temperature cells to currently available detectors.

Structural information such as the average solvent structure around a solute is more difficult to obtain directly. Time-resolved structural techniques such as electron paramagnetic resonance and resonance-enhanced Raman spectroscopies used in conjunction with pulse radiolysis or flash photolysis are of particular utility here.¹⁷⁵ Very few such apparatuses are available worldwide, and these methods deserve much more widespread development and application. Over the past several years, important advances have been made in scattering methods (e.g., neutron^{165,166} and X-ray scattering¹⁶⁷), which enable detailed structural information about the first solvation shell to be obtained. These methods have been applied to stable species, and the extension to transient species (e.g., radicals) remains a challenge. In most cases the use of molecular simulation techniques has played an important role in refining the structural information.^{166,168} These approaches have recently been extended to study the effects of temperature and pressure on the solvation structure.^{165,168,176}

Modern electronic structure theory has advanced significantly over the past decade,¹⁷⁷ and its use on high-performance computers provides a practical approach to calculate energetics, structures, and properties of molecules in the gas phase. Calculation of energetics (e.g., bond dissociation energies) are now possible with near chemical accuracy for molecules that are sufficiently small.¹⁷⁸ Indeed, for small molecules, chemical properties can often be calculated with wave function-based methods as well or better than they can be measured. For example, the heat of formation of OH radical has recently been determined experimentally using photoionization methods and high-level *ab initio* electronic structure theory to be 8.85 kcal/mol, which is 0.5 kcal/mol above the previously accepted value.¹⁷⁹ To obtain such accuracy one must include not only the valence electronic energy contributions but also core-valence effects, scalar relativistic effects, and spin-orbit effects. In addition, reliable thermodynamic results require high-quality zero point energies and vibrational frequencies including anharmonic effects for the reliable prediction of enthalpies, entropies, and free energies. The principal barrier to the routine application of such electronic structure techniques continues to be the very rapid growth of computational expense with system size due to the scaling of CCSD(T)¹⁸⁰ and related methods as N^7 , where N is the number of basis functions. Consequently, there remains a continuing need for evolutionary algorithmic development in key components to allow scalable computational performance on massively parallel computer

architectures for the most demanding yet most accurate theories. Alternative lower cost methods based on functionals of the density [e.g., density functional theory (DFT)]¹⁸¹ can provide useful and simple models. The most popular DFT methods employ functionals that are parametrized to experimental data, such as B3LYP,¹⁸² which also includes a contribution from the Hartree-Fock exchange interaction. However, DFT methods are not as accurate or reliable as the best wave function-based theories, especially for the characterization of transition-state structures and barriers and also for weak intermolecular interactions. There remains a continuing need for improved functionals, which include correct descriptions of exchange and correlation, have the correct asymptotic form and good scaling, and approach rigorous theoretical limits.¹⁸³

Considerable progress has been made toward extending the success of electronic structure methods from the gas phase to the condensed phase, albeit it has mostly concentrated on treatment of stable closed-shell solute molecules.¹⁸⁴ This work follows two general directions, depending on whether the solvent is represented by continuum or discrete molecules; hybrid models combining features of both approaches are also in use. Each of these approaches has its particular strengths and weaknesses and presents challenges to reliable application, especially for radicals and ions that are relevant to the field of irradiated solution chemistry.

Dielectric continuum models provide an efficient and practical means to simulate bulk effects of polar solvent. Such continuum models can predict free energies of solvation for stable closed-shell ground-state species in some cases with mean errors of <1 kcal/mol.¹⁸⁴ However, empirical parameters for certain energetic components are required to reach such accuracy. There are significant deficiencies for small organic radical ions, with mean errors of 1 order of magnitude larger (several kilocalories per mole) and with errors as large as 20 kcal/mol having been demonstrated, in contrast to the ~1 kcal/mol accuracy that is required for near-quantitative predictions.¹⁸⁵ These large errors are due in part to the cavity parametrization protocol, and there is a critical need to extend the protocols to determine physically correct sizes and shapes of molecular cavities to cover a much wider range of chemical and ionic functionalities and of transition-state structures. Recent work has also shown the importance of the solvent reaction field representation, such as whether volume polarization is included, in these calculations.¹⁸⁶ Large errors are also due in part to inadequate treatment of specific solute-solvent interactions, such as hydrogen bonding, and it will probably require going outside the framework of continuum theory to properly bring in these effects.

