Upgrade of Laser Initiated Time-Resolved X-ray Facility for Photochemical Research

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Abstract

An instrumentation upgrade is proposed for a laser initiated time-resolved (LITR) X-ray absorption spectroscopy (XAS) and wide-angle X-ray scattering (WAXS) user facility at Beamline 11-ID-D. The upgrade consists of a new high repetition rate laser and two new high throughput high time resolution detectors. We will complement the instrumentation upgrade with a beamline upgrade, which will enhance the versatility, reliability, and throughput of the facility, and create unique opportunities for new hard X-ray XAS and WAXS experiments. The design goals for this upgrade are to improve the throughput of time resolved measurements by 2-3 order of magnitude and to enable the measurements to be performed during the majority 24 bunch standard APS operating mode as well as during the hybrid timing mode. The upgrades will provide the basis for a world-leading facility for first-of-a-kind structural and electronic dynamics studies measured at length scales from 10^{-12} to 10^{-8} meters and at time scales from 10^{-11} to 10^{-6} seconds coupled to photochemical reactions that underlie fundamental mechanisms in solar energy conversion, photocatalysis, molecular and solid state devices. These new capabilities are vital to current BES sponsored scientific programs as well as to a growing scientific community in LITR x-ray studies across different disciplines of basic and applied sciences within the DOE missions, such as material sciences, energy research, environmental and surface sciences.

1. Science

In order to understand and ultimately control fundamental mechanisms of chemical reactivity, we need to know not only the structures of reactants and the products in a chemical reaction, but also how and why they can be transformed from one to another. This kind of information can only be obtained by tracking atomic position changes along reaction paths that typically proceed though a series of intermediate stages. These atomic position changes govern the outcome of the reaction and the functions of the molecules. In order to determine atomic position changes along the reaction path, the chemical process must be synchronized among all molecules in the ensemble, and pulsed x-ray or electron sources with sufficient flux must be available. These two essential requirements are met by using ultrafast laser pulses as the trigger for the reactions and by using new generation pulsed x-ray and electron sources with unprecedented high flux as the probe to track the transient structures at different time delays from the trigger. The pump-probe cycle can be repeated for reversible processes until data with required signal-to-noise ratios are obtained. An important advantage of this approach is that the intrinsic time resolution of the measurement is only limited by the pulse duration of the pump or probe pulse, whichever is longer rather than by the detector response time. By measuring the time evolution of the characteristic absorption features for excited and intermediate states, this method provides information on the populations and the energetics of the transient species, and the correlation between different species as a function of the delay time from the pump pulse, the trigger of the reaction. Although some optical measurements, such as time-resolved resonant Raman spectroscopy, can provide structural information through indirect measurements, such as vibrational frequencies, details of nuclear movements and the structures of the intermediates that enable the chemical reaction in general are far from clear when based on optical spectroscopic results only, and are often heavily reliant on theoretical models from quantum mechanical and molecular mechanical calculations without verification by direct structural measurements with atomic resolution.

Hence, extending the pump-probe approach to the x-ray regime became a forefront activity in chemical sciences as soon as intense pulsed x-ray and electron sources became available during the past decade. Compared to sophisticated dynamics measurements by ultrafast lasers, structural measurements by x-rays in short time regime are still in the early stages, because the key requirements for such measurements, x-ray pulses sufficiently short in duration and high in flux, sophisticated optics that manipulate x-rays with ease, and x-ray detectors with high sensitivity, high dynamic range and fast time response, have only become available in recent years. Several third generation synchrotron sources including the Advanced Photon Source (APS) at Argonne National Laboratory, have begun to provide x-ray pulses of 30 – 100 ps fwhm with unprecedented brilliance and photon flux, enabling several pioneering time-resolved structural studies. Meanwhile, ultrafast laser driven plasma x-ray sources and x-ray diode sources, as well as ultrafast soft x-ray sources via high harmonic generation, have been constructed in several laboratories, where x-ray pulses with < 50 fs fwhm were generated and applied to studying structural changes in various photoinduced processes. Moreover, several accelerator based ultrafast x-ray sources are planned or under construction in the near future. Hence, significant progress in ultrafast x-ray applications is expected in the future when the dream of visualizing molecular motions during real chemical reactions becomes reality.

