

Fundamental Interactions in Chemical, Atomic and Molecular Physics Team

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Executive Summary

A modern scientific challenge has been to observe, understand and control the relationship between structure and function in complex systems on the intrinsic time and length scales associated with electrons, atoms and molecules. Due to technical limitations, experiments seeking structural information on the atomic length scale have emphasized time-independent or slowly varying properties. For the past century x-ray diffraction has been the cornerstone of structural science. Newly emerging time-resolved x-ray methods permit tracking atomic and electronic motions on the ~ 100 ps timescale at synchrotrons and, in the near future, the ~ 100 fs timescale at hard x-ray free-electron lasers. Tracking the response to controlled excitation of a system initially at equilibrium yields deep insight and is a step toward the fundamental understanding required to control function at the molecular level. The Short Pulse X-ray (SPX) Source at the Advanced Photon Source will extend time-resolved capabilities to the important 1-ps timescale while retaining the powerful characteristics of synchrotron radiation, user-controlled continuous tunability of energy, polarization and bandwidth combined with exquisite x-ray energy and pulselength stability over a wide energy range. The 1-ps stroboscopic images can freeze molecular rotations, capture photoexcited molecular transition states, stress/strain wave propagation, magnetic domain wall dynamics, phase transitions, energy relaxation and the coupling between electron, phonon and spin degrees of freedom in condensed matter systems. The very high average flux ($\sim 10^{13}$ /s) of the proposed SPX combined with high repetition rate excitation methods and year-round operation, will enable time-resolved studies with unprecedented precision – yielding joint resolution of picoseconds and picometers for a variety of atomic, molecular, chemical and material systems. These enhanced capabilities provide a compelling reason to locate proposed Energy Frontier Research Centers at Argonne.

Introduction

The first half of the twentieth century witnessed explosive growth in understanding of the atomic and molecular basis for what we observe in the world around us. Because of technical limitations, the overwhelming emphasis in those developments was on time independent or slowly varying properties of physical and biological systems. The latter half of the twentieth century witnessed the development of tools that permitted extension of our understanding to include many aspects of the time dependences of atomic and molecular processes of all kinds. The time resolution available to investigators shrank from milliseconds in the 1950's, to microseconds and nanoseconds (ns) by the end of the 1970's, to picoseconds (ps) and femtoseconds (fs) by 2000, and now to attoseconds (as) in the first decade of the twenty first century. In fact, studies on all of these time scales are needed to understand real world processes. Again because of technical limitations, comparable time resolution was not available across the spectrum of experimental methodologies, in particular not for structural studies by x-ray or electron diffraction. Yet it is arguable that we have learned more about the structure of matter from diffraction measurements than from any other single method, and the creation of technology that permits the time evolution of structure to be studied is likely to yield similar advances in understanding, since it will permit unraveling of the relationships between physical processes and function. It is now possible to generate short x-ray pulses with either fs or ps duration; the former will be generated at the Linac Coherent Light Source (LCLS) as ~ 100 fs duration SASE pulses, and the latter can be generated by the Short Pulse X-ray facility (SPX) proposed for the APS as ~ 1 -ps duration synchrotron pulses. Atomic and molecular processes occur over so wide a range of timescales that both are needed for the proper study of matter and its transformations, and for both the physical and biological sciences. Indeed a very important subset of those processes, take place on the few ps to few ns time scale and are optimally studied with a source that generates ps x-ray pulses with high repetition rate, stable pulse shape, and high average intensity. Moreover, time resolved x-ray spectroscopy in all its variants requires that the x-ray source be tunable. The proposed SPX facility at the APS satisfies both of these requirements, whilst an FEL source, although generating shorter x-ray pulses with very high intensity, has relatively low repetition rate, does not have stable pulse shape, and is not conveniently tunable by the user. Thus, the two sources serve complementary purposes. A comparison between the SPX and the LCLS is shown in Figure 1 and Table 1.

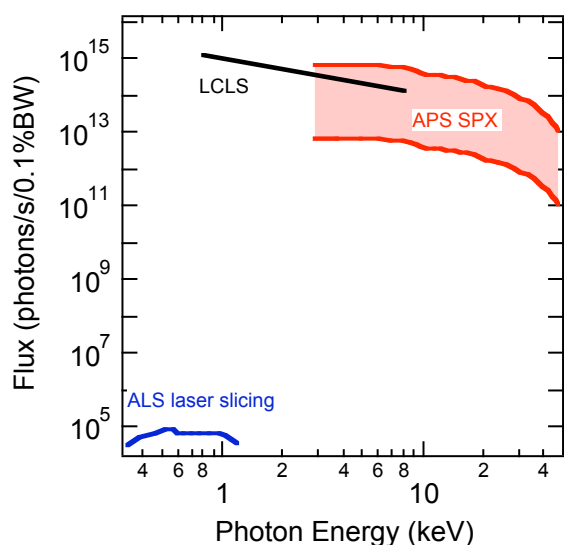


Fig 1. Photon flux for various accelerator-based short pulse x-ray sources. The LCLS has a projected pulse duration of ~ 230 fs, the ALS laser slicing source has a pulse duration of ~ 200 fs and the APS SPX has a projected pulse duration of ~ 1 ps. The LCLS photon energy is discretely specified under accelerator operator control, whereas both synchrotron-based sources (APS SPX and ALS laser slicing) are continuously tunable under local user control thus enabling time-resolved spectroscopy. The high average flux of the APS SPX enables all x-ray techniques currently in use: spectroscopy, scattering, diffraction, microscopy, imaging. The extension of APS SPX to higher x-ray photon energies allows higher spatial resolution. (The APS SPX curves are based upon Undulator A, 3.3 cm period). Two other synchrotron-based laser slicing sources at the Swiss Light Source and BESSY have performance similar to the ALS laser slicing source.

Table 1. Operating parameters for SPX and LCLS

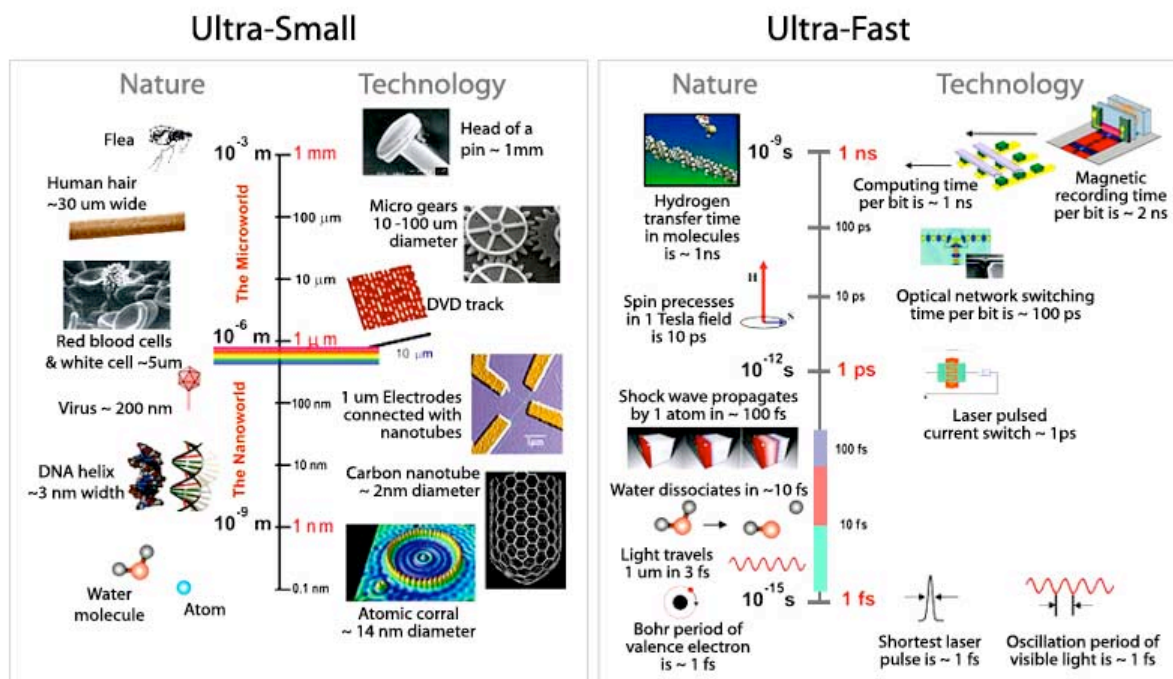
Property	SPX	LCLS
Pulse duration (FWHM)	1 ps^{1,2}	230 fs
Repetition rate	6.5 MHz	120 Hz
Photons/pulse @ 8 keV	10⁶	10¹²
Energy range	500-100000 eV	800 – 8000 eV
Tunability	Local-user control continuous	Accelerator-operator control discrete points
Average flux @ 8 keV	6.5 x 10¹² photons/s	1.2 x 10¹⁴ photons/s
Pulse-to-pulse stability	Excellent	Limited by SASE

¹ SPX can be operated with variable pulse length from 1 ps to 100 ps. The flux values in the table should be increased 100× for 100 ps operation.

