X-ray Capabilities on the Picosecond Timescale at the Advanced Photon Source

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The Advanced Photon Source (APS) operates with a timing structure advantageous for ultrafast dynamics experiments and, as a result, X-ray time-resolved studies on the 100-picosecond timescale have flourished. The standard operating mode, 24-bunch mode, runs 65% of the time and a hybrid singlet mode runs 15% of the time, yielding a total of 80% of beamtime easily accessible for studies of ultrafast dynamics using laser-pump/X-ray probe techniques. This article highlights recent enhanced capabilities for time-resolved studies at the APS.

Enhanced time-resolved X-ray capabilities at Sector 7

In the past few years, the general infrastructure at Sector 7 has been improved to enhance capability, reliability, and user-friendliness. These improvements have fostered ultrafast dynamics research in solid-state physics, material science, chemical science, and next generation of optoelectronics.

A Ti:Sapphire laser (50 fs, 2.5 W, 1 or 5 kHz) for pump-probe experiments has been synchronized to the X-ray pulses with a jitter < 2 ps. Higher-repetition-rate oscillator pulses (30 fs, 0.4 W, 88 MHz) can also be delivered to experimental hutches to use the 324-bunch APS-operation mode. An off-line lab was commissioned with an independent Ti:Sapphire laser system (50 fs, 1 W, 1 kHz). This lab allows sample characterization using optical/THz pump-probe methods before or after laser-pump/X-ray probe experiments.

To go beyond the time resolution limit due to the APS stored electron bunch length (~100 ps), an X-ray streak camera with ~2 ps resolution was installed. It uses a normal-incidence photocathode of 100 to 150 nm CsI on Lexan film and a magnetic lens to focus the entrance slit onto the phosphor. The suite of supporting infrastructure includes: 1) pre-adjusted, interchangeable set-ups for experimental techniques of laser-pump, X-ray-probe liquid-phase absorption spectroscopy and diffraction on kinematic mounts; 2) a high-speed X-ray chopper to match the X-ray repetition rate to that of the laser, thus reducing the X-ray damage of the sample and the photocathode; 3) beryllium lenses with continuously variable focal length. The streak camera was used recently in the study of the photoexcited ligand-substitution reaction in iron pentacarbonyl (Fe(CO)5) dissolved in ethanol. It was found [1] that the substitution occurs largely within a few ps in a cooperative motion of a CO group and an ethanol molecule.

Experiments at Sector 7 have played a major role in a recent ground-breaking experiment led by SLAC scientists demonstrating ultrafast optical control of ferroelectricity in PtTiO3 (PTO). The experiment uses above-band-gap laser photons to generate free carriers in the PTO thin film. The free carriers screen the depolarization field and enhance the internal polarization in the material. The team obtained a very systematic set of time-resolved data at Sector 7 in one run (Figure 1). Armed with these promising data, the team was granted beam time at the LCLS and improved the temporal resolution to sub-ps (Figure 1 inset). The result will appear in *Phys. Rev. Lett.* [2].

High-repetition-rate laser capabilities

A challenge for time-resolved experiments involving synchrotron X-rays and lasers has been the mismatch between laser and X-ray pulse repetition rates. The amplified laser systems required to achieve sufficient excitation of a sample have traditionally operated in the range of 1–5 kHz whereas the repetition rate of the X-ray pulses at the APS in the standard 24 bunch operating mode is 6.52 MHz. Because of this large mismatch, the high flux available at the APS has generally not been fully utilized for time-resolved measurements leading to data of inferior quality compared to that obtained for steady-state measurements.