Discrete models that include explicit solvent molecules in the calculation, which are being increasingly developed and used, are limited by the size of the system that can be treated explicitly. At the most fundamental level, all molecules in the system are treated quantum mechanically. Currently, the most powerful incarnation of this approach is found in the

Car–Parrinello *ab initio* molecular dynamics approach based on DFT,¹⁸⁷ in which the condensed phase is approximated by periodic boundary conditions. Currently available functionals do not represent weak intermolecular forces very well, and improvement of the functionals in a systematic way remains a high priority. Recent advances in *ab initio* molecular dynamics now allow propagation of the density matrix based upon molecular orbital methods using Gaussian-type orbitals.¹⁸⁸ These approaches can provide information about averaged solvation structure, although the computational effort to obtain proper statistical sampling of the solvent degrees of freedom makes the calculations of free energies inaccurate at this time. Alternatively, hybrid methods that combine mixed quantum-classical models for the solute–solvent interactions together with classical MM methods for the solvent–solvent interactions are denoted QM/MM methods.⁹³ The replacement of computationally intensive electronic structure calculations with MM interactions allows large numbers of molecules in the simulations and increased statistical sampling compared to the pure quantum mechanical approaches. The quality of the total QM/MM interactions depends on a balanced description between the separate electrostatic and van der Waals contributions. Important recent advancements have come from careful adjustment of parameters and the use of polarizable intermolecular potentials. However, expediency still requires that the interactions be highly oversimplified through assumed functional forms with most parameter values dictated at the outset, making it difficult to properly respond to changes in the charge distribution, hybridization, or electronic state of the solute. There is a pressing need for significant enhancements to the current *ad hoc* construction of solute–solvent interactions in QM/MM models, particularly in representing free radical solutes where information needed for parametrization is scarce.

Computational approaches based on first-principles, supermolecule-continuum approaches are also being used to predict the solvation free energies of ions. In this approach, part of the solvent surrounding the solute is treated quantum mechanically, and a dielectric continuum model is used to approximate the remaining bulk solvent. With this approach, the calculated results can systematically be improved by increasing the number of quantum mechanically treated solvent molecules. This approach has been used to calculate the free energies of solvation of the proton, hydroxide anion, and aqueous electron.¹⁸⁹ The $\Delta G_{\text{hyd}}^{298}(\text{H}^+)$, $\Delta G_{\text{hyd}}^{298}(\text{Li}^+)$, $\Delta G_{\text{hyd}}^{298}(\text{HO}^-)$, and $\Delta G_{\text{hyd}}^{298}(\text{F}^-)$ values have been predicted to be -262.4 , -125.1 , -104.5 , and -104.3 ± 0.7 kcal/mol, respectively. The size of the error limits on these values is on the order of ± 1 kcal/mol, and the values are in agreement with the best derived experimental estimates. For example, the calculated difference of 137.3 kcal/mol between the absolute hydration free energies of the proton and Li^+ is in excellent agreement with the experimental differences of 137.5 kcal/mol from the latest collection of experimental data and of 137.0 kcal/mol from earlier experimental data. The sum of

the absolute hydration free energies of the proton and hydroxide ion, $\Delta G_{\text{hyd}}^{298}(\text{HO}^-) + \Delta G_{\text{hyd}}^{298}(\text{H}^+)$, is -366.9 kcal/mol, in excellent agreement with the experimental thermodynamic value of -366.6 ± 0.1 kcal/mol. The calculations show that the thermal motion and bulk solvent effects can qualitatively change the relative thermodynamic stability of different structures of a hydrated anion based on a cluster of a given size and that the most stable structure in solution is not necessarily the most stable one in the gas phase.¹⁸⁹ Explicit inclusion of the solvent molecules significantly increases the cost of the computation and raises other issues for future studies, including the treatment of anharmonic and quantum mechanical effects on nuclear motion in the cluster.

An alternative and highly productive vantage point on the solvation structure and energetics of species in aqueous systems is provided by the study of clusters.^{190,191} Particularly valuable insight is obtained on the relative importance of specific interactions between solute and nearby first-shell solvent molecules versus dielectric contributions of bulk solvent. This field enjoys a unique synergism between theory and experiment, and a review of the theoretical and experimental advances in this field and the future challenges has been presented by Dykstra and Lisy.¹⁹¹ One particularly valuable role played by cluster studies is in establishing a firm connection between a given solute–solvent structure and its spectroscopic signatures. Once identified, these spectroscopic signatures can be interpreted when they are observed in solution. In addition, solute–(water)_{*n*} clusters also tend to form hydrogen-bonded bridges between donor and acceptor sites on a molecule, thereby enabling the study of key solvent structures that can facilitate fast proton transfer along the solvent bridge.¹⁹²

Coe and co-workers¹⁹³ have developed an approach to predicting enthalpies and free energies of solvation on the basis of the extrapolation of gas-phase cluster results to solution values. This approach has significantly lowered the error bars on previous experimental values, and it has provided a reconciliation of different excitation energies, such as the vertical photoionization energy (VPE), the photoemission threshold (PET), the vertical detachment energy (VDE), and the photoconductivity threshold (PCT), in bulk phases of water as shown in Figure 8.