² SPX pulse duration is a monotonically decreasing function of the x-ray energy (see Figure 10). At 500 eV photon energy the pulse duration FWHM is ~ 5 ps.

Key Science Drivers

The frontier of the ultrafast and ultrasmall world can be explored with the SPX which provides joint resolution on the picosecond and picometer scale. Both natural and technological phenomena can be explored *in situ* and in real time using hard x-rays with sub-Angstrom wavelength, high penetrating power and short pulse duration that provide ultrafast stroboscopic snapshots as shown below. The understanding of photoabsorption and subsequent energy transfer and dissipation in complex systems is a key scientific goal, one which will lead to a richer understanding of, e.g., the structure-function relationship in molecules relevant for efficient solar energy conversion. Molecular-scale electronics represent the technological future; device timescales fall in the terahertz domain and become accessible by the SPX. A few specific examples of scientific opportunities in fundamental atomic and molecular, chemical and materials physics are given below.



Control of Atomic/Molecular Dynamics

A fundamental and enduring challenge in science is achieving control, at the atomic/molecular level, of dynamical processes, specifically control of electron and atomic motion. Quantum control is enabled by recent advances in laser technology that tailor phase and amplitude of electromagnetic pulses from the visible to infrared. This is the subject of the 2006 National Academy Report "Controlling the Quantum World" and was issued as a Grand Challenge. With this technology, we can attempt to realize the dream that has existed since the inception of the laser. Can one steer molecular processes to a desired outcome? Can one control electron flow in semiconductors? Can one control non-radiative processes in semiconductors to enhance solar conversion efficiency? Combining this "photonic reagent" technology with short pulse x-rays will allow us to view laser-controlled phenomena on ultrafast timescales with atomic-scale resolution.

Strong electromagnetic fields (~ 0.1 - 1 V/Å) are commonly employed in exercising control over molecular and electron motion. The non-resonant interaction of a laser field with a molecule's polarizability can be used to reversibly modify potential energy barriers and thus control the outcome of photochemical reactions, and strong fields have been used to induce phenomena such as transient bond hardening or softening. The use of strong non-resonant laser fields to align and orient molecules has permitted forefront applications, examples of which are tomographic imaging of molecular orbitals, enhanced generation of high harmonic radiation, and serial crystallography of large molecules in the gas phase. X-rays allow one to probe the response of the molecular framework to the laser-aligning fields and through experimental/theoretical collaborations achieve a predictive theoretical understanding of molecular behavior in well-controlled, extreme environments. Strong electromagnetic fields can be used to modify x-ray absorption of atoms in a reversible manner, via electromagnetically induced transparency (EIT), which may lead to an x-ray pulse shaper enabling fs laser pulse shapes to be imprinted onto x-ray pulses. Photonic control methods such as STIRAP (Stimulated Raman Adiabatic Passage) can effect population transfer from the ground state into target states with almost unit efficiency and thus markedly enhance x-ray measurements of excited state structures. In general, the use of x-rays to probe phenomena created by strong-field laser interactions with matter is in its infancy and poised for discovery pulse shaper enabling fs laser pulse shapes to be imprinted onto x-ray pulses. Photonic control methods such as STIRAP (Stimulated Raman Adiabatic Passage) can effect population transfer from the ground state into target states with almost unit efficiency and thus markedly enhance x-ray measurements of excited state structures. In general, the use of x-rays to probe phenomena created by strong-field laser interactions with matter is in its infancy and poised for discovery (see Figure 2).

Laser-dressed potential energy surfaces: The laser field couples the potential energy surfaces of the field-free molecule. In this way, new potential energy minima and, hence, molecular structures emerge. The laser intensity necessary for studying laser-dressed potential energy surfaces is most easily obtained by employing a pulse duration below 100 ps. Most useful is structural information measured at an essentially constant intensity within the temporal and spatial profile of the laser pulse. The 100 ps x-ray pulses currently available at the APS are too long. Using a 10-ps laser pulse with energy of 2 mJ focused to a focal diameter of 40 microns, one can reach a peak intensity of about 10^{12} W/cm². This is about an order of magnitude below the intensity needed to saturate multi-photon ionization, and it is more intense by a factor of ten than the intensity needed to align molecules. In this intermediate regime, one expects to see a pronounced laser-dressing effect on the molecular structure. Using 1 ps x-ray pulses, it will be possible to perform in situ measurements of the resulting molecular structures.

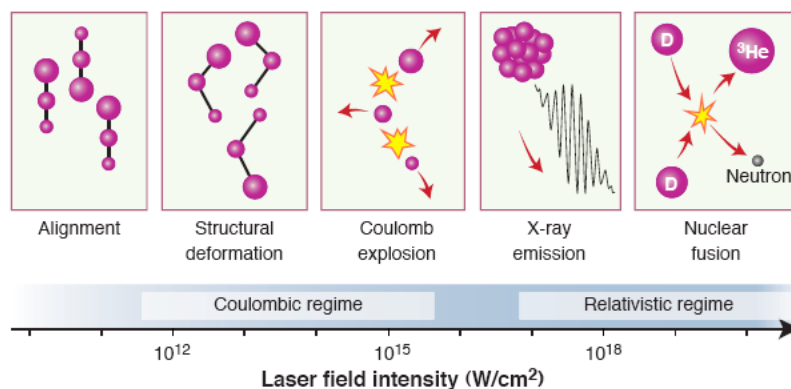


Fig 2. Strong optical laser field interactions with matter.
 [From K. Yamanouchi, *Science* **295**, 1659 (2002).]