We have implemented a high-power, high-repetition-rate laser system in the 7ID-D hutch at Sector 7, capable of operating at repetition

rates from 54 kHz up to 6.52 MHz, matching the X-ray repetition rate in the standard operating mode (3). The laser is a commercial master-oscillator power-amplifier system (Time Bandwidth Products, Duetto), customized for synchronization. It operates at two pulse durations, 10 ps and 130 ps, and produces 10 W power at 54 kHz (185 μJ/pulse), and 16 W at 6.52 MHz (2.5 μJ/pulse), at 1064 nm. The second (532 nm), third (355 nm), and fourth (266 nm) harmonics are produced in the 10 ps mode of operation with efficiencies of ~80%, ~40%, and ~20% respectively. As these pulse energies are less than the ~1 mJ energies provided by traditional kHz amplified systems, in order to achieve fluences for efficient excitation of the sample we focus the laser to a small spot (~25 μm FWHM) and use a microprobe geometry (4) to focus the X-rays to ~5 μm FWHM to probe a region of more uniform intensity and efficient optical excitation. The laser beam is actively stabilized on target to 5 μm and synchronized with the X-rays to a precision of ~250 fs.

A key feature is the ability to select the repetition rate that is most suitable for a particular experiment. Lower repetition rates may be advantageous for experiments where longer times are probed, larger laser pulse energy is needed, or sample recovery or replenishing time is a limiting factor. Figure 2 depicts an example of a time-resolved X-ray absorption measurement, carried out on a metalloporphyrin molecule in solution at 135 kHz. The sample flow rate of ~5 m/s allowed a fresh sample volume for each laser pulse. A laser-excited spectrum exhibiting clear changes from the ground-state spectrum was obtained in a single one-hour scan. By comparison, at 1 kHz and with a similar count rate, the same measurement would have taken 147 hours.

High-repetition-rate methods allow collection of higher quality data, measurements on dilute samples, and more X-ray-flux-demanding techniques such as X-ray emission spectroscopy and X-ray diffuse scattering.

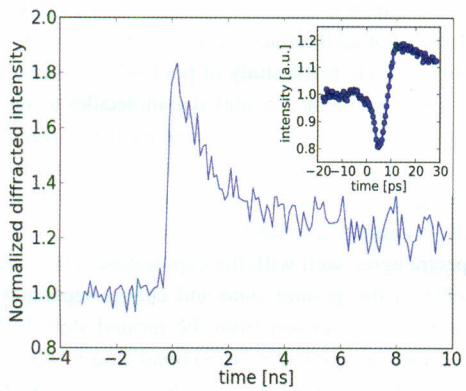

Figure 1: Time-resolved X-ray diffraction from 40-nm PbTiO3 thin films on SrTiO3 following 400-nm excitation, measured on the low angle side of the (004) diffraction peak. Measurements taken at APS Sector 7 with 100 picosecond time resolution. (Inset) Femtosecond measurements taken at LCLS on the low angle side of the (003) diffraction peak.

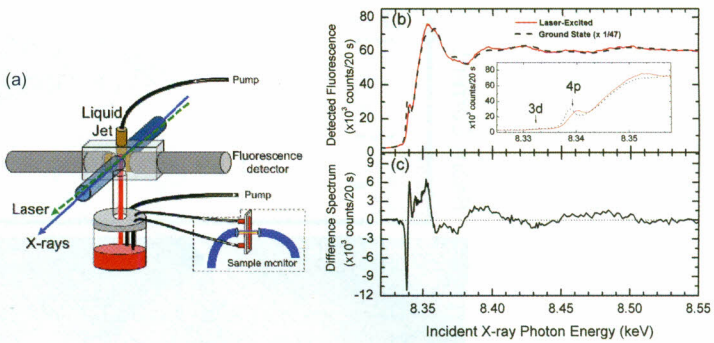

Figure 2: (a) Experimental arrangement for the time-resolved XAS of 2 mM Ni (II)-tetramesitylporphyrin in toluene at a laser repetition rate of 135 kHz. (b) XAS fluorescence at the Ni K edge collected in a single scan lasting ~1 hour. Ni Kα and Kβ fluorescence collected with an APD detector simultaneously for laser-pumped and ground state molecules. X-ray probe 50 ps after 5μJ laser pump. (c) Difference spectrum between the laser-excited and ground-state spectra shown in (b). Figure adapted from [3].