Calculations on solute–water aggregates of tractable size are also extremely valuable to help interpret observed spectra, and conversely the experiments provide benchmarks for systems with well-defined composition that are urgently needed to improve computational tools.^{38,194} Photofragmentation studies can provide information on radical–water binding energies.¹⁹⁵

3.2.2. Dynamics of Radical and Ionic Species and Coupling to Solvent Dynamics in Aqueous Systems

Research Issues. Detailed information about the factors controlling the dynamics of radical species and coupling to solvent dynamics is important to the understanding of diffusion and reactions in aqueous systems. At the heart of a chemical reaction lies the

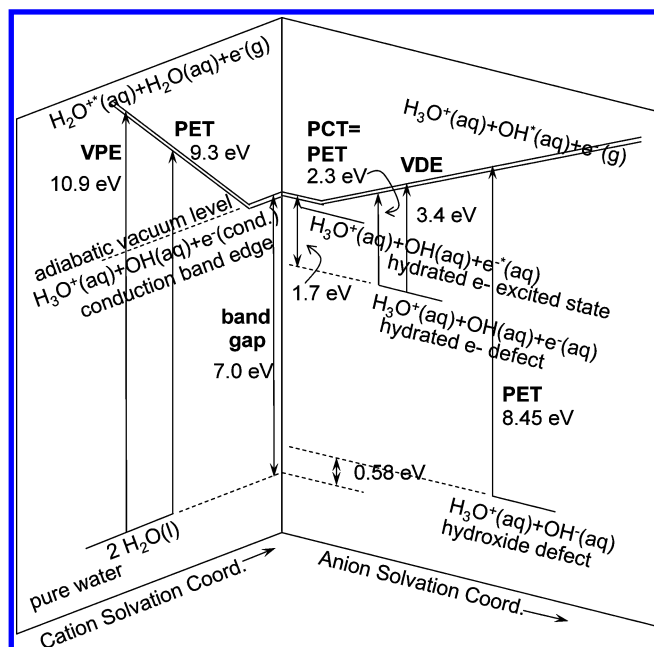


Figure 8. Bulk energy diagram for water as a function of solvent reorganization about charge species. See text and work of Coe and co-workers¹⁹³ for more details.

rearrangement of chemical bonds in two or more partners within an encounter complex to produce new chemical species. The most important information required is the size and shape of the energy barrier. Solvent participation has been shown to play a key role in reaction rates, particularly because of the effect on reaction barriers. The solvation structure around the reacting species will alter as the two reactants approach, and the solvation can significantly affect the stability of the encounter complex and its subsequent dynamics. Reactions of radical species will be affected by the solvent structure around the radical species and how this solvent structure changes as the radical approaches a reactant. For radical–radical association reactions the solvent structure around one radical species can be affected by the proximity of another radical, thereby affecting the interaction energies as the two species approach. Solvent can also be intimately involved in the structure of the complex, with solvent molecules assisting or catalyzing the reaction.¹⁹⁶ New channels involving proton transfer and/or electron transfer may also become favorable through solvent participation. As for isolated species, cluster models can probe short-range solvent contributions to reaction energetics. Long-range, collective solvent contributions to the reaction energetics may also be important. With ions, the relative importance of contact pairs and solvent-separated pairs must be understood, along with an expected strong dependence of these phenomena on ion concentrations. For radicals, the interaction of the open-shell species with another reactant may lead to the possibility of low-lying excited states. The influence of solvent molecules on the energetics of these states needs to be understood. The interaction of two radical species gives rise to different spin multiplets (e.g., singlets and triplets in the case of two interaction doublets such as OH interaction with OH). An understanding of the effects of solvation on the

energetics of these different spin states and on their coupling is needed.

Solvent dynamics as well as energetic effects of the solvent can influence both chemical reactions and diffusion. Both the local dynamics of a small number of solvent molecules and the global, collective dynamics of solvent reorganization can influence diffusion and reaction of solute species. As discussed above, recent experimental studies have raised issues about the factors controlling the diffusion of radical species. Although much has been learned about the diffusion of closed-shell ions, particularly the effects of solvent density and temperature on ion diffusion, there remain significant gaps in our understanding of radical diffusion in aqueous systems. Discrete water molecules may also be direct participants in aqueous radical chemistry, for example, through forming water bridges between hydrogen-bond donor and acceptor sites on a radical that facilitate proton transfer in a product-forming reaction step.¹⁹⁶ Solvent molecules can also create a solvent cage, and the dynamics of the local solvent molecules (e.g., in the first solvation shell) can greatly influence the reaction dynamics. Effects of collective solvent dynamics, such as solvent friction or polarization effects, can also affect the reaction dynamics. For example, recent simulation studies have shown that coupling between ion and solvent dynamics can be quite large; large solvent fluctuations were seen to be required before proton transfer could occur in water.¹⁹⁷ These types of effects are also expected to be important in the diffusion and reaction of the hydrated electron. It will also be important to understand the contribution of solvent reorganization in the dynamics of neutral radical species. The dynamics on multiple electronic states, as well as how coupling to solvent dynamics also influences these dynamics, needs to be considered. For example, electron-spin effects in the recombination of two radical species can lead to successful recombination after unsuccessful encounters. How the coupling of the different spin states is affected by the dynamics of the solvent needs to be understood. Important questions that should be addressed include the following:

- How do the solvation structure and energetics change as two reactants approach each other, and how does this change vary with temperature, pressure, and ionic strength?
- Does the open-shell nature of radical species affect the solvation structure and energetics of radical–reactant complexes?
- How are different electronic states of radical–reactant and radical–radical interactions affected by solvation?
- How do solvent dynamics change as reactant species approach each other? Does the solvation dynamics of an encounter complex of two radical species differ from that of an isolated radical, and if so, how does the change in solvation dynamics affect the association/reaction process?
- How does solvation dynamics differ for neutral and ionic, open-shell and closed-shell systems?
- How do different components of solvent dynamics (e.g., exchange in the first solvation shell, collective

solvent reorganization) affect diffusion? How do these components change with changing conditions (e.g., T , P)?