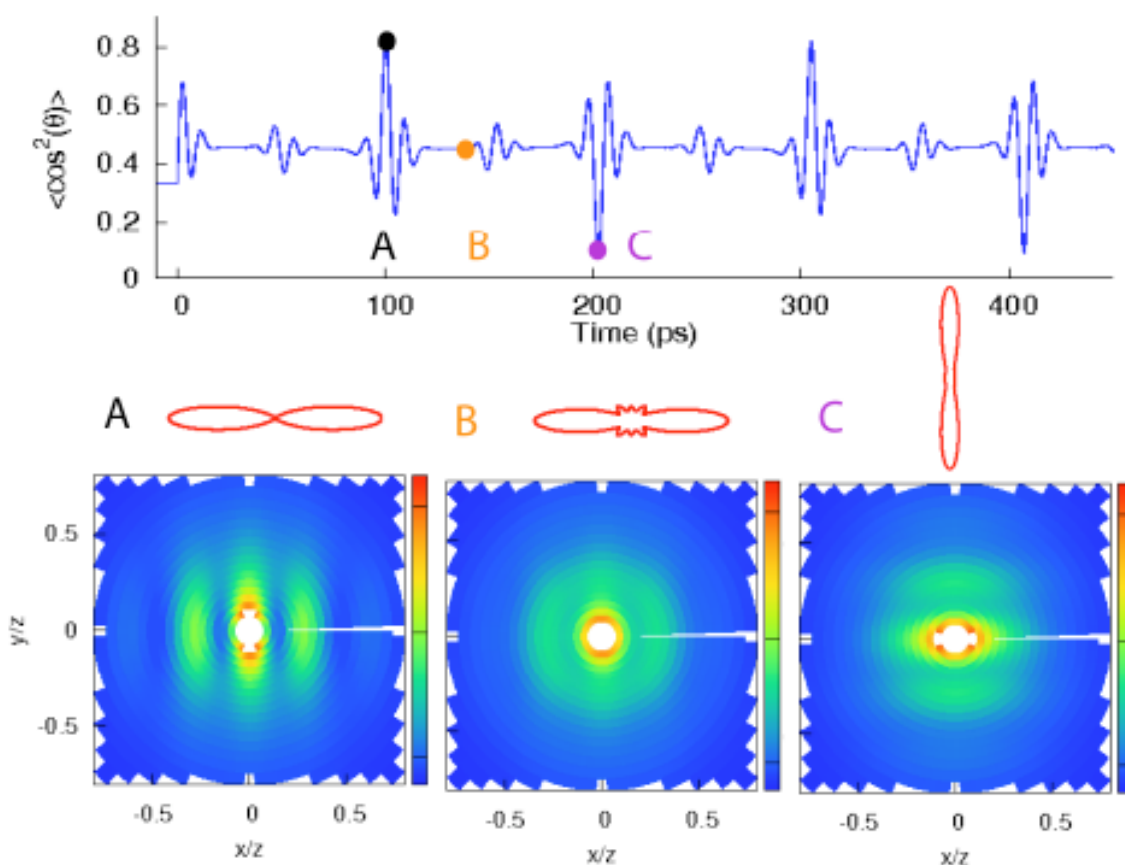


Fig. 3. Ultrafast x-ray diffraction imaging of rotational wave-packet dynamics of bromine molecules (1 K) kicked by a horizontally polarized 50-fs laser pulse, centered at $t=0$, with a peak intensity of 10^{13} W/cm². The top panel shows the time evolution of the ensemble average of the cosine squared of theta, where theta is the angle between the molecule's principal axis and the laser polarization axis. The probability to observe a given theta is shown in the middle panel as a polar plot. At time delay A, the molecules are highly aligned along the laser polarization axis. At time B, there is partial alignment, and at time C, the molecules are anti-aligned with respect to the laser polarization axis. The x-ray diffraction patterns (20-keV photon energy, 1-ps pulse duration) reflect the molecular alignment at the three different time delays A, B, and C.

Field-free molecular alignment: If the laser pulse duration is short in comparison to the characteristic rotational time scale of the molecule, then the laser-molecule interaction launches a rotational wave packet that undergoes periodic alignment and de-alignment, as illustrated above, where calculations are shown for bromine molecules at 1 K exposed to a horizontally polarized 50-fs laser pulse, centered at $t = 0$, with a peak intensity of 10^{13} W/cm². Theta is the angle between the molecule's principal axis and the laser polarization axis. The expectation value of the cosine squared of theta is thus a measure of the degree of alignment of the molecular ensemble. As may be seen in Figure 3, the molecules are highly aligned at the time delay A. This is about 100 ps after the laser pulse is off, when the molecules are no longer perturbed by the laser field. In order to exploit this phenomenon of field-free alignment, one has to be able to probe the molecules in the extremely short time interval during which the alignment persists. This is not possible using 100 ps x-ray pulses. However, 1 ps x-ray pulses are ideal for this purpose, as is shown in the three bottom panels of the figure. X-ray diffraction patterns, calculated assuming a 1-ps, 20-keV x-ray pulse probing the molecular ensemble at three different time delays after the laser pulse, clearly reflect the dynamics of the rotational wave packet. An important potential application of such impulsively aligned molecules is the measurement of

x-ray-induced electron angular distributions with respect to the molecular frame. Photoelectron and Auger electron emission patterns normally detected are rotationally averaged, resulting in a loss of information about the electronic structure of the target molecule. Recent applications of molecular-frame electron angular distributions include the identification of the excitation mechanism of the satellite accompanying the C 1s photo-line of the CO₂ molecule and ultrafast probing of core hole localization in N₂. So far, the measurement of molecular-frame electron angular distributions requires the complete fragmentation of the target molecule. In principle, each fragment must be an atomic ion. These ions are then collected on a position-sensitive detector and, assuming that fragmentation is fast in comparison to a rotational period of the molecule (axial recoil approximation), it is possible to reconstruct the spatial alignment of a given molecule from the fragmentation pattern. Evidently, for this technique to work, not only must ultrafast and complete atomic ionization and fragmentation take place upon x-ray absorption, which is not generally the case in polyatomic molecules, but the measurement must be done effectively with only one molecule at a time. The beauty of laser-induced alignment is that (a) it is not limited by the axial recoil approximation, (b) it may be applied to polyatomic molecules, and (c) it may be applied to a large number of target molecules, thus enabling more rapid data accumulation. A recent measurement of photoelectrons generated via strong-field ionization of impulsively aligned molecules found the first experimental evidence of the dependence of the electron angular distributions on the relative orientation between the molecule and the polarization of the ionizing laser field.

Molecular alignment in the liquid phase: One frontier area is the extension of studies of isolated molecule rotational alignment to the liquid phase, to investigate whether strong-field alignment survives in dense environments and the degree to which decay and decoherence can be photonically controlled. Although the theoretical work is just beginning one can expect laser alignment to become a versatile tool in chemistry once the effects of dissipative media are properly understood. Obvious applications of 3D molecular alignment in liquids range from control of chemical reactions to means of controlled assembly at the molecular level. The unique coherence properties of intense laser alignment should allow the disentanglement of decoherence from population relaxation. Already, laser alignment and trapping of nanoscale objects in solution has been achieved.

Controlling and Probing Vibrational and Electronic Motion: Although the rotational motion and alignment of molecules can be controlled and probed on the ps timescale, the vibrational and electronic motions of molecules typically take place much faster. Although direct time-domain studies of such motions are beyond the reach of even 1 ps x-ray pulses, these motions can still be studied by using alternative approaches. For example, stimulated Raman scattering and stimulated Raman adiabatic passage (STIRAP) techniques with shaped fs laser pulses can be used to transfer a large fraction of the sample to selected, highly excited vibrational levels. Such levels often sample very different portions of the potential energy surface than the ground vibrational state, and probing these selectively prepared molecules by using x-rays could provide direct information on how molecular geometry and structure change for different vibrational modes of the molecule. Even if the experiments were not time-resolved, this approach would be interesting if existing control techniques were used to drive molecules along the reaction coordinate for decomposition or isomerization.

Similarly, while electronic rearrangement takes place on a timescale much shorter than 1ps, excited state lifetimes are typically much longer than this. Thus, short-pulse lasers could be used to prepare selected electronic states and monitor the structural and spectroscopic changes that occur. While some work along these lines is being pursued in the condensed phase (see, for example, the work of Chen and Moffat), essentially no work has been done in the gas phase, and the untapped potential for this approach is enormous. The situation becomes even more interesting when the excited state undergoes a radiationless transition by internal conversion or intersystem crossing. Note that, in many such cases, 1ps resolution may not be sufficient to

resolve the radiationless transition rate; however, x-ray probes of the structure of the triplet states or high vibrational levels of the ground state would be of considerable interest. In such a case, it should be possible to pump a significant fraction -- i.e., more than half -- of the molecules into the triplet state. X-rays have the potential to provide unique structural information on high vibrational levels of both low-lying triplet states and the electronic ground states. The acetylene molecule provides an interesting example. Excitation in the near ultraviolet pumps the molecule from the linear ground electronic state to the trans-bent A^{\sim} state, thus inducing large structural changes in the molecule. Perhaps even more interesting, it is thought that some levels of the A^{\sim} state couple with highly excited cis-bent levels, and that this coupling drives the isomerization from the acetylene structure to the vinylidene structure. X-ray probes of levels exhibiting such large-amplitude motion could provide tremendous insight into the isomerization process.