These methods will play an important role in the utilization of the Short Pulse X-ray (SPX) Facility, described in the last section of this article.

Phase contrast imaging of supersonic fuel sprays with pulsed X-rays

Understanding the instability and disintegration of liquid jets has been of theoretical and experimental interest for more than one hundred years because of their wide scientific significance and technological applications. Attempts made with conventional laser optical visualization techniques were not successful in the near-nozzle region where complex multiphase flow is optically dense.

Using high-intensity and high-brilliance synchrotron X-ray beams, the morphology of the sprays can be captured with X-ray phase-contrast imaging with ns temporal resolution [5]. With one of the special X-ray timing modes at the APS, the hybrid-singlet mode (Figure 3A), an X-ray microimage of a supersonic spray was captured when it was injected at 200 MPa. The image, shown in Figure 3B, was taken 1 ms after the start of the injection during a 2-ms injection event when the injection was in a quasi-steady state, using only the X-ray singlet pulse.

More interestingly, the other part of the pulse train can be used to study the dynamics of the sprays. For example, we used two of the eight septuplets (17-ns wide and 51-ns apart) in the timing mode and developed structure tracking velocimetry as illustrated in Figure 3A. The doubly exposed image of the spray (Figure 3C) was used to calculate the speed of the supersonic sprays. By tracking the movement of microscopic liquid features in the double-exposure image, even without using seed particles common in optical tracking techniques, we have been able to extract a quantitative velocity distribution of the sprays. The velocity map is obtained by using local autocorrelation analysis of the double-exposure images of the entire sprays and during the entire injection events. The correlation function shown in Figure 3D has two

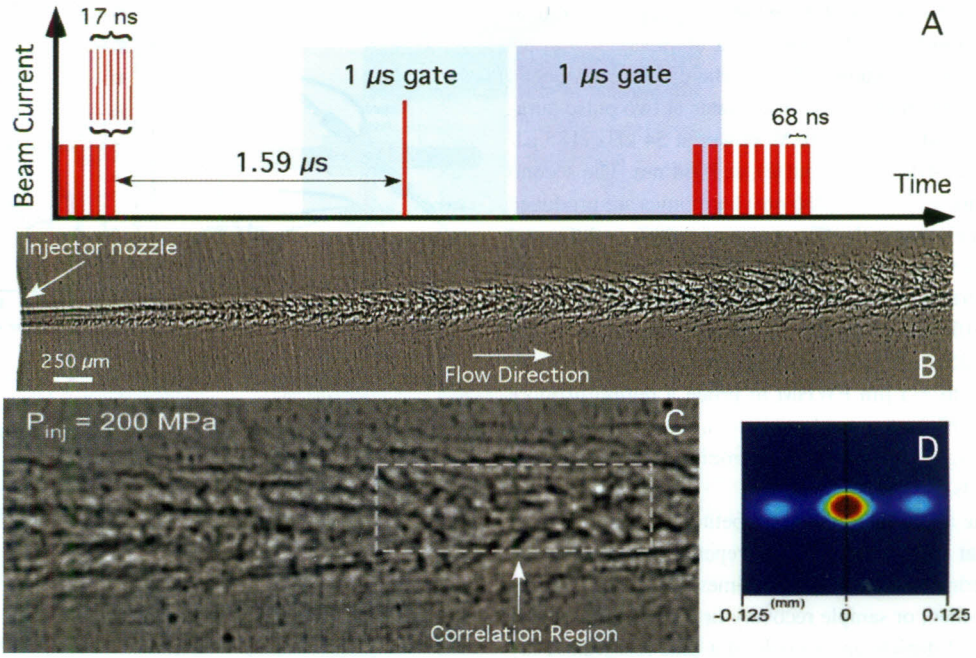

Figure 3: a. Hybrid-singlet bunch pattern at APS; b. Microimage of supersonic fuel spray; c. Doubly exposed image for velocimetry; d. Autocorrelation peak for velocimetry.

distinctive and well-defined correlation peaks essential for the velocity evaluation. The axial velocity of the jet reached over 600 m/s for diesel fuel injected at 200 MPa [6].

