

Letter of intent for experiments at LCLS for new exciting science (B)

Molecular-Level Understanding of Energy-Driven Ultrafast Processes in Aqueous Systems

Team Leader: Anders Nilsson

Stanford Synchrotron Radiation Laboratory
650-9262233 (Phone), 650-9264100 (FAX), nilsson@slac.stanford.edu

Team:

Kelly Gaffney

Stanford Synchrotron Radiation Laboratory
650-9262382(Phone), 650-9264100 (FAX), gaffney@slac.stanford.edu

Louis Corrales

Pacific Northwest National Laboratory
509-375-2404(Phone), rene.corrales@pnl.gov

James Cowin

Pacific Northwest National Laboratory
509-375- 6330 (Phone), jp.cowin@pnl.gov

Gregory Kimmel

Pacific Northwest National Laboratory
509-375- 2501 (Phone), gregory.kimmel@pnl.gov

Gregory Schenter

Pacific Northwest National Laboratory
509-375- 4334 (Phone), greg.schenter@pnl.gov

Lai-Sheng Wang

Pacific Northwest National Laboratory
509-375- 8709 (Phone), ls.wang@pnl.gov

Sotiris Xantheas

Pacific Northwest National Laboratory
509-375- 3684 (Phone), sotiris.xantheas@pnl.gov

Peter Rossky

Institute of Theoretical Chemistry, University of Texas, Austin
512- 471-3555 (Phone), 512- 471-1624 (FAX), rossky@mail.utexas.edu

Thomas Orlando

School of Chemistry and Biochemistry and School of Physics
Georgia Institute of Technology
404-894-4012 (Phone), 404-385-0155 (FAX), Thomas.Orlando@chemistry.gatech.edu

Water is the most important substance for all life on Earth. The aqueous environment plays a critical role not only in biological systems, but also in processes that humans manipulate to improve the quality of life. Throughout the world, water is a key component in the production of energy and materials. In these processes, pollutants are created and transported by water throughout the ecosystem. High-energy radiation is known to induce physical and chemical transformations in aqueous systems. Typical sources of high-energy irradiation include nuclear waste, where radiolysis in aqueous solutions leads to the production of hydrogen gas; nuclear reactors, where deterioration is accelerated when irradiated materials come into contact with aqueous environments; and high-energy electromagnetic radiation used to destroy waste, to process materials, to probe functionality in biological system (diagnostics) or to destroy specific targets (e.g. cancer cells). These processes occur under a variety of conditions from ambient temperatures and pressures in biological systems to high temperatures and pressures in nuclear reactors and waste destruction. In addition, the processes in aqueous systems occur with a variety of solute molecules and interfaces present, from chemicals such as chlorinated hydrocarbons to enzymes and DNA to metal and oxide surfaces. A better understanding of these processes will lead to safer storage of high-level waste, cheaper destruction of hazardous chemical wastes and processing of materials in industrial applications, control of the deterioration of materials in nuclear reactors, and a better predictability of radiation effects in biological systems. This is a research topic of high interest for the Department of Energy (DOE) in the field of radiation chemistry. Recently a workshop was held at the Pacific Northwest National Laboratory in 2002 sponsored by DOE on this topic where a written report was generated and can be downloaded from the Basic Energy Sciences (BES) website.

http://www.sc.doe.gov/production/bes/chm/Publications/WaterWorkshopReport_final.pdf

The interaction of high-energy radiation and particles (with energies of keV and higher) with aqueous systems creates a cascade of ionization events. Each ionization event can produce low-energy, secondary electrons typically with energies below 100 eV that induce a variety of physical and chemical processes (excitation, ionization, chemical reaction, *etc.*). Electrons with energy above approximately 5 eV can induce electronic excitations in a water molecule (and solute or impurities) on subfemtosecond time scales. These precursor-excited states rapidly decay to form a wide range of high-energy species that include electrons, radicals and ions that are solvated and can exist in ground or excited states. The most sophisticated mechanisms have been inferred from stochastic simulations of track structures to reproduce experimental measurements of yield and spatial distribution of species such as the solvated electron (e^-_{aq}), H_3O^+ , OH, H, and H_2 in pure liquid water.

The solvated electron, discovered more than 40 years ago, has received intense theoretical and experimental interest over the past decades and its nature remains a challenging problem for the scientific community. Elucidating the dynamics of excess electrons in water leading to the solvated electron is a fundamental problem, essential for understanding many chemical reactions involving solvation and charge-transfer processes. Early ultrafast observations of solvated electrons in preequilibrium states and

a number of quantum-molecular dynamics simulations laid the foundations of the solvated electron dynamics. The generation of solvated electrons involves rich dynamics over a large temporal range; ultrafast librational dynamics (in the order of ~ 10 fs), localization of the electron in preexisting traps (~ 100 fs), solvation dynamics involving translational motion of surrounding molecules (< 300 fs) and relaxation from excited states (“wet” electron) to the hydrated electron (~ 500 fs). The localization and trapping of the electron is of fundamental importance to the subsequent dynamics. In the past most time resolved measurements of electron induced processes in water have been conducted by optical lasers. However, it is not clear how relevant optical lasers are to study the effect of ionizing radiation. In this sense ultrafast x-rays is the appropriate source to be utilized for time resolved studies of the early dynamics in aqueous systems. The initial stage of relaxation after hard x-ray absorption generates a primary photoelectron that relaxes, in part, by creating a cascade of secondary electrons. Molecular dynamics simulations indicate that the secondary electron cascade occurs on the ultrafast time scale, but the absence of high-energy ultrafast sources has precluded resolving this process in real time. However, with LCLS a new opportunity for generating ionizing radiation in the femtosecond time domain exists that can be used to study the time evolution of electrons and various dissociation products.

We propose two classes of pump-probe experiments:

1. Transient measurements of the visible absorption of the solvated electron following x-ray absorption will provide a direct monitor of the electron cascade process. The different steps involved in the formation of an equilibrated solvated electron can also be determined by measuring the time dependent spectrum of the photoelectrons. In addition to solvated electrons, other products of ionizing radiation (OH, etc.) can also be monitored optically.
2. We envisage that a development of a delay line for one colour x-ray pump-probe experiments will provide unique capabilities. The initial x-ray pulse can pump the system and the following probe pulse can be used for characterization. It will allow for a full synchronization of the pump and probe pulses. The probe detection can involve x-ray scattering, x-ray Raman scattering and O K edge x-ray emission spectroscopy. X-ray scattering provides information about the structural rearrangement in the solution during the electron cascade event. X-ray Raman scattering probes the O K edge x-ray absorption spectrum and will provide information about newly formed species such as OH⁻ and H⁺ and changes in the hydrogen bonding network. Non-resonantly excited O K edge x-ray emission spectroscopy probes the occupied electron states. The full valence band projected on the oxygen atom in water will allow to directly follow the population and energetics of the solvated electrons and how the valence band of water is affected.

All these classes of experiments can provide information that can not be obtained by other techniques and could lead to a large step in understanding electron driven processes in aqueous systems.

Most of the instrumentation for these experiments is expected to exist at the LCLS facility and can be coordinated with other proposals such as:

Frequency tunable femtosecond laser from near IR to UV

Delay lines for one colour x-ray pump and probe experiments

x-ray scattering detectors

x-ray Raman spectrometer

The extra equipment that will be needed for these classes of experiments utilizing the O K edge x-ray emission spectroscopy is the following:

X-ray Emission spectrometer	200k
-----------------------------	------

Endstation	100k
------------	------