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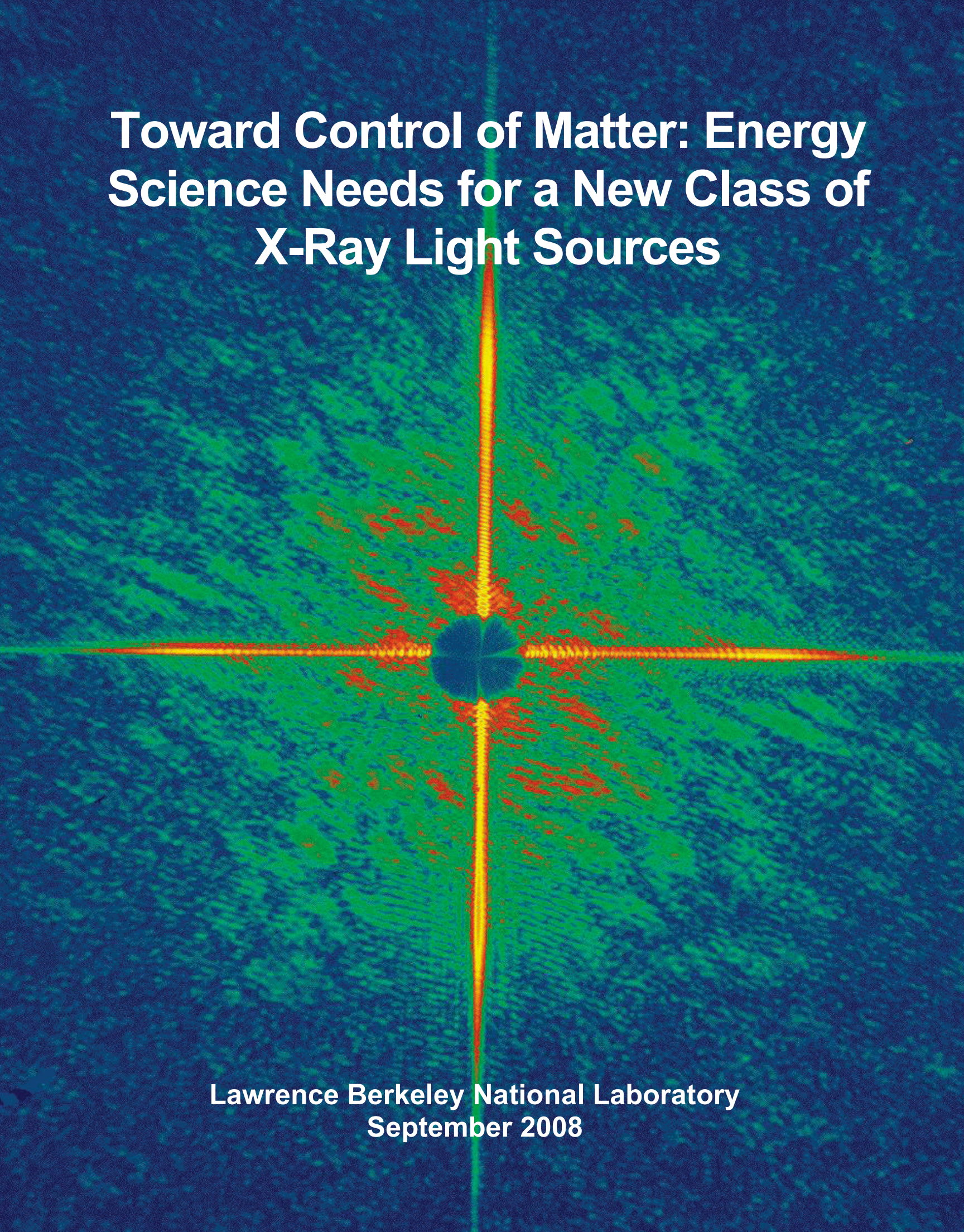
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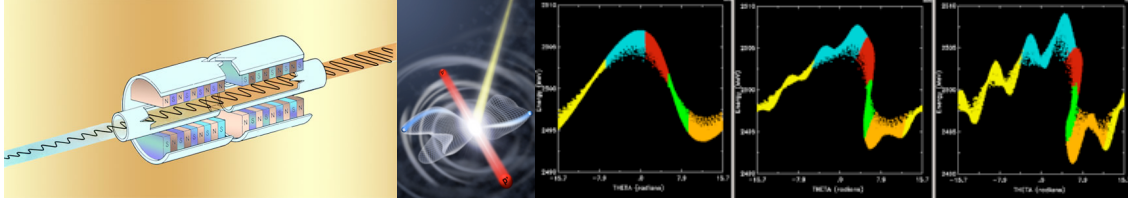


Toward Control of Matter: Energy Science Needs for a New Class of X-Ray Light Sources

Lawrence Berkeley National Laboratory
September 2008

[Cover Caption]

Ultrafast FEL diffraction pattern from a single 25-fs exposure at a wavelength of 32 nm at the FLASH FEL at DESY presented by Henry Chapman (Lawrence Livermore National Laboratory) at the workshop “Science for a New Class of Soft X-Ray Light Sources” held in Berkeley in October 2007. The image of a test object reconstructed from the diffraction pattern achieved the diffraction-limited resolution of 62 nm. [H. Chapman et al., “Femtosecond diffractive imaging with a soft-x-ray free-electron laser,” *Nature Physics* **2**, 839 (2006)]



Toward Control of Matter: Energy Science Needs for a New Class of X-Ray Light Sources

**Report of the Workshop on Science for a New Class of
Soft X-Ray Light Sources, October 8–10, 2007, Berkeley, CA**

Report Contributions from Elke Arenholz, Ali Belkacem, Lew Cocke, John Corlett, Roger Falcone, Peter Fischer, Graham Fleming, Oliver Gessner, M. Zahid Hasan, Zahid Hussain, Steve Kevan, Janos Kirz, Bill McCurdy, Keith Nelson, Dan Neumark, Anders Nilsson, Hans Siegmann, Malcolm Stocks, Ken Schafer, Robert Schoenlein, John Spence, and Thorsten Weber.