Finally, it must be emphasized that most net chemical reactions in solution have multiple steps, and there may be cross connections between the various elementary steps leading to several competing pathways. The relative probability of each channel may be strongly dependent on temperature, pressure, and other reaction conditions. To be able to reach a predictive capability to control the identities and relative yields of the final long-lived products, all issues raised above must be understood for each elementary step of the overall reaction process.

Research Approaches. Information about the energetic factors controlling the dynamics of chemical reactions is difficult to obtain directly, and most information about energy barriers comes from kinetic studies. Activation energies obtained from the temperature dependence of the rate constants are kinetic measures and include dynamical effects (e.g., recrossing and tunneling effects) as well as information about the free energy of activation, which includes both energetic factors (i.e., changes in energy along the reaction coordinate from the reactant to the transition state) and entropic factors that reflect the change in vibrational modes from the reactant to the transition state. Transition-state spectroscopy^{198,199} offers the opportunity to directly probe reaction barriers. This approach has provided detailed information about the potential energy surface for the $\text{OH} + \text{OH}$ and $\text{OH} + \text{H}_2\text{O}$ reactions.¹⁹⁸ In recent years, these methods have been extended to studies of reaction in clusters,¹⁹⁹ but these techniques have not been extended to the study of reactions in aqueous systems. Pulse radiolysis is a premiere tool for obtaining kinetic information about radical reactions in water. UV-vis transient absorption spectroscopy is the workhorse detection technique thanks to the red-shifted spectra of free radicals relative to their parent compounds and shot-noise-limited sensitivity. Signal-to-noise continues to improve in time-resolved EPR spectroscopy with developments in microwave technology and new resonator geometries. Both one- and two-dimensional, time-resolved Fourier transform EPR spectroscopies have been used for studies of transient free radicals in water. The presence of chemically induced dynamic electron polarization in the transient spectra provides a completely unique spin probe of dynamics and mechanism.²⁰⁰ Photoacoustic calorimetry and photothermal methods¹⁷² also hold promise for measurements of aqueous radical kinetics.

Direct information about solvent dynamics during a reaction is more difficult to obtain experimentally than the kinetic parameters, because the time scale for the solvent dynamics is typically very fast. Over the past decade tremendous advances have been made in ultrafast multidimensional spectroscopies that allow the solvation dynamics to be probed during a reactive process.^{28,201} Although most of this work has focused on excited-state charge-transfer processes, a tremendous amount of understanding of the solvent response has been obtained from these stud-

ies. Extension of these approaches to understand the role of solvent dynamics in reactions of radical species, and particularly neutral ones, remains a challenge.

Significant advances have also been made in theoretical and computational approaches, which are essential to complement and guide experimental efforts in all of these areas. A significant amount of the detailed information about dynamics of molecules in aqueous systems has been obtained from computer simulations that are closely coupled to experimental studies. A number of challenges must be met to achieve the goal of reliably simulating the dynamics of radicals in water. For meaningful results, it is necessary to evaluate the underlying interaction potentials accurately. In direct simulations, these potentials must be calculated billions of times in large-scale statistical simulations that run for hours or days on the computer, with that computational time corresponding to only picoseconds or, at most, nanoseconds of real time. The time scale for diffusion or reaction simulations is generally much longer. As outlined below, the competing requirements of accuracy and efficiency will require development of new simulation technologies, with a sustained effort to validate simulation models.

The interaction potentials that govern the reactive motion between reacting species, and between reactants and aqueous solvent, must be evaluated. Reasonably accurate descriptions of interacting potentials have been developed for water-water and for water with closed-shell ionic and neutral reactant species,^{41,97,202} but there is little experience in the characterization of radical-water interactions, and these interactions are difficult to calculate. Accurate calculation of the interaction for some radicals, such as the H atom, is especially difficult because of the weakness of the interaction between the radical and water molecules. Development of reliable and systematically improvable interaction potentials describing water-radical species is a special challenge, because the unpaired radical electrons can give rise to unusual structures and bonding motifs and, in some cases, more than one electronic quantum state can participate. Certain features of the interaction potential are crucial. For example, the charge cloud of a negatively charged ion is especially deformable, and its proper treatment has been established as necessary for a correct description of anion behavior.⁴² Developments in this area call for more intensive collaboration between specialists in high-level ab initio calculations and condensed-phase simulation experts.

