

The LCLS Experimental Program: Call for Letters of Intent

## Probing Ultrafast Structural Reorganizations in Photochemical Reactions: from Molecules to Nanoparticles

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#### Abstract:

We present a research program that uses the unique characteristics of the LCLS to investigate the response and evolution of reactants during the early chemical events that are initiated by photon-induced electronic redistributions. We intend to explore ultrafast events coupled to chemical reactivity in systems ranging in complexity from diatomic molecules in the gas phase to nanocrystalline materials in the condensed phase. A full experimental, theoretical, and instrumentation program will be developed that puts minimum demands on the exact x-ray energy delivered by the beam line by using non-resonant spectroscopic and scattering techniques. A maximum amount of information will be gathered by simultaneously utilizing final-state x-ray fluorescence spectroscopy and wide angle x-ray scattering with the full intensity of the FEL photon output.

## Introduction

The fundamental processes governing chemical reactivity are the electronic and structural dynamics that take place on the femtosecond (fs) to picosecond (ps) timescale. These ultrafast events determine the ensuing outcome of chemical reactions. Our goal is to gain a detailed knowledge of the response and evolution of reactants during the early chemical events that are initiated by photon-induced electronic redistributions. The capability to exploit these fundamental phenomena is critical for the development of new technologies in areas such as catalysis, artificial photosynthesis, and molecular devices. This proposal explores ultrafast events coupled to chemical reactivity in systems ranging in complexity from diatomic molecules in the gas phase to nanocrystalline materials in the condensed phase.

Presently these processes are intensively studied at Argonne National Laboratory (ANL) with the complementary techniques of ultrafast laser pump-probe spectroscopy and time-resolved x-ray structural techniques at the Advanced Photon Source (APS). Whereas the optical studies have given us a wealth of information about electronic and vibrational dynamics as well as the coherence of excited species with fs time resolution, the x-ray experiments have provided us with structural information of excited states limited to 100 ps time resolution. This mismatch of time resolution has limited us to observing only thermally equilibrated states at relatively long times following photo-excitation. Our proposed beamline at the LCLS will allow structural information to be obtained on the same time scale as ultrafast laser spectroscopy, and hence enable entirely new concepts for reaction control to be explored that use light-initiated non-equilibrated and coherent states for manipulating reaction pathways.

Our proposed end station and experimental designs exploit the fact that the FEL delivers narrow-band radiation and accounts for the fact that it is not readily tunable and has large shot-to-shot intensity fluctuations. A key feature of our end station design is the simultaneous utilization of final-state x-ray fluorescence spectroscopy (FSXFS) and wide angle x-ray scattering (WAXS) with the full intensity of the FEL photon output. The flexibility of this design will permit the implementation of other complementary and novel experimental techniques. The following pages outline a program divided into four interdisciplinary research topics that explore the common theme of electronic and structural dynamics, followed by a description of the experimental techniques and instrumentation.

## Molecular Motions and Transition State Structures in Chemical Reactions

Excited states of photo-active molecules are powerful reagents for conversion of light to other forms of energies. Excited state chemistry can be used to drive a variety of critical chemical, biological and physical processes<sup>1</sup> including photocatalysis<sup>2</sup>, photosynthesis<sup>3-4</sup>, and molecular photonics<sup>5</sup>. Hence, resolution of photo-excited state dynamics and channeling of light energy to targeted reaction directions is the key for establishing fundamental mechanisms for solar energy conversion and storage. Metallo-organic complexes have been used in light-harvesting and photo-induced charge separation due to their intense optical absorption in the solar spectrum and their complex, adaptable, excited-state electronic structures<sup>6</sup>. The initial fundamental events in these light energy conversion processes are light-driven electron density redistributions, coupled with nuclear movements on a time scale from fs to longer which are ultimately responsible for the outcome of the reactions<sup>7</sup>. Therefore, knowing the mechanism of the coupling between the electronic and nuclear movements is essential for gaining control of photochemical processes. Using synchrotron x-rays, we have developed pump-probe x-ray absorption spectroscopy to capture thermally equilibrated excited state structures of metal complexes in solution<sup>8-12</sup>, and extensively applied the WAXS method on solving molecular structures with metal complexes as building blocks in solution during photochemical processes<sup>13-16</sup>. The intense fs x-ray pulses from the LCLS afford unprecedented opportunities to follow real-time atomic motions coupled to the electron redistribution in the initial excited state prior to thermal equilibration. As an example, our recent work on the excited state dynamics of Cu(I)(bis-dimethylphenanthroline) [Cu(I)(dmp)<sup>2+</sup>] using fs transient absorption spectroscopy revealed evidence of sub-ps Jahn-Teller distortion from the initial Franck-Condon state to the thermally equilibrated excited state due to the metal-to-ligand-charge-transfer induced by light<sup>9</sup>. The LCLS will be an ideal source to investigate such a structural change as well as the solvent reorientation accompanied this process.