The spatial and temporal dependence of the spray velocity will help illustrate the fluid dynamics of multiphase flow, the break-up of the liquid jet, and the interaction between the spray and surrounding gas. The X-ray-based structure velocimetry is a unique and practical application of the pulsed X-ray structure for fluid engineering research at the APS.

Upgrade of pump-probe X-ray capabilities at Sector 11

The time-resolved (TR) program at the11-ID-D beamline focuses on electronic and structural dynamics of processes associated with energy conversion or storage. The beamline was equipped with TR X-ray absorption spectroscopy (XAS) and X-ray scattering (XS) tools, covering length scales from 10^{-12} to 10^{-8} meters and at time scales from 10^{-11} to 10^{-6} seconds. Recent upgrades enhance versatility, reliability, and throughput.

A 10 W, femtosecond Ti:Sapphire laser system (3–10 kHz) with optical parametric amplifier was installed in an enlarged laser hutch. With the existing 1 kHz, ps, Nd:YLF laser system, a broader range of excitation wavelength (200 nm to 2 μm) and repetition rate are now available. A new hybrid pixel array area detector, a Pilatus 2M, was also incorporated. Compared to the charge coupled device (CCD) detectors previously used, the Pilatus detector provides a higher dynamic range and detection efficiency. More importantly, the Pilatus 2M allows electronic gating of single X-ray pulses to select the experimental repetition rate. In combination with the new 10 kHz laser, the data collection efficiency of TR-XS experiment can be improved 20-fold.

The TR experiments at 11-ID-D were originally optimized for liquid solution samples. Capabilities have been extended to accommodate studies of reactions in photovoltaic devices and photocatalytic cycles that occur on surfaces or at an interface under real-working conditions.

One recent example is the study of photo-driven interfacial charge transfer from transition metal complex dye molecules to semiconductor nanoparticles [7]. Using TR-XAS, we have measured transient electronic and geometric structures of a ruthenium dye undergoing interfacial photoinduced charge separation, mimicking DSSCs. Figure 4 compares experimentally measured and theoretically calculated XAS signals; the calculated spectra agree well with the experiment. The structural parameters of RuN3 in the ground state and charge-separated state were extracted. Upon the conversion from the ground state RuN3/TiO_2 to $RuN3^+/TiO_2^-$, the average Ru-N(NCS) bond length shortens by about 0.06 Å, from 2.05 Å to 1.99 Å, whereas the average Ru-N (dcbpy) bond length only changes within the experimental error from 2.04 Å to 2.05 Å. The different responses in the Ru-N bond lengths in dcbpy and NCS ligands are rationalized by the interplay between two important factors governing the metal to ligand bonds, bond order and steric hindrance.

This work demonstrates the great potential of time-resolved X-ray techniques to investigate the fundamental structural dynamics linked to solar electricity and fuel generation.

Single-shot X-ray imaging at Sector 14

BioCARS is located at Sector 14 of the APS and specializes in single-bunch 100-ps resolution pump/probe experiments. An X-ray pulse from a single electron bunch at sector 14 contains nearly $\sim 4 \times 10^{10}$ photons [8] and for time domain measurements from 100 ps to seconds, this flux is competitive with Free Electron Laser (FEL) sources. Until recently, BioCARS has primarily been a time-resolved (TR) macromolecular crystallography beamline. However, not all proteins form crystals and those that do may not survive the structural rearrangement that accompanies photoexcitation with their crystal structure intact. For example, human hemoglobin crystals fracture as the molecule undergoes its allosteric transition. For these systems, TR biomolecular solution scattering is a low-resolution alternative to single-crystal scattering. To meet this need, we have developed a solution scattering capability [9, 10] and are now accepting proposals from this rapidly expanding community.