Usually, computer simulations (e.g., MD or MC) of condensed-phase systems rely on compact mathematical description of interaction potentials. These computationally efficient forms can be determined by fitting to experimental data on solvation energies, to neutron and X-ray diffraction data, and to high-level ab initio calculations of small molecular clusters. However, sometimes the potentials are too complicated for such parametrization. To meet this challenge, the new field of ab initio simulation^{187,188} calculates the interaction potentials by electronic

structure methods at each simulation step. This promising technology is especially important for the description of chemical reactions, and until recently, only modest levels of electronic structure calculation were implemented. Such advanced, intermediate-level QM/MM methods are discussed more fully in the previous section. An additional concern for the use of these methods for chemical reactions is the separation of the fast electronic response of the solvent from its slow orientational (inertial) response, which will be necessary to describe nonadiabatic processes in solution, such as electronic excitation, electron-transfer, and charge-transfer processes.

Although significant progress has been made over the past decade in theoretical and computational methods for calculating rate constants for reactions in solution, the accurate calculation of condensed-phase rate constants is a continuing challenge. Chemical reactions occur relatively infrequently on the time scale of molecular events in dilute solutions, and it is usually impractical to run dynamical computer simulations until they occur. This has spurred the development of simulation techniques for infrequent events, such as the transition path sampling method used in liquid simulations²⁰³ and accelerated MD methods used in materials simulations.²⁰⁴ The related methods that have evolved rely on stochastic methods to locate the reaction path for the rare event and special sampling that focuses computational effort on the rare events of interest. Accurate benchmark calculations do not exist to validate the developing approximate techniques, and it is not clear that there are enough accurate experimental rate data for benchmark purposes. A systematic development that takes into account limitations in the descriptions of molecular interaction and statistical mechanical sampling must be made for significant progress to be made in the future.

A common limitation to standard molecular simulation methods is that they rely on classical mechanics to describe the nuclear motion. Whitnell and Wilson²⁰⁵ conclude in their 1993 review of simulation methods that "a more accurate analysis of many reactions, including some of the ones that have already been simulated using purely classical mechanics, will ultimately require some form of quantum mechanical methods". Significant steps have been taken toward developing theoretical approaches and computational tools for quantum dynamical simulations in condensed phases including the centroid molecular dynamics method²⁰⁶ and the semi-classical initial value representation approach.²⁰⁷

Transition-state theory (TST)²⁰⁸ has played an important role in calculating and analyzing rate constants for chemical reactions in condensed phases. Over the past decade, significant progress has been made in developing approaches based on TST that explicitly include the effects of solvent. At the most basic level, TST for reactions in solution utilizes the equilibrium solvation approach, in which the free energy of activation in solution is evaluated by adding the difference in free energy of solvation between the saddle point and reactants to the gas-phase free energy of activation.²⁰⁹ Because the rate constant is

extremely sensitive to changes in the free energy of activation, the accuracy of this quantity is crucial. As discussed in the previous section, significant progress has been made in developing methods to evaluate energetics in aqueous systems, and these same approaches can be used to directly calculate energy barriers for chemical reactions. At the next level of sophistication, effects of solvent dynamics should be included. Reviews²¹⁰ of theoretical approaches to treating activated barrier crossing in dissipative systems presented the advances made in this area through about 1995. Although significant advances continue to be made, the need for further work in this area remains. As an example, the inclusion of quantum mechanical effects in the calculations of rate constants for condensed-phase reactions still presents a major challenge. The extended nature of the condensed-phase system makes it necessary to make approximations in the calculations. A recent comparison of several approximate computational approaches to calculating quantum mechanical rate constants for a model reaction in solution showed large differences in the rate constants for the different methods.²¹¹ A major difficulty is that benchmark calculations do not exist for these extended systems, and this work points to the need for systematic approaches to understand the regions of validity of the different approximations. Reactions of hydrated electrons involve a charge-transfer process for which solvent dynamical effects (e.g., solvent reorganization) will be very important. Methods based on a solvent reorganization energy or energy gap as the reaction coordinate, as first introduced by Marcus,²¹² have been widely applied to electron-transfer reaction in solution.²¹³ During the past several years, some of the limitations of these methods have been recognized, and new approaches have been developed.²¹⁴ Even so, new approaches for reactions of a hydrated electron, which properly treat the strong correlation between the electron's energy and orbital size and the solvent dynamics, are still necessary.²¹⁵

Kinetic isotope effects (KIEs), particularly for H isotopes, have historically played an important role in elucidating reaction mechanisms and in allowing reaction energetics (e.g., barrier heights) to be estimated from the activation energy. Valuable insight into H atom reactions have been obtained from studies of muonium (Mu), which is a light isotope formed with a positive muon nucleus having a mass only one-ninth that of hydrogen. Measurements on reactions of the muonium atom with various scavengers in supercritical water²¹⁶ show that the high-temperature rate constants fall well below an Arrhenius plot extrapolated from near room temperature, even at temperatures well below the critical regime ($T_c = 374$ °C for water). These results were interpreted to indicate that solvent dynamics effects (e.g., solvent caging) were responsible for the decrease in the rate constant. Other important benchmark reactions include the addition of H to benzene (which apparently slows at high temperature), abstraction of hydrogen from methanol, and reaction with O₂ to give the hydroperoxyl radical. Theoretical modeling

of the H/Mu KIE for the H reaction with benzene indicated that the amount of tunneling contributing to the Mu rate constant was greatly reduced by the coupling of solvent dynamics to the reaction coordinate motion.²¹⁷