Chemical Reaction Dynamics: Structure of the Transition State

A chemical reaction almost always generates a change in the structures of the molecules involved. Although we know a great deal about the initial structures of reactants, and the final structures of products there is, excepting a few gas phase electron diffraction results, no direct experimental information about the atomic pathways that are involved in these structural changes. Some reactions, for example direct fragmentation following absorption of a photon, occur on the fs time scale. Other reactions, such as photo-fragmentation via a metastable state, photo-isomerization and ring closure, can be many orders of magnitude slower, especially when large-scale atomic motion is involved in the formation of the product. And the time scale of a reaction is usually different in the gas phase and in solution. The availability of high repetition rate, stable pulse shape, intense, ps duration hard x-ray pulses will permit study of the evolution of molecular geometry in a substantial class of chemical reactions, including determination of the transition state between reactants and products. Only a short pulse x-ray source can be used to study structural changes accompanying chemical reaction in both the vapor and solution phases. It is clear that determination of the structures of transition states in chemical reactions will transform our understanding of molecular dynamics by providing information about the displacement pathways of all of the atoms involved, thereby replacing the simplistic descriptions now employed.

Studies of the evolution of structure along the pathway from reactant to product are restricted, for technical reasons, to either unimolecular reactions or reactions initiated in a preformed bimolecular complex. Despite this restriction, there are so many important chemical reactions that choice of systems for study will be targets of opportunity. Isomerization reactions, both in the gas phase and in solution, are prime targets for study, as they involve large atomic displacements and are involved in the first stages of photosynthesis and of vision. Despite decades of study using spectroscopic probes the mechanism of isomerization about a carbon-carbon double bond, and/or multiple double bonds, remains uncertain. There is new theoretical evidence that such reactions are determined by so-called conical intersections of potential energy surfaces, which occur in polyatomic molecules with multiple electronic states. Calculations of the change of electronic structure as a molecule undergoes the geometric changes that characterize the isomerization suggest that x-ray structural studies can provide crucial information about the reaction mechanism and dynamics.

That time resolved x-ray diffraction measurements can be carried out on a reacting molecule in solution, on the 100 ps time scale, has been demonstrated at ESRF (see Figure 4). The proposed SPX source will generate shorter x-ray pulses with greater flux than was available for those experiments. Indeed, there should be ample intensity available for studies of the unimolecular reactions of isolated molecules in the vapor phase since the density need only be low enough that the time between collisions is much greater than the pulse length and much greater than the characteristic reaction time. The x-ray diffraction experiments can be carried out on freely rotating molecules, in which case the structure is determined by fitting to model structures, as is

conventional in electron diffraction experiments. Alternatively (see previous Section), the x-ray diffraction experiments can be carried out on aligned molecules, to greatly increase the information content of the diffraction pattern and reduce uncertainty in the structure determination. The effect of inert gas (solvent) collisions on the evolution of the structure can be determined from measurements in, say, a He environment. The determination of the time dependence of the molecular structure in solution is complex because of the need to account for scattering from the solvent and the influence of the evolving reactant on the solvent, but also offers the opportunity to learn how solvent structure influences the reactant molecule structure and its evolution. Methods for separating the contributions to the scattering from reactant molecule and solvent have been developed. We expect that determination of, say, the transition state structure in the isomerization of gaseous stilbene and related molecules in a He atmosphere, and then in solution, will test our understanding and challenge our conceptual description of these and other isomerization reactions (e.g. the ring expansion of toluene to heptatriene, and of reactions that occur in the refining of oil).

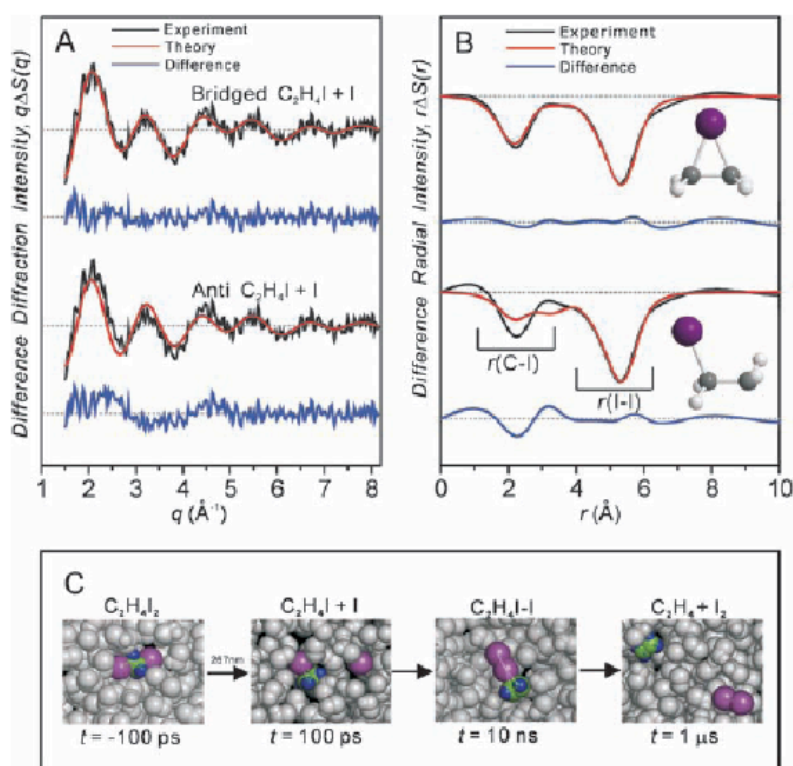


Fig 4. Structure determination of the C₂H₄I radical in methanol at $t=100$ ps. The contribution from C₂H₄I alone is isolated by subtracting other contributions from the raw data, allowing comparison with the gas-phase model of the anti and bridged structures. (A) Theoretical (red) and experimental (black) difference intensities for two possible reaction channels. The difference between the theory and experiment are also shown in blue. The upper curves are for the formation of the bridged C₂H₄I radical and the lower ones are for the classical anti structure. (B) Corresponding radial density functions for the two possible reaction channels, and molecular structure (iodine, purple, carbon, gray). (C) A schematic reaction mechanism based on time-resolved x-ray diffraction in solution. From Ihee et al., *Science* **309**, 1223 (2005).

There are many photochemical reactions of metal complexes that are relevant to solar energy conversion. For example, multiple metal center complexes are involved photo-induced water splitting reactions, where single photon events are coupled with multiple electron redox reactions. It is challenging and ultimately important to visualize how and how fast the reaction

coordinates correlated with electronic configuration changes induced by photons lead to the transformation from the Franck-Condon (F-C) state to products. Such information will help us to design molecules and learn how to control structural factors correlating with electronic transitions and to direct chemical reactions to desirable directions via photonic excitation. The concepts developed in these experiments can be applied to capturing the transition state during photochemical reactions, such as substrate binding to metal complex photo-catalysts.

F-C states have not been directly observed in condensed phase photochemical reactions, where the nuclear geometry relaxation, both internal vibrational relaxation and solvent cooling, are on a time scale of <1-10 ps. By coupling a laser pump pulse with a ps x-ray pulse it becomes possible to directly observe electronic and nuclear structural changes simultaneously with x-ray absorption spectroscopy and solution x-ray diffraction. For example, the S_1 excited state of nickel porphyrin undergoes an electronic π - π^* transition, followed by internal energy transfer to generate a transient d-d excited state that relaxes to an expanded porphyrin macrocycle geometry. Although the resulting electronic configuration and nuclear geometry have been observed with 100 ps x-ray pulses, the correlation of the electronic transition with the ensuing nuclear geometry change could not be resolved. With 1 ps x-ray pulses, the timing for generating the excited state $3d$ configuration and the porphyrin expansion can be investigated.