**Experimental:** Initial experiments will be with molecules that we have had vast experience with such as the copper complex mentioned above and iron, nickel and zinc porphyrin complexes. All of these molecules undergo large structural changes upon photoexcitation ranging from symmetry changes (tetrahedral to square-planar) to bond breaking and photodissociation<sup>9,12</sup>. We will use laser and x-ray techniques shown to be sensitive to these electronic and structural changes around metal centers such as final state x-ray fluorescence spectroscopy (FSXFS) and wide angle x-ray scattering (WAXS). We have developed numerical analysis methods that correctly interpret the WAXS data and extract the information that was not readily available before. The combination of high x-ray flux and innovation in analytical methods allows fine structures of solute and solvent structural rearrangements after photoexcitation to be revealed. Such studies will bring fundamental understanding of solvation of excited state molecules and will continue to have significant impact in many chemical and biological processes.

Since these experiments do not involve zero-background measurements in that they attempt to discern structural differences based on the changes in absorption and scattering by the small subset of molecules that are excited, we have developed numerous methodologies for optimizing sample concentration and experimental geometry that enable us to excite and probe the largest concentration possible while avoiding nonlinear effects such as multi-photon excitation from the pump laser.

### **Real-Time Structural Dynamics in Size-Selected Clusters**

The nature of chemical reactions and phase transitions is determined by atomic motions leading to structural rearrangements on the subpicosecond timescale. The effect of structural changes on the physical and chemical properties can be drastic in the case of small clusters - nanoparticles consisting of only a handful of atoms. Since the properties of small clusters can change dramatically with particle size (by adding or removing one single atom from the particle), uniform size-selected particles are a prerequisite for such studies. The ultimate goal is to study the motion of atoms in such particles with femtosecond time resolution, in order to elucidate the correlation between the structural dynamics and the properties of the investigated systems. Isomerization rearrangements and especially phase changes are the processes of greatest importance. The ultrashort laser- and x-ray pulses available at the LCLS will make the tracing of the evolution of structures possible. Deepest insight into the underlying mechanisms and structures involved will come from theoretical calculations and modeling. The unique combination of a femtosecond x-ray probe, cluster size-selection with atomic precision and state-of-the art theoretical approach will enable us to address the fundamental issue of dynamic structural and phase transformations that determine the properties of small particles. The proposed integrated experimental and theoretical work has two main streams. The first lane will be the investigation of the temporal evolution of metal cluster clusters structures (e.g. Au<sub>n</sub>, Ag<sub>n</sub>, Co<sub>n</sub>) for variable cluster sizes. The second lane will be devoted to the study of the dynamics of phase transitions in two-component clusters (e.g. alkali halides). The findings from these studies will contribute, for example, to the detailed understanding of chemical reactions taking place on the active site of nanocatalysts governed by structural/phase changes during a course of a chemical reaction.