Cluster studies offer the potential for obtaining detailed information about the influence of solvent molecules on reaction dynamics. Recent advances in spectroscopic techniques have made it possible to obtain detailed information about the dynamics of weakly bound neutral clusters.²¹⁸ The application of photofragment and photoelectron methods and the imaging technique to the studies of molecular cluster anions have provided detailed information about the effects of solvation on the electronic structure and reactivity of negative ions in heterogeneous and homogeneous cluster environments.²¹⁹ To date, these approaches have not been applied to aqueous clusters, and there is great opportunity for work in this area. Larger radical-(H₂O)_n or ion-(H₂O)_n clusters have the potential for formation of networks of hydrogen bonds about the radical or ion center. Here, the balance between solute-water and water-water interactions could be probed directly in the infrared spectra of the clusters. The development of these spectra with growing cluster size can provide evidence for size-dependent chemistry. The ion-(H₂O)_n clusters offer the distinct advantage that size selection is straightforward, enabling the study of their spectroscopy as a function of cluster size. Size selection in radical-(H₂O)_n clusters will require double-resonance spectroscopies, like those that have been employed successfully in molecule-(H₂O)_n clusters with stable neutral molecules.²²⁰ Photodissociation of a free radical precursor in a water-containing cluster can lead to further reaction with the water molecules or, in large enough clusters, to caging and radical-radical recombination. Finally, superfluid helium clusters may provide a useful medium for studying radical-water interactions, because free radical and water pick-up in the helium cluster can be separated from one another. Indeed, the unusual characteristics of superfluid helium can be used to freeze out unusual structures for the radical-(H₂O)_n clusters or to trap two radicals in configurations from which they cannot recombine with one another.²²¹

3.2.3. Interfacial Processes

Research Issues. Interfacial processes must be considered explicitly. The concentrations of additives and scavengers are certain to be different at walls, liquid/particulate interfaces, and near biological membranes than in bulk liquid. Diffusion of radical species to/from interfaces and reaction at interfaces can lead to new products via catalytic processes and can exacerbate corrosion of walls. Reaction barriers as well as charge-transfer processes will be different at walls and interfaces than in solution. The fact that chemical microenvironments exist must be dealt with explicitly, and this may necessitate the inclusion of flow and transport models with the chemical kinetic models. Such microenvironments are also important in geochemical and biogeochemical processes.

It is well documented that the first few monolayers of water on a solid surface are distinctly different

from bulk water. In many respects they more closely resemble ice than liquid. Important questions include the following:

- Can these monolayers sustain and stabilize excess electrons? Can they react with electrons or contribute to their production?
- Would the electron localize at the periphery, similar to localization on small water clusters, or would it trap in a deeper layer?
- Does the surface contribute to its stabilization?
- What are the dynamics of the stabilization process?

These questions of immense scientific basic interest need to be addressed theoretically as well as experimentally. Existing molecular dynamics methodologies and ultrafast experimental instrumentation are ripe to address the question of interfacial solvation.

Research Approaches. Reactions involving aqueous radicals and ions can be especially significant near solid surfaces, for example, through exacerbating corrosion of waste-tank walls or by producing oxide buildup in reactor pipelines. Diffusion of ions and radicals near interfaces may be entirely different from that in the bulk, changing product ratios due to altered local concentrations of additives and scavengers. Catalysis of reactions by solid interfaces or by suspended particulates can further lead to entirely new products. For example, the preferential reaction of oxidizing products of water radiolysis with cladding surfaces shifts the total balance of radiation-induced chemical reactions toward production of reducing species,²²² including potentially flammable hydrogen gas. Ionizing radiation can also initiate reductive dissolution of oxide-scale buildup in water-cooled reactors. The mechanisms of the radical reactions in these technologically important processes are not known. Identities of the species on the surface and in the solution, their dependence on pH, temperature, surface composition and surface geometry, and the energetics and rates of their primary reactions all need to be determined. The largely unknown influence of interfaces on electron-induced processes has already been recognized in the Chesterton report,⁹⁹ which recommends emphasis on research into interfacial processes in all of the subcategories outlined therein.

It is clearly necessary to understand transport of species near interfaces. However, there is a key problem hindering creation of a diffusion-based stochastic model of radical reactions with a surface boundary condition to describe the near-wall radiolysis, in that many unknown diffusion coefficients and reaction cross sections at the surface are needed. This is extremely important for the understanding of radiation-induced corrosion and catalysis. The whole problem of radical and ion diffusion near the surface is further complicated by local changes in the liquid water structure (solvation effects), electrical fields near the surface, adsorption/desorption equilibrium, etc.