An unique and important advantage of the proposed upgrade is the capability to conduct both LITR-XAS and WAXS experiments at the same beamline, on the same sample, and at the same time, so that transient structural information can be extracted on different length scales with the identical sample conditions. For many metal complex supramolecular systems used in photocatalysis for solar fuels and organic semiconductors, such a combined approach will greatly augment our knowledge on the electronic and geometry of the metal centers as well as the overall structures of the system during the photochemical reactions, which otherwise can not be obtained.

Another area of growth will be in the development of techniques which probe the interfaces of organic and inorganic materials. In almost all applied fields the efficiency of the final device is determined by an efficient charge separation and the details of charge transfer at the organic/inorganic interface, and the trapping of carriers on grain boundaries. Only very indirect experimental techniques are available to probe the basic mechanism of these effects. Core level spectroscopy with its element selectivity and surface X-ray scattering with its high spatial resolution are perfect tools to probe the electronic and structural response of these hetero structures. The measurement of X-ray standing waves is one example of how scattering and spectroscopy measurements can be combined. The periodic intensity variation of an X-ray standing wave field perpendicular to the surface of a crystalline substrate caused by the crystal structure of the substrate itself, is used to spectroscopically probe the electronic structure of surfactants. By changing the Bragg condition of the substrate, the vertical intensity profile can be changed and a full depth profile with sub-angstrom resolution can be achieved. Charge transport can be triggered by laser excitation of the cathode or anode, so that a complete spatial and temporal profile of the charge distribution can be determined. This kind of experiment will result in unique insight into the basic transport properties of hetero structures. They require high flux, high brilliance to achieve a small vertical focus, and a very efficient spectroscopy detection system, to make optimal use of the emitted fluorescence photons and therefore to limit sample damage produced by X-rays and laser photons. Other experimental developments are anomalous surface truncation rod X-ray scattering and grazing incidence small/wide angle X-ray scattering (GISAXS/GIWAXS) techniques, which can be used to probe the vertical and lateral structural response of molecular materials polymers on crystalline surfaces. We have already successfully performed initial static GIWAXS experiments to test the

beamline optics and detection requirements for time dependent experiments. These developments will fully benefit from the expertise of existing users of 11-ID-D, who are experts in these techniques, presently only statically performed.

2. Added Value:

The proposed laser and detector systems are highly optimized for time-dependent experiments and will allow bunch-to-bunch time resolution in the standard 24-bunch mode without the use of an x-ray shutter. In combination with the ongoing beamline upgrade of 11-ID, the LITR x-ray facility upgrade will reduce the required acquisition time by 2 - 3 orders of magnitude, will enable time-resolved experiments to be scheduled for 80% of the available time (as opposed to the current 20%), and will allow a wider range of sample systems to be studied. Table 1 summarizes the various enhancements expected from the upgrade. This will create a facility supporting a general user community dedicated to the investigation of charge transfer and structural time dependent effects in materials across a broad range of liquid, powder, and interfacial states. The large throughput and the highly developed optimized beamline environment will allow us to offer the use of laser pump and X-ray probe experiments to a large community in basic and applied science, which is not versed in the utilization of large facilities. As in the past, with this facility we will develop new techniques and experimental approaches which will address the needs of these communities.