**Experimental:** The clusters of chosen single size will be extracted from the cluster beam using a mass filter, and will be either trapped in an ion trap<sup>12,13</sup> or deposited under well defined conditions (temperature, impact energy) on naked surfaces or surfaces covered by noble gas layers. A femtosecond UV-VIS/IR pump pulse will be used to trigger the structural transitions, and the temporal evolution of the cluster structure will be probed employing a delayed femtosecond X-ray pulse by recording the time dependent WAXS and FSXFS patterns. In the case of metal clusters, the studies will include investigations under vacuum conditions and in the presence of inert, "heat-bath" and reactive gases as well. The latter studies will address the issue of dynamic structural fluxionality of small clusters that reflects itself via the propensity of clusters to change their structure during a chemical reaction, thus altering the reaction barrier or the selectivity. Experimental development and preliminary (steady-state) x-ray experiments will be performed at ANL and the Advance Photon Source, in the time period of the LCLS construction.

**Theory and Modeling:** The outlined experimental program will be carried out in close contact with theoretical/computational work that will include high-level computations of cluster structures, elucidation of

mechanisms of structural transitions, and detailed time-dependent dynamics of structural transformations and phase transitions<sup>14-19</sup>. The theoretical component will also guide the choice of appropriate model systems for the experimental studies. The theoretical tools will include quantum mechanical methods, notably density functional theory, particularly for treating relatively small metal clusters. For larger clusters, effective potential methods will have to be used, so in the intermediate size region both methods will be used to validate and determine the extent of reliability of the more approximate methods. Molecular dynamics simulations will be used to explore the time-dependence of processes. For alkali-halide and other ionic clusters the simplified Born-Mayer model will be utilized as it has been shown to yield a good approximate description of structural and phase changes in these systems.

### Semiconductor Nanostructures

Semiconductor photocatalysis using nanoparticulate TiO<sub>2</sub> has proven to be a promising technology for use in a variety of photocatalytic reactions, from contaminated water to nanocrystalline solar cells<sup>20-23</sup>. Titanium dioxide, in particular, could be the catalyst of choice for a large variety of applications because it is cheap, non-toxic, and has redox properties which are favorable both for oxidation of many organics and for reduction of a number of metal ions or organics in aqueous solution. The mechanism of semiconductor assisted photocatalysis is based on the principle that particulate semiconductors behave as miniature photo-electrochemical cells. Although TiO<sub>2</sub> is very effective from an energetic point of view, it is relatively inefficient. The main energy loss in all investigated semiconductor particulate systems is due to the recombination of charges generated by the illumination of the particles. Therefore, the main focus of future research for the application of semiconductor assisted photocatalysis is to improve separation of charges and at the same time preserve or improve their redox properties. Understanding the events that take place in the early stages of photocatalytic reactions is a necessary step for the design and optimization of efficient artificial photocatalytic systems.

**Experimental:** This program is designed to understand the interplay between structure and electronic properties by studying the precursor and localization dynamics of charge carriers in nanoparticulate semiconductor films particularly time-dependent lattice deformations during thermalization of charge carriers after short-pulse optical excitation. Excitation of nanocrystalline TiO<sub>2</sub> with photon energies larger than its band gap results in formation of conduction band electrons and valence band holes. The localization of conduction band electrons into lower energy electronic (trap) sites can occur as fast as within 2 ps. Localization of charge carriers is manifested with a change of local symmetry that in turn alters their electronic structure. The electronic structure and energy levels of charge carriers ultimately determine their fate and their capability to perform subsequent redox reactions. We have previously shown that the surface of metal oxide nanocrystalline particles (TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>) differs from that of the respective bulk materials, and is characterized by a highly reactive under-coordinated surface<sup>24</sup>. We have also shown, using steady-state XANES and XAFS, that when electrons are electrochemically injected into TiO<sub>2</sub>, a change in the local symmetry of the surface Ti sites is detectable<sup>25</sup>. Similar changes were seen in chemically reduced TiO<sub>2</sub> (Ti<sub>2</sub>O<sub>3</sub>) samples. XANES is particularly sensitive to both the oxidation state and symmetry around the Ti allowing us to readily differentiate Ti<sup>4+</sup> and Ti<sup>3+</sup> as well as the change from the D<sub>2d</sub> symmetry of anatase TiO<sub>2</sub> nanoparticles and the D<sub>3d</sub> symmetry of Ti<sub>2</sub>O<sub>3</sub><sup>26</sup>.