Adsorption of radicals on surfaces plays a key role in mediating many of the important chemical processes taking place there. Localization of the unpaired spin of a radical at a particular site or its

mixing into any of the solid electronic bands depends on the relative energies of the band and the radical, on the specific binding geometry of the fragment to the surface, and on the distance from the surface. Advances in surface spectroscopies, especially in surface-enhanced Raman, combined with rapid developments in microscopy, are promising tools to determine the chemical identity, the geometry of the bound species, and the electronic interaction between the species and the surface, at the level of a single molecule, a single particle, or a single site.²²³ This unparalleled sensitivity, combined with the extraordinary specificity of vibrational spectroscopy, should be used not merely in materials research but in biophysical studies as well. The technology is now available to identify specific sites of radiation damage in single biomolecules adsorbed on metallic surfaces.²²⁴

Radiation-induced secondary electrons released from walls and from particles suspended in solution can cause decomposition of solutes and initiate a chain of radical–molecule and radical–radical reactions; chlorinated hydrocarbons are a prime example.²²⁵ There is a lack of experimental and theoretical information on the electron-transfer reactions between short-lived radicals and surfaces. Reaction barriers as well as charge-transfer processes will be different at surfaces and interfaces from those in solution. Recent technological enhancements of computer power have led to computational tools that provide reasonably accurate calculations of energies and structures of species adsorbed at the surface of metal oxides.²²⁶ Extensions to the aqueous environment should be made, allowing for computational studies on aqueous ions and radicals interacting with various metal and oxide surfaces of practical importance. The reactivity of the primary water radiolysis products, as well as the reactivity of the electron–hole pairs from the solid, could then be outlined. Strategies to maximize or minimize production of water radiolysis or redox products in the solid could be offered depending on the practical need.

Interfacial processes are also expected to be a major factor affecting the biological roles of reactive intermediates. This follows because biological membranes provide both a means of compartmentation and a reactive interface.²²⁷ Among the most biologically important reactive species are superoxide (O_2^-), nitric oxide (NO), nitrogen dioxide (NO_2), and carbonate (CO_3^-) radicals, as well as non-radical reactive transients derived from them: for example, peroxyxynitrite ($ONOO^-$), nitroxyl (HNO), hydrogen peroxide (H_2O_2), and hypochlorous acid (HClO). The most important parameter that governs the ability of an intermediate to react outside a microcompartment of its origin is the permeability coefficient. This parameter is closely related to solvation energetics in water and membrane, but it remains unknown for most biologically significant radicals and transient molecules. In addition, metal ions such as the Fe^{3+}/Fe^{2+} redox couple, which also involve radical species, can play important roles in biological systems and can be transported into the membrane or into extracellular lipopolysaccharide matrix. Simulations of such species involved

in the interactions of biological membranes with metal oxide mineral surfaces are just beginning.²²⁸ Biological membranes often contain large amounts of readily oxidizable and reducible species such as lipophilic quinones and proteins. The interfacial reactivity of these species toward radicals produced by radiolysis also remains largely unexplored. Clearly, quantitative mechanistic assessments of the biological roles of radicals will require further research that addresses these important issues.

4. Summary

Because of the complexity inherent in treating electron-driven processes in water, important questions regarding the primary chemical events remain after decades of inquiry. The excitation, relaxation, and reaction processes driven by electrons in aqueous systems span a wide range of energies and time scales: from thermal energies up to tens of electronvolts and from femtoseconds to microseconds or longer. These processes include scattering of electrons from molecules with relative translational energies up to tens of electronvolts, the dynamics of highly excited (electronic, vibrational, and rotational) states, the relaxation of energy in the condensed-phase environment, chemical reactions under highly non-equilibrium conditions, and the reactions of thermalized, but highly reactive, radical species. In all of these processes the role of water is poorly understood, if at all. Until very recently, one would have been tempted to conclude that the sheer complexity of the problem would preclude any attempts to establish realistic reaction pathways.

On the other hand, the progress of our understanding of the dynamics of electrons and molecules in the gas phase, in clusters, and in condensed media has been so profound that the primary chemical events following energy deposition are now within reach. The past several years have seen the development of new experimental and theoretical techniques to examine the structure, energetics, and dynamics of aqueous-phase systems. For example, model systems (clusters and designed films) provide unique structures for the evaluation of theories and models of aqueous processes, single-molecule spectroscopies directly reveal molecular level data, ultrafast lasers allow detailed probing of early-time dynamics, and computational advances enable the treatment of systems with ever increasing complexity. These new techniques have enabled the development of new insights into the role water plays in a variety of fundamental processes, such as electron and ionic relaxation and solvation and the subsequent reactions of ions and radicals.

A fundamental understanding of the complex collection of processes driven by low-energy electrons will enable progress in addressing longstanding issues in understanding radiation effects in aqueous environments including those related to energy production and waste processing and in biology.

An understanding of the molecular scale processes controlling the chemistry driven by low-energy electrons in aqueous systems poses a variety of challenges for experiment, theory, and computations. The

fundamental challenges identified by this review include the following:

- probing the electronic structure of aqueous phases, including obtaining information about electronically excited states;
- obtaining detailed information about the effects of aqueous environments on electron-water scattering cross sections for ionization, excitation, and dissociative attachment including the effects of changing temperature and pressure;
- understanding how the local aqueous environment affects the dynamics of electronically excited states and their intermolecular migration;
- exploring the molecular scale mechanisms of relaxation and reaction processes occurring under highly nonequilibrium conditions;
- understanding the complexities that arise from the existence of aqueous interfaces with large molecules such as DNA and with solid materials including catalysts; and
- understanding the solvation structures, energetics, dynamics, and reactions of radicals and ionic species in aqueous systems including interfaces.