Table 1. Enhancement factors for LITR-XAS/WAXS experiments with the upgrades

UPGRADE	LITR-XAS	LITR-WAXS
Beamline insertion device and optics	Photons/bunch 2-5 times higher	Photons/bunch 2-5 times Higher (additional factor 80 for polychromatic beam)
Laser	Repetition rate 10 times More selections in excitation wavelengths	
KETEK Detector Arrays	Total count rate 50 times Usable beam time 4 times	N/A
Pilatus Detector Arrays	N/A	Signal to noise ratio
Total estimated enhancement factor for an individual experiment	up to 2500	up to 8000

3. Expected user communities

Research done at this facility has been highly beneficial to core research activities of BES in solar energy utilization, and will play an important role in future energy related research on solar energy, hydrogen generation, chemical imaging, catalysis, and electrochemistry. At present, more than ten Principal Investigators (most of whom are funded by BES) support our proposal, and have full intentions of becoming regular users/collaborators (see Partnerships and user interest). We expect the demand for time-resolved x-ray experiments will further grow in the future. However, the

demand can only be met after upgrades on the LITR-XAS/WAXS instrumentation, beamline optics , and infrastructure.

4. Enabling technology and infrastructure

a. Implications of the Beamline Upgrade for LITR-XAS/WAXS Experiments and optimization of insertion device ($1400K)

The upgrade of the beamline 11-ID-D is intended to capitalize on the high electron energy of the storage ring (7 GeV) to provide an exceptional photon beam in the hard X-ray range, perfectly suited for hard X-ray spectroscopy and scattering experiments. It consists of two inline undulators (already installed), one designed for full energy tunability over the range 4.5 - 25 keV for XAFS experiments, and the other designed to produce an extremely high flux at selected energies (12 keV, 18 keV, 24 keV) for scattering experiments. Together with optimized beamline optics and a high heat load monochromator, we expect a photon flux of $5 \times 10^{13\text{-}14}$ photons/sec with a beam size of 50×400 μm^2 and an energy bandwidth of 0.01%. The design of the optics also allows the use of a KB-mirror system to adjust the optimum x-ray beam size for pump probe experiments (smallest beam size ~250×250 nm^2). An additional broadband multilayer monochromator (with energy bandwidth 1%) will be installed, increasing the photon flux to 10^{16} photons/sec for scattering experiments. To reduce radiation damage the system will be combined with a relatively slow heat-load chopper. As far as we are aware, this will be the most powerful beamline in the world designed for laser pump X-ray probe experiments in the hard X-ray range.

To utilize this unique potential, we need to have a detection system capable of simultaneously handling the much higher photon flux and having a time response faster than the bunch to bunch interval in the standard 24-bunch operating mode at the APS (i.e. 154 ns). While the requirements on sample, infrastructure, x-ray optics and x-ray source characteristics are comparable, the requirements for the detection systems for XAS and WAXS experiments are very different from each other. XAFS experiments require detectors with an energy resolution of 2-3%, usually achieved by pulse-height-analysis of the produced charge from the x-ray absorption in the detector, but they do not require spatial resolution. In contrast, the WAXS detector must have spatial resolution but does not require significant energy resolution. In a typical geometry, the required spatial resolution is about 150×150 μm^2 to 200×200 μm^2.

b. The XAS Detector upgrade ($2100K)

In order to simultaneously meet requirements for energy-resolution, response time, and count rate, we propose the use of a multi-element silicon drift detector (SDD) in single photon counting mode for x-ray fluorescence detection (2x203-elements). The primary advantage of using fluorescence detection (rather than transmission) is the ability to work with dilute samples. The majority of LITR-XAS experiments carried out at the current facility are on relatively dilute samples ranging from 1 - 2 mM concentration for several reasons: 1) the dilute samples will be efficiently excited by the laser pulses (10^{14} photons/laser pulse) to create an excited state population of up to 30%, allowing the XAS spectrum of the transient species to be extracted from the overall measured spectrum; 2) many samples of interest have limited solubilities (even less than 1 mM concentration); 3) many interesting samples, especially metalloproteins, are synthesized only in very limited quantities by

research laboratories; and 4) additional unintended photoprocesses, such as excited state annihilation and quenching, could take place in high concentration samples.

c. The WAXS detector upgrade ($900K)

The proposed WAXS detection system (PILATUS M2) is a hybrid pixel array detector, where each pixel is provided with independent signal processing, gating and counting circuitry, operating in a single photon counting mode. Compared to a charge coupled device (CCD) detector, the proposed detector will provide higher dynamic range, more efficient detection of low count rate signals, faster readout and easy gateability by means of electronic signals. As an integrating detector, a CCD provides superior high count rate signal detection, but this is less important in our application.