Although the focus of the beamline is primarily biology, we also accept physical science proposals under the APS General User Program. Several recent physical science projects include the measurement of excited-state structures of small molecules [11], photoinduced phase transitions [12], and a novel X-ray pump/laser probe experiment that utilizes a laser tuned to the GaAs band gap to study the effect of an intense X-ray pump pulse [13]. In this experiment, the Durbin group measured optical transmission through a ~60-mm-thick GaAs sample as a function of pump-probe delay and laser wavelength, which was scanned across the bandgap (Figure 5). The sample transitioned from being strongly absorbing to nearly transparent in less than 100 ps when the laser photon energy was tuned above the band gap. When the laser photon energy was tuned below the bandgap, X-ray induced optical opacity was observed. The X-ray induced transmission increased nearly 50 times compared to the "dark" state.

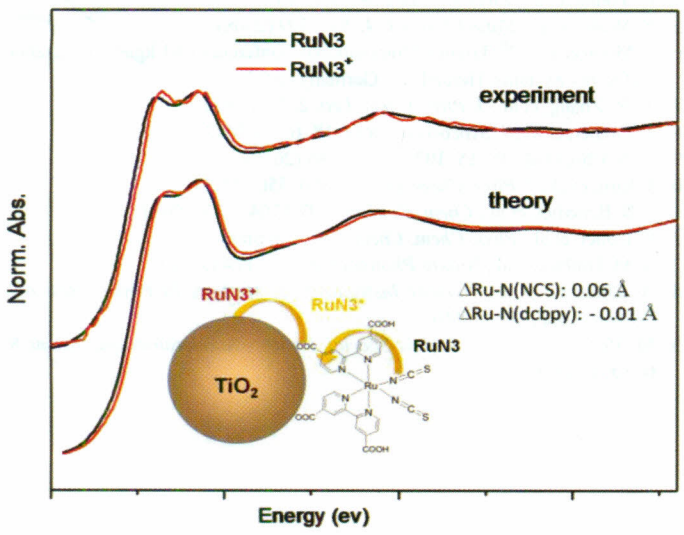

Figure 4: The XAS spectra of the ground (black) and excited (red) state for RuN3 dye-TiO_2 nanoparticle conjugate. Both experiment and calculated XAS spectra are shown. Inset: Schematic of MLCT excitation of RuN3 followed by interfacial electron injection from excited RuN3 to TiO_2 nanoparticle.

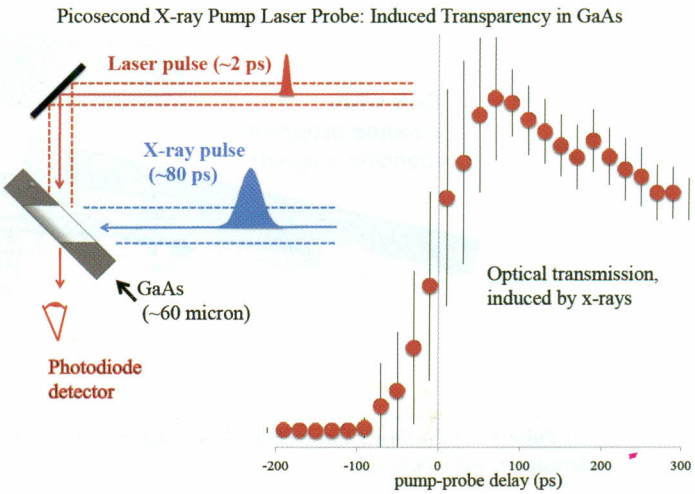

Figure 5: X-ray induced optical transmission of an 860-nm laser pulse through a GaAs sample as function of pump-probe delay. Absorption of the X-ray pump beam strongly perturbs the valence and conduction bands, indicated as the light shading of the GaAs sample. For photon energies just above the band gap, absorption is transiently blocked by the filled conduction band for nearly the full 60 micron thickness of the specimen, turning the sample transparent within the ~100 ps X-ray pulse duration.