This review highlights the opportunity in the scientific community to create a research thrust aimed at developing a fundamental understanding of electron-driven processes in aqueous systems. Successful research programs in radiation chemistry and condensed-phase chemical physics provide the foundation to build such an effort. This new effort could be highly leveraged by the unique experimental and computational resources currently used by the Department of Energy (DOE) radiation chemistry and chemical physics programs and through additional utilization of current and planned user facilities, including X-ray light sources.

5. Acknowledgment

On September 26–28, 2002, a workshop titled “Understanding the Role of Water on Electron-Initiated Processes and Radical Chemistry” was held in the William R. Wiley Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory in Richland, WA. The Chemical Sciences Division of the DOE Office of Basic Energy Science provided support for the workshop. The workshop brought together physical chemists and chemical physicists—particularly those working on understanding effects of aqueous solutions on molecular processes—with researchers in the fields of solution chemistry, radiation chemistry, and environmental sciences. The workshop broke up into three writing teams to prepare a final report to the DOE. This review is a result of the workshop and the final report.

6. Glossary of Acronyms and Terms

ASW	amorphous solid water
BEB	binary-encounter Bethe (model)
BED	binary-encounter dipole (model)
CFC	chlorofluorocarbon
DEA	dissociative electron attachment

DFT	density functional theory
DIET	desorption induced by electronic transitions: atoms, ions, molecules are desorbed from surfaces as a result of electron or photon bombardment (ESD or PSD)
DNA	deoxyribonucleic acid
TD-DFT	time-dependent density functional theory
EICS	electron-impact cross sections
EID	electron-induced dissociation: electron bombardment of molecules coadsorbed with films of ice can induce dissociation, which is revealed in measurements using XPS, IR absorption, TPD, etc.
EPR	electron paramagnetic resonance
ESD	electron-stimulated desorption
ESR	electron spin resonance
ESDIAD	electron-stimulated desorption ion angular distribution: ion desorption directions are directly related to orientation of bonds at surfaces
exciton	excited state of an insulator or semiconductor that allows energy to be transported without transport of electric charge; often referred to as a bound state of an electron and a hole
<i>G</i> value	yield of a species from radiation (radiation term comparable to quantum yield); old units are species per 100 eV of energy deposited—normally 1–5; SI unit is moles per joule (micromoles per joule is approximately $1/10$ of the “old” definition of <i>G</i> value)
IR	infrared
IXS	inelastic X-ray scattering
KIE	kinetic isotope effect: ratio of rate constants for chemical reaction with different mass isotopes
LEAF	Laser-Electron Accelerator Facility (at Brookhaven National Laboratory)
LCLS	linear coherent light source
LIF	laser-induced fluorescence
LET	linear energy transfer: the amount of energy transferred to the solution per unit path length; typical LET for an electron (low LET) is ~ 0.2 eV/nM, which means that if a typical event is 50 eV, ionization events are separated by 250 nM; for an α particle (high LET), the range of energy loss might be 100–200 eV/nm, which means an ionization separated by 0.2–0.5 nM
MC	Monte Carlo (simulation)
MD	molecular dynamics (simulation)
MM	molecular mechanics
NMR	nuclear magnetic resonance (spectroscopy)
PAC	photoacoustic calorimetry
PCT	photoconductivity threshold
PES	photoelectron spectroscopy: ionization of core or valence electrons
PET	photoemission threshold
PSD	photon-stimulated desorption
QM/MM	hybrid methods that combine mixed quantum-classical models for the solute–solvent interactions together with classical molecular mechanics (MM) for the solvent–solvent interactions
REMPI	resonant-enhanced multiphoton ionization
RPES	resonant photoelectron spectroscopy: resonant enhancement of the photoionization cross section at core level thresholds
SLAC	Stanford Linear Accelerator Center
SPPS	subpicosecond photon source
Spur	localized high concentration of species, normally created by the effect of a single electron ejected by the primary ionizing event that has sufficient energy to create further ions

STM	scanning tunneling microscopy
TPD	temperature-programmed desorption: an ice-covered surface, coadsorbed with other molecules, is heated at a linear rate to cause thermal desorption; products are detected using a mass spectrometer
Track	ionization region caused by high LET radiation
TST	transition state theory: theory for calculating rate constants of chemical reactions based on the approximation that the reactive flux through the transition state dividing surface is equal to the forward flux toward products
TUHFF	Table-Top Terawatt Ultrafast High Field Facility (at Argonne National Laboratory)
UV-vis	ultraviolet-visible (radiation)
VDE	vertical detachment energy
VPE	vertical photoionization energy
VUV	vacuum ultraviolet (spectroscopy)
XAS	X-ray absorption spectroscopy: core electron excitation into unoccupied states
XES	X-ray emission spectroscopy: decay of occupied valence electrons to core hole
XPS	X-ray photoelectron spectroscopy
XRS	X-ray Raman spectroscopy: inelastic X-ray scattering proving core excitations

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