All of our experiments to date have been steady-state due to the rapid thermalization and trapping and/or recombination of photolytically produced electron hole-pairs. The LCLS light source will be an ideal source of x-rays for studying the ultrafast photophysics and photochemistry of a variety of nanoparticle semiconductors. Initial experiments will involve single and multi-photon laser excitation of TiO<sub>2</sub> films and structural probing using FSXFS and WAXS. We will investigate both bare films as well as films under potentiostatic control in an x-ray spectroelectrochemical cell similar to one that we have successfully used at the APS. The cell design allows us to make simultaneous x-ray and optical measurements during photo-induced detrapping. Investigation of the changes in structure, both in situ and in real time, will enable observation of the response of structure to charge carrier localization. Modification or hybridization of the nanoparticle surface will allow us to study the effects of surface chemistry on charge carrier lifetime giving

us new insights into what the structural nature of trap sites is and how, with surface modifications, to increase the lifetime and redox efficacy of the charge carriers.

### **Coherent Control**

Coherent control of chemistry, i.e., guiding a chemical reaction along a particular pathway with a spectrally synthesized laser pulse, is an emerging topic in chemistry. X-rays can provide vital information about the structural and electronic changes that occur during the controlled quantum dynamics, and the time resolution of the LCLS is needed in most cases. The x-ray techniques to be applied include FSXFS (see techniques section) which will provide information on the changes in chemical speciation (oxidation state, etc.), x-ray scattering to show evolving bond lengths, and atom-resolving holography<sup>27,28</sup> to provide information on both, bond lengths and orientation. The molecules to be studied can be oriented by several means, i.e., attaching them to a substrate, pre-orienting them in a strong electric field from a laser, or by selectively exciting molecules in a particular rotational state and orientation. The latter technique is the basis of an LDRD pre-proposal, we submitted at Argonne National Lab<sup>29</sup> with the purpose of developing an alignment technique, and at the same time do a first test experiment of probing coherent control (here of the external, rotational degree of freedom) with x-rays: using a frequency- and polarization-chirped laser pulse, a rotational sub-ensemble of molecules in the gas phase (we consider specifically Br<sub>2</sub>, I<sub>2</sub> and digermane H<sub>3</sub>Ge-GeH<sub>3</sub>) is excited on the Raman ladder to a high vibrational state<sup>30</sup>. Only those molecules whose rotational frequency is commensurate with the polarization chirp of the exciting laser pulse will undergo full excitation; all others drop out early<sup>31</sup>. Due to their anharmonicity, the bonds (Br-Br, I-I, or Ge-Ge) in the excited molecules are lengthened. Depending on the timing of the x-rays relative to the laser excitation, the rotational sub-ensemble will have a well-defined orientation. X-ray scattering from the sample will then show a corresponding anisotropy in the nearest-neighbor correlation peak, and likewise, near-edge spectroscopy will exhibit anisotropy with regard to the x-ray polarization. Our estimates show that in the gas phase, alignment coherence of the molecules is preserved long enough to show these effects even with the time resolution of the APS. At the LCLS, the same experiment will be done on a about 1000-fold faster time scale, thus providing a unique opportunity of a seamless transition from a current 3rd-generation x-ray source to the LCLS. Further development of the program will involve the study of coherently controlled dynamics of internal degrees of freedom in the above and more complex molecules in the gas and liquid phase. All of these extensions beyond the simple test experiment depend crucially on the LCLS because the typical oscillation periods of internal degrees of freedom (vibrational and electronic) lie in the subpicosecond domain, and the same is true for the collisional decoherence in the liquid phase and internal decoherence due to dissipation among the many internal degrees of freedom in a complex molecule.