We believe that the first determinations of transition state structures in isomerization reactions will be paradigm changers. Continuation of such measurements in a thematic program to determine transition state structures in many reactions will yield a data-base that can be used to suggest new concepts and to test old concepts vis a vis the relationships between structure and reaction mechanism; the results of such data mining are likely to greatly advance our understanding of chemical reaction pathways. The need for information concerning transient structures in chemical reaction pathways is so great, and the diversity of chemical reactions is so great, that we anticipate widespread demand from the community for time for such studies.

Fundamental responses of materials to applied fields

A unifying theme in condensed matter and materials science is the development of an understanding of the response of materials to applied fields including mechanical stresses, and magnetic, and electric fields. Materials respond to applied fields by developing internal strains, electrical or magnetic polarizations, or with dramatic phase changes. The dynamics of the relationships among structure, magnetism, polarization, and applied fields in solids extends from very long times to times as short as 1 ps or less.

The relationships between applied fields and responses are the key to the phenomena underpinning nanomagnetism, nonlinear optical materials, ferroelectric devices, and metamaterials. The responses to applied fields are also the key to understanding correlated electron systems such as sliding charge density wave conductors and colossal magnetoresistive oxides. The fundamental problem is that although quantitative tools for probing the magnetism and structure of the ground states of materials are highly advanced, there are few probes capable of looking at structures driven into transient states far from equilibrium. The SPX facility can address these questions by providing the opportunity to perform time-resolved x-ray diffraction and scattering studies with samples driven into short-lived transient states. Many materials exhibit a slowing down (and concomitant growth in the spatial scale) of phenomena near phase transitions. The soft-mode dynamics of ferroelectrics are an excellent example of this.

The magnetic multiferroic oxides provide an important example of the opportunities involved in manipulating these responses, as shown in a diagram developed by Spaldin and Fiebig (see

Figure 5). The applied magnetic and electric fields \mathbf{H} and \mathbf{E} and the mechanical stress σ lead to responses in magnetization \mathbf{M} , electric polarization \mathbf{P} , and strain ϵ . The coupling among these degrees of freedom is only beginning to be understood and essentially nothing is known about dynamics of the relationships between the magnetism and applied fields in these materials.

These phenomena have a fundamental structural and magnetic basis that can be probed directly and quantitatively using x-ray scattering and spectroscopy. X-rays are unique in this sense because they are largely non-perturbative, penetrate complex sample environments, and can provide information across a wide range of time- and length-scales. The fundamental scales of the responses of materials vary, but the large-scale responses have times corresponding to tens to hundreds of picoseconds. Phenomena associated with domain dynamics and the conventional linear constitutive relations such as elasticity or polarizability all have characteristic time and length scales.

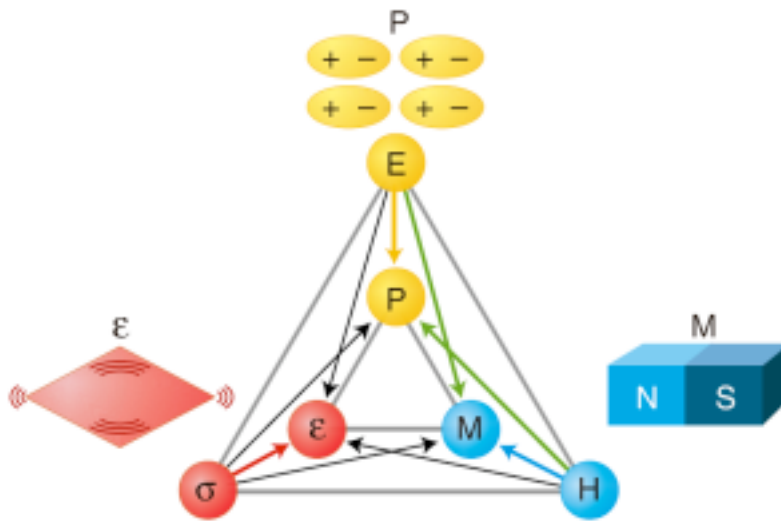


Fig 5. The response of materials to applied fields.
 [From Spalding and Fiebig, *Science* **309**, 391 (2005).]

The time resolution of structural measurements at the proposed SPX facility will be comparable to the fundamental timescales associated with these phenomena. Electronic and magnetic phenomena can be driven at the high repetition rates available at the SPX and benefit from the inherent flexibility of the high-repetition rate approach. X-rays couple to these phenomena with via a wide range of quantitative scattering mechanisms including resonant- and non-resonant magnetic scattering, diffuse scattering, and coherent scattering. The 100 ps resolution available presently is too long in duration to match the fundamental times associated with these responses. The following presents several areas in which the few-ps time resolution of the proposed SPX would be essential.

Dynamics in nanomagnetism. Nanomagnetism is the field that arises from the intersection of the physics of magnetic materials and the capability to fabricate and understand nanostructures. The long-length scale dynamics of magnetism involves the control of magnetic domains and domain walls and has resulted in devices such as giant magnetoresistive sensors, and device concepts such as magnetic racetrack memories. In addition, nanomagnetic structures provide the means for discovering new phenomena in magnetism, such as spin-transfer torques.

Magnetic domains are linked to a small magnetostrictive distortion of the magnetic solid, so

domain wall velocities are typically limited to be approximately the same as the speed of sound, kilometers per second, or nanometers per picosecond. A picosecond source of x-rays has fundamentally the appropriate time resolution for the study of magnetic domain dynamics and phenomena linked to them.

The magnetism of thin film structures can be manipulated using spin-polarized currents of electrons. The coupling of the spins carried by the spin-polarized current to the remnant magnetism of the layers results in magnetic forces that can cause the magnetization of ferromagnetic layers to precess, nucleate magnetic vortices, and ultimately switch the magnetization. In addition to the potential to switch the stored magnetization in devices electrically, the resonance itself is interesting because resonance frequencies can exceed 10 GHz, even in relatively large devices and because these frequencies can be electrically tuned. These devices are beginning to incorporate more complex materials, including the magnetic multiferroics. These materials can be reconfigured using applied fields and require structural and magnetic characterization tools with sufficient time resolution.

Metamaterials and materials at THz frequencies. Lithographic structures with sizes smaller than or comparable to optical wavelengths can have surprising and useful optical properties, including effectively negative indices of refraction. These structures are rapidly evolving to incorporate materials with properties that can be manipulated with external fields. Laser-pumped optical switches with single-cycle THz pulses can drive these materials. The potential to probe the structure of the metamaterials during their operation could be extremely valuable. The pulse duration of the SPX facility will be an excellent match for the timescale of the optical pulses in non-linear metamaterials systems, and for the THz radiation and THz optical properties of materials.

High frequency MEMS and NEMS. The range of frequencies at which nanomechanical systems can operate is already above 1 GHz and will reach higher frequencies. At present, these systems are studied using lumped parameters such as the resonance frequency and understood using simulations. The potential to examine the structural distortion locally in operating devices will dramatically improve the potential to design these structures.

Ferroelectrics and multiferroics. Ferroelectric materials have a remnant electrical polarization that can be manipulated with applied electric fields. As in magnetic materials, the response of ferroelectrics to applied fields includes domain wall motion, which typically involves times of many nanoseconds. Shorter times effectively freeze the domain walls, allowing the intrinsic local response of materials to be studied at high fields, large strains, and highly unstable polarization-electric fields states. It has recently become possible to begin to develop and test predictions for the response of ferroelectric oxides to very high electric fields. The physics of ferroelectrics in this regime is fascinating because it is far outside the range of validity of conventional descriptions based on free energy models.