A typical WAXS pattern from a disordered sample is approximately radially symmetric with a general decrease of intensity with increasing momentum transfer (or Q). The detected scattering pattern is a sum of contributions from the solvent, the species of interest, and the solvation interface layer, whose structure is modified by the presence of the species of interest. The signal from the solvent is the dominant component and therefore the experimental challenge is to detect a small signal on a large background. Even in the areas of high intensity the scattered intensity is spread out over hundreds of pixels so the count rate per pixel is relatively low, and the use of a photon counting mode is not a limitation for the usable X-ray flux. In the case of the high Q-range the signal is taken from a very large number of pixels in each of which there is only a very small probability of detecting a photon. Here the single photon counting mode provides a large advantage in comparison to an integrating detection system where the additional read-out noise from each CCD pixel (typically about 1 photon) severely limits the high Q sensitivity of the measurement.

d. The laser upgrade including laser-hutch upgrade and infrastructure ($1100K)

The fourth key-element of the proposed upgrade is an ultrafast laser system with a repetition rate of 10 kHz with sufficiently high pulse energies at a variety of wavelengths. An ideal laser system for LITR-XAS/WAXS experiments at a synchrotron facility should have the following characteristics: 1) sufficient pulse energy, or number of optical photons per pulse, to excite a relatively high fraction (i.e., >20%) of the sample to the photoinduced transient states of interest to allow their structures to be extracted from the spectrum of a mixture with the remaining ground state molecules; 2) as high repetition rate as possible for more efficient data acquisition (as long as the sample has sufficient time to fully relax to its ground state); 3) a wide selection of excitation wavelengths to increase the range of samples which may be studied; and 4) easy operation and high reliability to minimize the possibility of losing valuable beam time. In addition we plan to offer a laser pump-probe apparatus which will be used to pre-characterize sample systems

5. Partnerships and user interest

Benjamin Gilbert Staff Scientist, Lawrence Berkeley Laboratory

Glenn Waychunas Staff Scientist, Lawrence Berkeley Laboratory

Michael D. Hopkins Professor and Chairman of Chemistry Department, University of Chicago

Joseph T. Hupp Professor and Chairman of Chemistry Department, Northwestern University

Himanshu Jain Professor of Materials Science, Lehigh University

Frederick D. Lewis Professor of Chemistry Department, Northwestern University

Jonathan S. Lindsey Professor of Chemistry Department, North Carolina State University

Gerald J. Meyer Professor of Chemistry Department, Johns Hopkins University

Martin Newcomb Professor of Chemistry Department, University of Illinois

Russell Schmehl Professor of Chemistry Department, Tulane University

Michael Wasielewski Professor of Chemistry Department, Northwestern University

2. *Estimated Budget*

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Equipment ($5,500K)

	Year 1	Year 2	Year 3	Year 4	Year 5	Total
M&S	$150K	$250K	$170	$70	0	$640K
Capital	$1450K	$1250K	$1400K	$1400K	0	$5500K
Total	$1600K	$1500K	$1570K	$1470K	0	$6140K

Year 1: new laser system & laser hutch expansion & high heatload monochromator + posdoc (M&S)

Year 2: PILATUS-detector & broad-band monochromator + posdoc (M&S)

Year 3: First unit of KETEK-detector (203-element) & micro-focusing instrumentation + posdoc (M&S)

Year 4: Second unit of KETEK-detector (203-element) & plane x-ray mirror