### **Required Instrumentation for the LCLS Chemistry Beamline**

The experimental challenge in this proposal is to probe both the structural and the electronic response of the samples to a perturbation. This will be achieved with an end station designed for simultaneous final state x-ray fluorescence spectroscopy (FSXFS) and wide angle x-ray scattering (WAXS) measurements described below. A number of characteristics of the LCLS must be addressed, namely the high peak intensity, the high transverse coherence, the low repetition rate, the large shot-to-shot intensity fluctuations in a small energy bandwidth, and a timing jitter which is larger than the pulse length itself. By avoiding resonant techniques, our design reduces the requirements on tunability and optics to a minimum while obtaining spectroscopic information for all elements heavier than titanium. By using a different detector system, even elements down to carbon can be studied. Future opto-mechanical and detector developments may allow additional and more complex techniques, such as using x-rays as the source of perturbation, to be integrated, thereby broadening and enhancing the scientific program.

The goal of the FSXFS experiment is to determine the localized charge and spin state of the absorber. Resonant XAFS techniques will be very demanding at the LCLS because of the high peak intensity, the shot-to-shot fluctuations and the limited source tunability. Instead, we will excite x-ray fluorescence well above the absorption threshold and measure its spectrum with large solid angle and medium to high energy resolution. The Coulomb and exchange coupling between the core hole of the final state and the localized electron distribution will result in a multiplet splitting of the fluorescence lines.

Through atomic multiplet theory and more advanced theoretical models, this will reveal the charge and spin state, localized at the absorber<sup>32,33</sup>. Due to the above-threshold excitation, the full pink beam without a monochromator can be used. With an incoming photon energy around 8 keV we will be able to investigate most of the heavier elements (titanium and heavier). A multi-crystal analyzer system will be radially arranged to the incident x-ray beam so that the WAXS scattering can be simultaneously detected. Using conventional spherical single crystal analyzers with a bending radius of 1 meter in the Rowland geometry, the achievable energy resolution is better than 1 eV. A system with 20 elements can achieve a solid angle of  $10^{-3}$ - $10^{-2}$  rad<sup>2</sup>. We will use an array of avalanche photo diode detectors (APD) in proportional mode because, depending on the sample, we expect up to  $10^4$  photons per shot at each detector element. The high energy resolution will also allow the separation of multi-photon absorption events causing multiply ionized sites - an essential condition for the interpretation of the data at high x-ray flux densities.

The time-resolved WAXS experiment will probe spatial configuration changes due to its high sensitivity to the arrangement of the core electrons surrounding nuclei in the systems being excited. The data obtained will be analyzed by applying algorithms known from powder diffraction, pair distribution function and small angle scattering measurements, so that the structural response of the entire system is probed<sup>34</sup> and can be correlated to the electronic response measured simultaneously using FSXFS. Because we intend to measure a wide range of ordered to strongly disordered systems, it is necessary that our proposed experimental setup must permit determination of the scattered intensity distribution over a large  $\mathbf{q}$ -range. However, because of the nanometer-sized molecules and particles being studied, only a moderate  $\mathbf{q}$ -resolution is required. The ideal detector for this experiment would be an energy resolving pixelated area detector covering a large solid angle. At a minimum, the required experimental flexibility could be achieved with current technology by a combination of a two dimensional and a linear CCD detector array combined with an optimized phosphor and lens system. The two dimensional detector would be placed in the forward direction and mounted on a rail to permit the sample-to-detector distance to be easily changed. The small divergence of the LCLS beam will allow the use of a detector with a central hole and a beam stop at the end which will permit easier heat dissipation due to the high intensity of the forward beam. To span the low to high  $\mathbf{q}$ -range, we will have an additional linear array in the vertical scattering geometry, which will cover the  $2\theta$  range between  $30^\circ$  and close to  $180^\circ$ . This arrangement will be compatible with the spectroscopy detectors, so that all three detector systems will be simultaneously available. If pixelated detectors should become available they will be used instead of the two-dimensional CCD. It must be emphasized that due to the high peak brilliance and low repetition rate of the source, the pixelated detector electronics will have to be modified so that the signal from the individual pixels can be stored in analog form and later multiplexed out.