Frontier Research in Photosynthesis and Molecular Solar Fuels Catalysis

Critical scientific challenges in solar energy and solar fuels generation as outlined in the DOE workshop on *Basic Research Needs for Solar Energy Utilization* derive from the need to couple ultrafast, single-electron, excited-state photochemistry in molecular photosensitizers to multiple-electron, proton-coupled, chemical fuels catalyses on transition metal complexes in a manner that avoids excited-state free energy loss, quenching, and chemical back reactions, and ultimately to accomplish all of this using renewable, naturally abundant materials. Biology has achieved the ideal of efficient solar initiated water-splitting coupled to reductive chemical energy storage using abundant, renewable, self-assembling “soft” materials, and emergent work is suggesting

synthetic pathways for achieving comparable solar fuels catalysis in organometallic and inorganic systems. However, progress in the development of solar energy converting materials is currently restricted by the lack of information on time-dependent photoexcited-state electronic and coordinate structure changes and resolution of how these structural dynamics are linked to energy-conserving chemistry. The development of Short Pulse X-ray (SPX) capabilities at APS would create opportunities for groundbreaking discovery of both electronic and atomic coordinate structural dynamics that underlie solar energy conversion across the full range of biological, organometallic, and inorganic photocatalytic materials, and would provide a strategy to accelerate solar fuels catalyst development by allowing information on structure-dependent excited-state energy conversion processes to be included in synthetic design. Particularly significant would be the development of SPX facilities that with capabilities for photo-excited structure mapping using short pulsed x-rays across a broad x-ray energy range, including i) tunable hard x-ray energies for combined high-resolution spectroscopy and anomalous scattering experiments, ii) high-energy pulsed x-rays for high-resolution time-resolved pair distribution function (PDF) analyses, and iii) low-energy x-rays for time-resolved electronic structure analyses of the complete 1st row transition metals and sulfur ligands.

The critical role that SPX facilities would contribute to frontier research in solar energy can be illustrated by considering the photoexcited-state reaction cycles for organometallic solar fuels catalysts. Significant recent synthetic work is directed at the challenge of synthesizing first-of-a-kind supramolecular ensembles composed of photosensitizers connected by electron conducting linkers to transition metal catalysts, with the goal of producing supramolecular ensembles that couple ultrafast, single-electron, excited-states to multiple-electron, water-splitting and hydrogen-evolving reactions. Comparable approaches are also being investigated using biological and inorganic light-harvesting materials. One example is illustrated in Figure 6, showing a molecular device composed of a cobaloxime-based hydrogen-evolving catalyst coupled to a ruthenium tris(diimine) photosensitizer moiety. This construct is the most efficient supramolecular photocatalytic system produced to date, although it operates with only about a 5% efficiency. Sources for the low yield have not been resolved, but even the “simple” two electron reduction of 2H^+ to produce H_2 requires the repetitive passage through two complex photochemical cycles that include the following dynamics. 1) Initial photo-excitation and subsequent ultrafast electronic structure relaxation involving vibronic (Franck Condon) transitions and, depending upon the photosensitizer, electronic reorganization such as intramolecule charge transfer (eg., metal-to-ligand charge-transfer, MLCT), intersystem crossing (S-T transitions), Jahn-Teller distortions, and photo-isomerization processes. These ultrafast electronic structure and coordinate structure dynamics are crucial for establishing the precursor

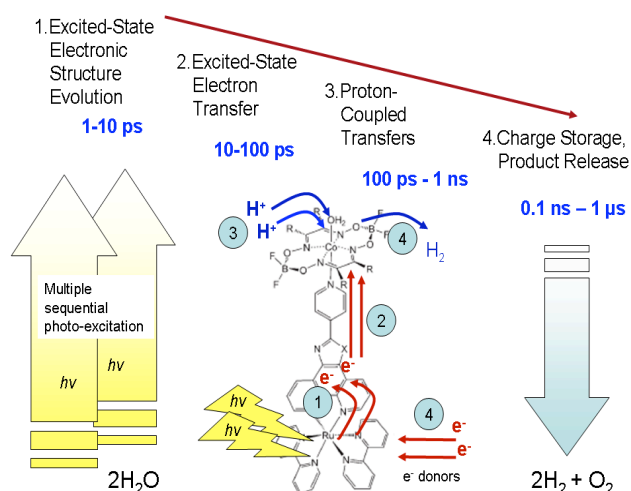


Fig 6. Excited-state reaction cycle for a photosensitizer linked to a hydrogen-evolving catalyst.

state energies and reactivities for subsequent chemistry. 2) Excited-state electron transfer from the excited-state photosensitizer to catalyst that theory has shown to be coupled to rate-determining inner sphere and outer sphere atomic reorganization, but have yet to be directly observed. 3) Proton-coupled transfers that are similarly coupled to rate-controlling inner and outer sphere reorganization events. 4) Bond changes and product release. Breakthroughs in solar catalyst design would be realized by resolving excited-state electronic structures throughout the photon-initiated reaction cycle, and correlating these structural dynamics to chemistry in organometallic, inorganic, and biological solar catalysis. Key questions include resolving possible electronic interactions between the

photosensitizer and transition metal catalysts in light-excited states, roles for microenvironments and second sphere ligand environments for tuning excited-state chemistry, and atomic-scale resolution of reaction mechanisms.

Milestone experiments have demonstrated the unique capabilities offered by time-resolved x-ray measurements. Excited-state electronic configuration changes (process 1 above) have not been directly observed in condensed phase photochemical reactions, where the nuclear geometry relaxation, both internal vibrational relaxation and solvent cooling, are on a time scale of <1-10 ps. By coupling a laser pump pulse with a ps x-ray pulse it becomes possible to directly observe electronic and nuclear structural changes simultaneously with x-ray absorption spectroscopy and solution x-ray diffraction. For example, the S_1 excited state of nickel porphyrin undergoes an electronic π - π^* transition, followed by internal energy transfer to generate a transient d-d excited state that relaxes to an expanded porphyrin macrocycle geometry. Although the resulting electronic configuration and nuclear geometry have been observed with 100 ps x-ray pulses, the correlation of the electronic transition with the ensuing nuclear geometry change could not be resolved. With 1 ps x-ray pulses, the timing for investigating excited-state electronic and configuration can be significantly shortened to allow them to directly address reorganization processes most critically coupled to energy converting events.

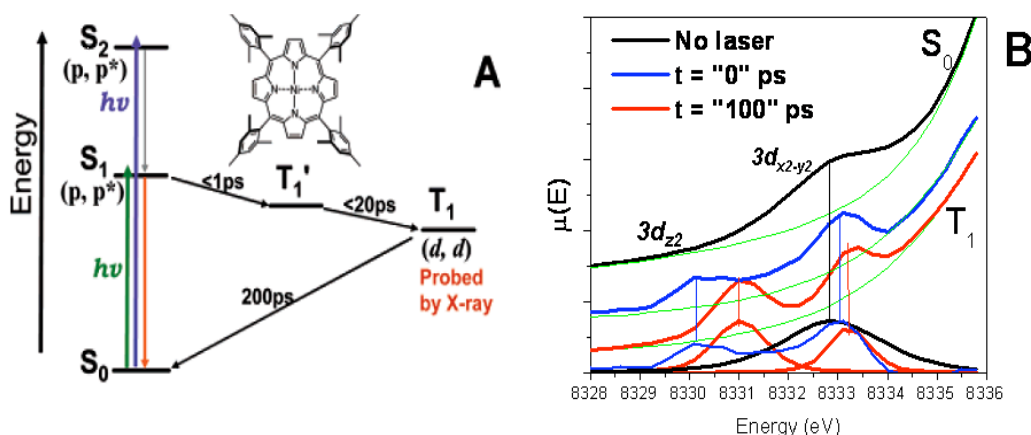


Fig. 7. Time-dependent electronic configuration changes for a photo-excited Ni-porphyrin measured by pump-probe time-resolved x-ray absorption (TR-XAS). The ground S_0 state is characterized by a $1s$ - $3d_{x^2-y^2}$ transition with a 2.2eV band width (290K) and 1.8 eV at 15K, showing evidence of structural diversity. The excited T_1 state: the singly occupied $3d_{z^2}$ and $3d_{x^2-y^2}$ MO in the XAS final state with a d-d splitting of 2.2 (± 0.2) eV and widths of the peaks are $<1\text{eV}$. The MO energies shift with probe delay time corresponding to an E-shift of $d_{x^2-y^2}$ MO by 0.3 eV from the GS. From Chen et al., *J. Am. Chem. Soc* 129, 9616 (2007).