Plans for a short pulse X-ray facility at APS

The Short Pulse X-ray facility (SPX) is planned as part of the APS Upgrade. This unique-in-the-world facility will provide tunable polarized X-ray pulses of variable duration (1–100 ps), repetition rate (1 kHz – 6.5 MHz), and bandwidth (10^{-4} or 10^{-2}) over a wide energy range (200 eV - 40 keV) at high average flux ($\sim 10^{15}$/s for the widest bandwidth, longest pulse duration). The variable pulse duration is enabled by incorporation of a pair of rf-deflection cavities in the APS storage ring, as originally suggested by Zholents et al. [14] and later modeled for the APS storage ring by Borland [15]. The first cavity chirps the 100-ps duration electron pulse such that different parts of the pulse acquire different vertical momenta, producing a fan of radiation as the pulse passes an undulator. The second cavity restores the beam to its original phase space. The

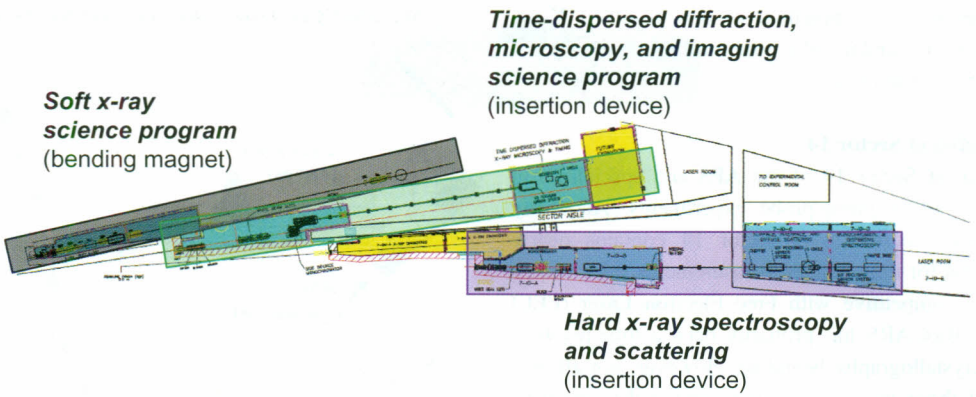

Figure 6: Short Pulse X-ray Facility. Plans include three independently operating beamlines covering the energy range 200 – 40000 eV, with variable pulse duration, polarization, and bandwidth.

variable repetition rate is easily achieved as interpulse time in the standard 24-bunch mode, 153 ns, can be mechanically chopped.

The envisioned facility (Figure 6) will have three independently operating beamlines and co-located ultrafast laser infrastructure. Two beamlines fed by insertion devices will operate in the hard X-ray regime. The hard X-ray spectroscopy and scattering beamline will extract short pulses with a slit and operate with interchangeable Si and multilayer monochromators, variable-speed chopper, and incorporate microfocusing capability. The hard X-ray microscopy and imaging beamline will accept the entire 1-mrad fan of X-ray radiation, which can be used for time-dispersed diffraction or coherent imaging. Planned endstation equipment includes a zoneplate-based microscope to study dynamics in nanoscale materials. The soft X-ray beamline (200–2000 eV) will be based on bending magnet radiation. In the bending magnet, the electron beam produces a vertically elongated source. Imaging a portion of the source will produce a short pulse and controlled/chopped polarization by selecting on- or off-axis components.

Significant progress toward SPX has been made in the past year. In collaboration with Jefferson National Laboratory, superconducting RF defecting cavities that meet SPX performance requirements have been constructed and tested in collaboration with the Argonne Physics Division. RF power amplifiers have been acquired and the design of mode dampers and a timing/synchronization system in collaboration with Lawrence Berkeley National Laboratory has progressed. Current plans call for a first test of the rf deflection cavities in the storage ring in late 2013.

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