In the event of significant detector, experimental, or theoretical developments, this experimental arrangement will provide enough flexibility to extend the scientific program using the described detectors or to integrate additional detector systems or x-ray crystal optics to support advanced techniques such as correlation spectroscopy and x-ray fluorescence holography<sup>27,28</sup> which has the potential to provide information similar to EXAFS.

**Required Lasers:** All of the proposed experiments will require a synchronized amplified Ti:Sapphire or similar short-pulse/broad bandwidth laser system preferably with an OPA for tuning the excitation wavelength to better match sample absorption bands (300 nm to 2  $\mu\text{m}$ ). For most experiments, pulse energies on the order of 20-100  $\mu\text{J}$  will be sufficient. The coherent control experiments will require a pair of acousto-optic programmable dispersive filters (one for each polarization) with the flexibility to Fourier synthesize a pulse including the polarization of each spectral component.

#### **Sources of Funding:**

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## Budget 2006-2011

1. Transition States
  - a. Staff scientist, 1yr: \$240K
  - b. Postdoc, 3yrs: \$240K
  - c. Sample environment: \$50K
2. Cluster
  - a. Staff scientist, 1yr: \$240K
  - b. Postdoc, 3yrs: \$240K
  - c. High flux cluster source (including vaporization laser, vacuum chamber and pumps) permanently located at LCLS: \$450K
3. Nanoparticles
  - a. Staff scientist, 1yr: \$240K
  - b. Postdoc, concurrent with 1.b
  - c. Sample environment: \$50K
4. Coherent Control
  - a. Staff scientist, 1yr: \$240
  - b. Postdoc, 3yrs: \$240
  - c. Acousto-optic programmable dispersive filter: \$100K
  - d. Sample environment: \$10K
5. Theory Effort
  - a. Postdoc (1at ANL, 1 at University): \$390K
  - b. Graduate student, 3yrs: \$85K
6. Instrumentation
  - a. OPA for laser system: \$75K
  - b. Crystal optics (with supporting mechanics): \$210K
  - c. Photo avalanche diode array (with supporting electronics): \$200K
  - d. Scattering detector for scattering experiments (1Mpx): \$2M est.
  - e. Customization of scattering detector
    - i. Application-Specific Integrated Circuit (ASIC) development for low repetition rate/high peak flux: \$1M
    - ii. Detector positioning mechanics: \$200K
  - f. Beamline optics (variable focus size): \$250K

<b>Research Personnel</b>	
David J. Gosztola <a href="mailto:gosztola@anl.gov">gosztola@anl.gov</a> Chemistry Division Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60440 Tel:(630)252-3541 Fax:(630)252-4993	Project coordinator, Staff Chemist Currently developing a multi-terawatt laser based sub-picosecond MeV electron source for time-resolved radiolysis studies. Experienced in the uses of ultrafast laser spectroscopy x-ray absorption and electrochemistry. Research interests include the study of the structural changes in molecules during photo-excitation, electron transfer, and adsorption at surfaces. Expertise in optical and electronic instrumentation design and development for time-resolved spectroscopies.
Bernhard W. Adams <a href="mailto:adams@aps.anl.gov">adams@aps.anl.gov</a> Experimental Facilities Division Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60440 Tel: (630)252-6454 Fax: (630)252-0279	Physicist X-ray optics, relevant for beamline design issues such as focusing and wavelength dispersion. Time-resolved laser pump, x-ray probe spectroscopy (currently working on time-resolved x-ray spectroscopy of the GaAs band structure and on high-energy-resolution spectroscopy of optical phonons in GaP). Coordinated the DESY workshop on nonlinear optics and ultrafast physics, which is incorporated into the Technical Design Report on the TESLA FEL.