Similarly, time-resolved solution x-ray scattering (TR-SXS) provide the new opportunity to directly observe nuclear geometry changes in the excited state. For example, Figure 8 shows single 100 ps x-ray pulse scattering pattern changes measured with variable time delays following a laser pulse for a Cu(I)[dimethylphenanthroline] complex (CuDMP). Upon photon absorption the CuDMP complex undergoes instantaneous MLCT followed by an excited state Jahn-Teller distortion and coordination change that is complete within 20 ps. The reconfigured MLCT state decays back to ground state in 350 ps in water. The "0 ps" TR-SXS transient measured with 100 ps pulses, shows a fully developed set of changes that includes small angle changes indicative of the coordination state change, and changes at higher angle that reflect outer sphere reorganization that includes change due to both the ligand structure and solvation layer. The outer sphere changes are seen to continue to evolve during the MLCT state lifetime. The current TR-SXS measurements are limited by the 100 ps pulse duration that can not resolve the early conformational changes in the excited state, and low experimental repetition frequency (1 kHz) that prevents the acquisition of high-signal-to-noise data.

The development of a multiple-energy SPX facility at APS would provide dramatically new opportunities for breakthrough discovery in solar energy research. Critical new capabilities would include the following. The use of tunable hard x-ray energies for combined high-resolution spectroscopy and anomalous scattering measurements that would enable precise

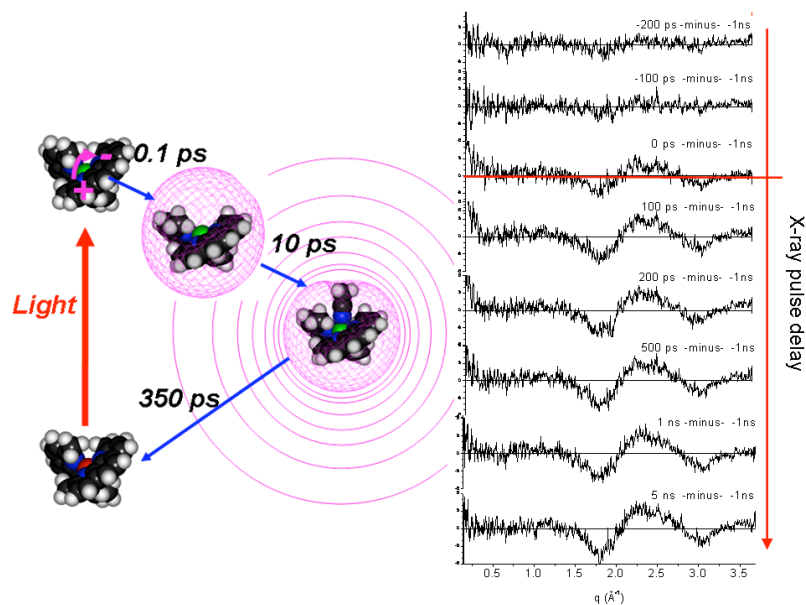


Fig. 8. Reaction scheme (left) and time-resolved difference x-ray scattering patterns measured using single 100 ps 12 keV x-ray pulses set at variable time-delays following laser excitation.

resolution of ultrafast electronic structure changes and inner and outer sphere nuclear geometry changes with 1 ps time resolution. The development of high-energy SPX capabilities that would create the entirely new opportunity for high-resolution PDF excited structure mapping, allowing the global scattering measurements to achieve a spatial resolution comparable to that obtained by metal-centered XAFS measurements. Finally, the development of low-energy SPX capabilities would enable electronic and metal-centered coordinate structure to be measured for the entire 1st row transition metals and sulfur ligand that are high-priority synthetic targets for solar catalyst development.

Significance of APS

The APS is poised to become the leading x-ray facility in the world for time-resolved studies at the 1-ps and longer timescale. There are presently only two hard x-ray synchrotron facilities in the world that can incorporate the Zholents rf-deflection cavity scheme to produce short pulse x-rays, the Advanced Photon Source and Spring-8. (The PETRA-III synchrotron, due to begin operation in 2009, may be able to incorporate this scheme. The ESRF is a 6 GeV machine, with smaller circumference and has no available real estate for superconducting rf cavities.)

Researchers at the Advanced Photon Source have performed extensive engineering studies for implementation of the superconducting rf-deflection cavities, and at this point in time are ahead of the Spring-8 group in planning. The relatively long 150-ns period between x-ray pulses in the standard 24-bunch operating mode facilitates recovery of samples and the gating of detectors for time-resolved studies.

Importantly, the APS has a strong community of world-leading researchers in time-resolved x-ray science spanning many fields: atomic and molecular physics, photochemistry, materials science, condensed matter and biology. To serve the biology community, a Laue diffraction beamline has recently been commissioned (BIO-CARS) that produces 100-ps pulses with 10^{10} x-ray photons/pulse at a 1 kHz repetition rate within a 3% bandwidth. This is suitable for time-resolved diffraction of crystalline materials with long recovery times at an incident energy ~ 12 keV. The SPX serves a complementary purpose by enabling studies of both non-crystalline and crystalline materials at higher temporal and spatial resolution, higher repetition rate and with widely variable photon energy, thus allowing the use of all x-ray spectroscopic, scattering, diffraction and imaging methods.

Scientific Community

We argue that the scientific community will benefit from the SPX at ANL in three complementary ways:

- (1) The opportunity to carry out a small set of "must do" experiments that address what are widely accepted premium problems in specific subject areas, the results of which are likely transformational. The experiments suggested are matched to the unique capabilities of the proposed SPX facility.
- (2) At the other extreme, the provision of a facility that can be used to study many systems and solve many problems, providing information not now obtainable by other means. The notion is that adding the capability for picosecond and longer time resolved x-ray measurements of all types will assist the solution of problems across almost all fields of the physical and biological sciences, and that provision of high throughput beam lines and stations available to the scientific public is a matter of national interest. The emphasis here is on the added value of an interwoven net of scientific measurements. Although very few experiments are of type (1), even type (1) experiments benefit from the web of knowledge gained from other less spectacular studies.
- (3) Intermediate between categories (1) and (2), the definition of a few thematic problems the solution of which will benefit from a coordinated generation of data from studies of many systems, from which new concepts and transformational developments will be gleaned. The notion is that selecting systems for study with reference to a central theme will draw complementary experiments on many systems, and the collection of data thereby obtained can then be used to test old theories, develop new theories and concepts, etc. Two models for this category are the Sloan Digital Sky Survey, which has radically altered cosmology and astrophysics by generating a data base that has been used to ask and answer entirely new questions, and the Protein Data Base, which has performed a similar function in advancing understanding of protein folding.

Researchers interested in ultrafast x-ray science span many scientific disciplines. A partial non-Argonne listing is shown below.