<p>Klaus Attenkofer  <a href="mailto:klaus.attenkofer@anl.gov">klaus.attenkofer@anl.gov</a>  Experimental Facilities Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel: (630)252-0383  Fax: (630)252-0365</p>	<p>Beamline Scientist at BESSRC/APS  Application and development of various spectroscopic techniques and the appropriate experimental set ups for XAFS, EXAFS, X-ray magnetic circular dichroism (XMCD), and resonant inelastic X-ray scattering (RIXS). Current research is focused on time-dependent X-ray spectroscopy at the APS (magnetic interactions, charge transfer, and structural response of molecules), utilizing laser and microwave pump techniques. This includes detector-, crystal optics-, micro focusing optics- and high heatload beamline optics-developments.</p>
<p>R. Stephen Berry  <a href="mailto:berry@uchicago.edu">berry@uchicago.edu</a>  The University of Chicago  Department of Chemistry  Office SCL 101  5735 S Ellis Ave  Chicago, IL 60637  Tel:(773)702-7021  Fax:(773)702-080</p>	<p>James Franck Distinguished Service Professor Emeritus,  Joint appointment at ANL as Special Advisor to the Director  Expertise in structures, dynamics, and statistical thermodynamics of clusters; special nature of phase changes of small systems, including first-order-like and second-order-like changes and their relation to bulk phase transitions; thermodynamics of finite-time processes; dynamics of protein folding and reactions; collisions and photoionization of atoms and small molecules; selection of neutral clusters of a single, chosen size. His contribution will include primarily theory of metal clusters, especially of binary nonmetallic clusters; analytic theory from models; the use of kinetic master equations; molecular dynamics, and Monte Carlo simulations.</p>
<p>Lin Chen  <a href="mailto:lchen@anl.gov">lchen@anl.gov</a>  Chemistry Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel:(630)252-3533  Fax:(630)252-9289</p>	<p>Staff Chemist  Molecular dynamics and structure determination in photochemical reactions including photoinduced electron and energy transfer in natural and artificial photosynthetic systems, light harvesting by metal complexes, semiconductor nanoparticles, and supramolecular systems. Expertise includes ultrafast laser spectroscopy, nonlinear optical spectroscopy, time-resolved laser pump, x-ray probe XAFS and XANES, as well as molecular modeling.</p>
<p>Julius Jellinek  <a href="mailto:jellinek@anl.gov">jellinek@anl.gov</a>  Chemistry Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel:(630)252-3463  Fax:(630)252-4954</p>	<p>Senior Scientist and Group Leader, Cluster Studies Group  Structural and phase transitions in clusters, in general, and metal clusters (one-component and alloys), in particular; development of new analytical and computational techniques for analysis of dynamical and statistical behavior of finite systems; density functional theory explorations of geometric, electronic, and magnetic properties of metal clusters and organometallic complexes; development of new semiempirical many-body potentials; theoretical/computational studies of cluster chemical reactivity; explorations of size-evolution of different cluster properties (e.g., the size-induced transition to metallicity)</p>
<p>Guy Jennings  <a href="mailto:jennings@aps.anl.gov">jennings@aps.anl.gov</a>  Experimental Facilities Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel: (630)252-0361  Fax: (630)252-0365</p>	<p>Beamline Scientist at the Advance Photon Source (BESSRC)  Experience with time dependent X-ray spectroscopy. Expertise in high speed electronic instrumentation and detector design. Expertise in design and implementation of high performance data acquisition systems. Development of data acquisition and analysis software</p>
<p>Eric C. Landahl  <a href="mailto:elandahl@anl.gov">elandahl@anl.gov</a>  Experimental Facilities Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel: (630)252-0278  Fax: (630)252-0279</p>	<p>Beamline Scientist at the Advanced Photon Source.  Operates the Sector 7 ultrafast laser facility. The research at this facility includes a variety of ultrafast laser pump / x-ray probe experiments. While at SLAC from 2001-2003, developed the X-band photoinjector for the Next Linear Collider X-Ray FEL. Role in the proposed work will be developing techniques for the synchronization and overlap of ultrafast x-rays and lasers.</p>