Yves Acremann (SLAC)	Nicola Armaroli (ISOF - CNR, Italy)
Jim Belak (LLNL)	Felix Castellano (Bowling Green State U.)
Phil Bucksbaum (Stanford University)	Michael Hopkins (U. of Chicago)
David Cahill (University of Illinois)	Chuan He (U. of Chicago)
Roy Clarke (University of Michigan)	Michael Hopkins (U. of Chicago)
Phillip Coppens (SUNY, Buffalo)	Joseph Hupp (Northwestern U.)
David Ederer (Tulane University)	Himansu Jain (Lehigh)
Paul Evans (University of Wisconsin)	Frederick D. Lewis (Northwestern U.)
Peter Fischer (LBNL)	Jonathan S. Lindsey (North Carolina State)
Eric Fullerton (Hitachi)	Braja K. Mandal (IIT)
Jacob Jones (University of Florida)	Gerald J. Meyer (Johns Hopkins)
Jorgen Larsson (University of Lund)	Martin Newcomb (U. Illinois Chicago)
Soo-Heyung Lee (KRISS, Korea)	Daniel Nocera (MIT)
Aaron Lindenberg (SLAC)	Kirk S. Schanze (U. of Florida)
Hector Lorenza (LLNL)	Russell Schmehl (Tulane)
Roberto Merlin (University of Michigan)	Michael Schmittel (Universität Siegen, Germany)
Martin Nielsen (Copenhagen University)	Michael R. Wasielewski (Northwestern U.)
Hendrik Ohldag (SLAC)	Glenn A Waychunas (LBNL)
Stanislas Pommeret (Commissariat à l'énergie atomique)	Luping Yu (U. of Chicago)
David Reis (University of Michigan)	Ling Zhang (Southern Illinois U.)
Ed Stern (University of Washington)	Jeffery Zink (UCLA)

Requirements and Capabilities

The proposed SPX facility at the APS, is based on the concept illustrated in Figure 9; it uses transverse deflecting rf cavities ("crab cavities") to impose a correlation ("chirp") between the longitudinal position of an electron within a circulating electron bunch and its vertical momentum. The x-rays emitted by each electron tend to travel along the path of the electron itself. By placing an undulator just downstream of the crab cavity one produces a chirped x-ray beam. At a sufficient distance (e.g., 30 m) from the undulator, this angular chirp evolves into a spatial chirp, so that there is a strong correlation in the x-ray pulse between arrival time and vertical coordinate. Use of vertical slits then permits filtering the pulse in the time dimension, allowing production of an x-ray pulse that is shorter than the electron pulse.

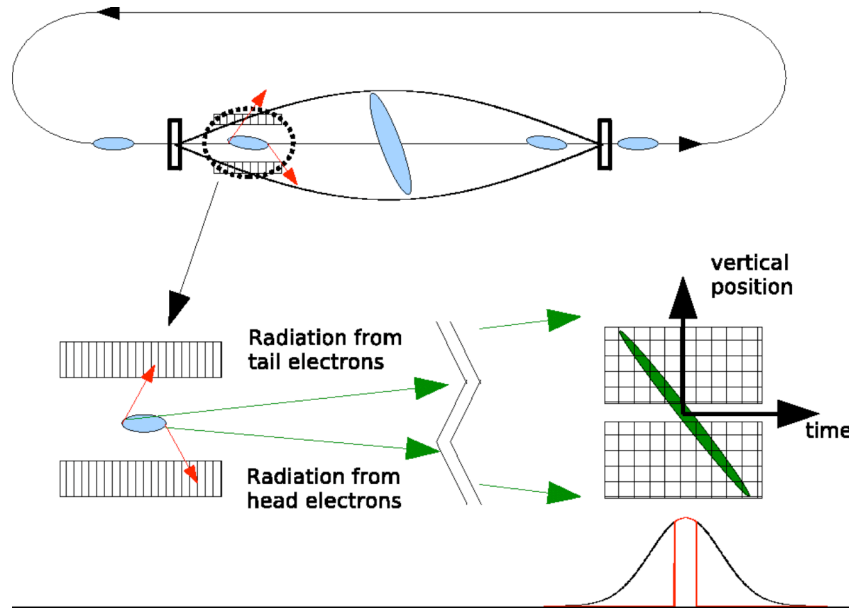


Fig 9. Illustration of Zholents' scheme for short x-ray pulse production using deflecting rf cavities in a storage ring.

As shown in the figure, two cavities are required; the second cavity cancels the effects on the electron beam of the first cavity and thereby avoids extremely large vertical emittance growth. The second cavity is placed at a vertical betatron phase advance of $N \cdot 180$ degrees downstream of the first, where N is an integer; at the APS this placement will be achieved by having the cavities separated by exactly n sectors and making slight adjustments to the electron beam optics. If N is greater than 1 the time-angle chirp of the electron beam will reappear at all intervening straight sections, thereby permitting time resolved x-ray studies to be carried out at a large number of beamlines. The cavities must have a deflecting mode frequency that is a harmonic h of the ring rf frequency, 352 MHz; the likely choice for the APS installation is $h = 8$ which corresponds to a deflecting cavity frequency of about 2.8 GHz. Ideally, the second cavity exactly cancels the effect of the first. In real systems, nonlinearities, errors, and other details destroy the perfect cancellation of the kicks, resulting in vertical emittance growth. Vertical emittance together with the natural opening angle of the undulator radiation results in smearing of the chirp, which limits how short a pulse, may be produced. As the deflecting voltage is increased, the emittance growth also increases and reduces the anticipated benefit. The emittance growth has been predicted by particle tracking simulations. Convolution of the predicted electron phase space with the single-electron radiation distribution from an undulator allows predicting

the effectiveness of slits in producing short x-ray pulses. Figure 10 shows the results of such simulations, for the case that the deflecting voltage is 4 MV and the vertical slits that are 30 m from the undulator are set to transmit 1% of the incident photons. A deflecting voltage of about 4 MV is sufficient to achieve x-ray pulse widths of 1 ps or so. Due to the large deflecting voltage and resultant power loss, the cavities will operate at 2° K to reduce losses.

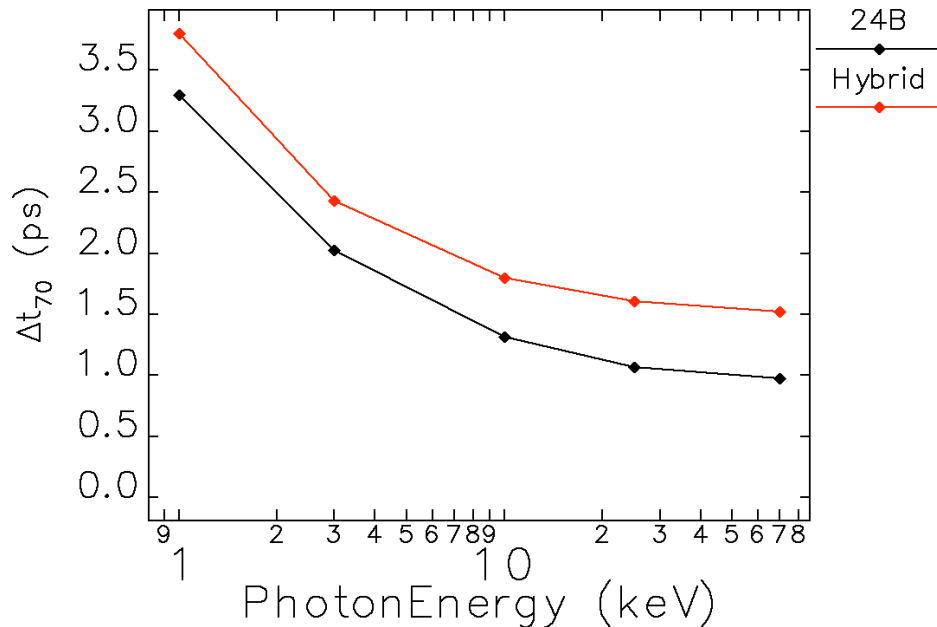


Figure 10: Predicted x-ray pulse duration (central 70%) as a function of the photon energy assuming 4 MV deflecting voltage and 1% transmission through the slits. “24B” is for 24-bunch mode, while “Hybrid” is for the intense bunch in hybrid mode.

Beyond the developments in the storage ring, it will be essential to have beamline infrastructure for scattering, spectroscopy, microscopy and imaging. Specifically, it will be essential to have high-repetition-rate, ultrafast excitation sources (e.g. lasers or electrical pulses) as well as gated pixel array detectors and software for scattering and multidimensional absorption spectroscopies. Careful planning of access modes to allow evolutionary development of complex experiments will be necessary.