<p>Tijana Rajh  <a href="mailto:rajh@anl.gov">rajh@anl.gov</a>  Chemistry Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel:(630)252-3542  Fax:(630)252-9289</p>	<p>Group Leader and Chemist, Radiation and Photochemistry Group  Surface modification of metal oxide semiconductor nanoparticles for electronic coupling of with surrounding environment. Investigations of the effects of surface modification on structural, dynamic and redox properties by XAS, electron paramagnetic resonance (EPR) spectroscopies and pulse radiolysis</p>
<p>Stuart A.Rice  <a href="mailto:s-rice@uchicago.edu">s-rice@uchicago.edu</a>  The University of Chicago  Department of Chemistry  Office RI 348  5640 S Ellis Ave  Chicago, IL 60637  Tel:(773)702-7199  Fax:(773)702-5863</p>	<p>Frank P. Hixon Distinguished Service Professor, Emeritus  Joint appointment at ANL as Special Advisor to the Director  Expertise in experimental and theoretical studies of inhomogeneous metals, specifically the liquid-vapor interface; theory of active control of chemical reactions and theory of unimolecular reaction rate, experience using Advanced Photon Source for various x-ray based studies of surfaces of liquid metals. Contribution will include theoretical support for the design and interpretation of experiments and theoretical description of processes observed.</p>
<p>Carlo Segre  <a href="mailto:segre@iit.edu">segre@iit.edu</a>  Illinois Institute of Technology  Physics Division, BCPS Dept.  3101 South Dearborn Street  Chicago IL 60616  Tel: (312)567-3498  Fax: (312)567-3484</p>	<p>Professor of Physics and Associate Dean, Associate Director of MRCAT  Involved in scattering and spectroscopy research for the past 17 years and have been responsible for construction and operation of the MR-CAT beamlines at the APS since 1994. Current research includes EXAFS and XANES on nanoparticle catalysts in working Direct Methanol Fuel Cells, EXAFS on magnetoelectric nanoparticles and electroluminescent phosphors, SAXS studies of nucleation and crystallization of supersaturated solutions of small organic molecules and x-ray optics development.</p>
<p>Gopal Shenoy  <a href="mailto:gks@aps.anl.gov">gks@aps.anl.gov</a>  Experimental Facilities Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel: (630)252-5537  Fax: (630)252-9303</p>	<p>Senior Scientist and Senior Scientific Advisor for the Advanced Photon Source.  Has been involved in the development of scientific cases for X-ray FEL Projects.</p>
<p>David Tiede  <a href="mailto:tiiede@anl.gov">tiiede@anl.gov</a>  Chemistry Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel:(630)252-3539  Fax:(630)252-9289</p>	<p>Senior Chemist and Group Leader, Photosynthesis Group  Expertise lies in the design and characterization of the structure and function of natural and artificial photosynthetic molecular assemblies, with particular expertise in the development and application of solution wide-angle X-ray scattering techniques for the resolution of molecular diffraction in liquids, including the development of atomic coordinate-based techniques for the modeling of solution diffraction data in terms of ensemble-averaged structure and configurational dispersions.</p>
<p>Stefan Vajda  <a href="mailto:vajda@anl.gov">vajda@anl.gov</a>  Chemistry Division  Argonne National Laboratory  9700 South Cass Avenue  Argonne, IL 60440  Tel: (630)252-8123  Fax:(630)252-4954</p>	<p>Staff Chemist  Studies of chemical reactions of size-selected clusters, femtosecond laser spectroscopy of clusters in the gas phase and laser controlled cluster dynamics. Study of the chemical properties of metal clusters, as well as on the investigation of temperature induced growth of deposited clusters by means of grazing incidence small angle x-ray scattering at the APS.</p>
<p>Michel Veenendaal  <a href="mailto:veenendaal@physics.niu.edu">veenendaal@physics.niu.edu</a>  Northern Illinois University  Department of Physics  Faraday West 223  DeKalb, IL 60115  Tel: (815)753-0667  Fax: (815)753-8565</p>	<p>Associate Professor of Physics, Deputy Director of the Laboratory for Nanoscience Engineering and Technology  Expertise in the studies of chemical reactions of size-selected clusters, femtosecond laser spectroscopy of clusters in the gas phase, laser controlled cluster dynamics. Research interests include the study of the chemical properties of metal clusters, as well as the investigation of the thermal stability of supported clusters by means of grazing incidence small angle x-ray scattering at the APS. Experience in vacuum instrumentation design.</p>