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[Title Page Caption]

Right three figures are scatterplots of predicted longitudinal phase space at different stages of an FEL cascade operating between wavelengths of 240 to 4 nm, produced by the GINGER FEL simulation code. [Courtesy, W.M. Fawley, Lawrence Berkeley National Laboratory]

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Executive Summary

Over the past quarter century, light-source user facilities have transformed research in areas ranging from gas-phase chemical dynamics to materials characterization. The ever-improving capabilities of these facilities have revolutionized our ability to study the electronic structure and dynamics of atoms, molecules, and even the most complex new materials, to understand catalytic reactions, to visualize magnetic domains, and to solve protein structures. Yet these outstanding facilities still have limitations well understood by their thousands of users.

Accordingly, over the past several years, many proposals and conceptual designs for “next-generation” x-ray light sources have been developed around the world. In order to survey the scientific problems that might be addressed specifically by those new light sources operating below a photon energy of about 3 keV and to identify the scientific requirements that should drive the design of such facilities, a workshop “Science for a New Class of Soft X-Ray Light Sources” was held in Berkeley in October 2007 (see Appendix). From an analysis of the most compelling scientific questions that could be identified and the experimental requirements for answering them, we set out to define, without regard to the specific technologies upon which they might be based, the capabilities such light sources would have to deliver in order to dramatically advance the state of research in the areas represented in the programs of the Department of Energy’s Office of Basic Energy Sciences (BES). This report is based on the workshop presentations and discussions.

Scientific Areas Addressed by New Light Sources

Plenary and parallel discussions covering five broad scientific categories took place over the two and one-half days of the workshop. It is highly noteworthy that the themes emerging from these discussions closely mirror those found in the forward-looking Basic Energy Sciences Advisory Committee (BESAC) report: *Directing Matter and Energy: Five Challenges for Science and the Imagination*. There was also broad agreement that a new user facility that provides an array of simultaneously operating stations with broadly tunable beams (tunable in pulse length from picosecond to attosecond, pulse frequency up to 100 kHz, flux, energy, polarization, etc.) would have a transformational impact on all areas of research examined by the participants.

(1) Chemical Physics. Both gas-phase and condensed-phase chemical processes, including those at surfaces, were considered. The frontier theme identified was the attosecond manipulation of electronic motion on its own time scale. Two research directions in attosecond science offering new conceptual paradigms were (1) the ubiquitous role that non-Born–Oppenheimer chemical dynamics, in the form of dynamics at conical intersections, plays in excited state chemistry and (2) the creation of a coherent superposition of electronic states of a molecule for coherent core-hole correlation spectroscopy. Intense attosecond and femtosecond pulses in the soft x-ray region will be essential to addressing both of these problems, among others in chemical physics.

(2) Atomic, Molecular, and Optical Physics. Gas-phase targets, including clusters were discussed, and experiments on the time scale of electron dynamics emerged again as a central theme, encompassing two major research directions. Probing electron correlation in atoms and molecules on the attosecond time scale is one of the greatest challenges in AMO physics today, and although current experiments have certainly demonstrated the promise of attosecond x-ray science, they barely scratch the surface of this new area of inquiry. The complete and detailed understanding of dynamics at conical intersections in small molecules is another challenge for this area, and no less difficult.

(3) Magnetization and Spin Dynamics. Here, the common theme that emerged was the exploration of the origin of magnetic interactions at both fundamental time and length scales. Capabilities of new soft x-ray light sources at femtosecond time scales and nanometer length scales are expected to open new avenues of research, such as the generation of magneto-electronic anisotropies or the all-optical control of spin and magnetization for future magnetic technologies. Element-selective x-ray dichroism effects link spin and orbital moments with magnetic anisotropies and will enable the detection of even subtle changes in advanced magnetic materials, such as multiferroics or magnetic semiconductors. Soft x-ray sources capable of producing intense femtosecond pulses will launch experiments that drive magnetization far from equilibrium and allow the study of the stochastic behavior of internal spin structures.

(4) Correlated Materials. The central challenge in this area of condensed-matter physics is to understand and ultimately control exotic phenomena in complex materials that emerge from the effects of electron correlation and its coupling to nuclear motion. The importance of ultrafast time-resolved soft x-ray measurements in these systems lies in the capability to drive them out of correlated equilibrium on time-scales shorter than the underlying correlations, and then disentangle the interactions by probing their time response as the correlation develops. Once again the issues of non-Born–Oppenheimer dynamics play a major role in the science that might be accomplished with ultrafast soft x-ray pulses. In the opposite regime, narrow bandwidth (relatively long duration) soft x-ray pulses, with high average flux, will also be very important for high-resolution inelastic x-ray scattering studies of low-energy correlated excitations in complex materials.

A remarkable common thread between the discussions in chemical physics, atomic and molecular physics, and the discussions of correlated materials was the tantalizing prospect that two-dimensional x-ray spectroscopies might be possible. Two-dimensional NMR and IR spectroscopies have of course already had great success. There may be intrinsic limitations to the application of these ideas at x-ray wavelengths, but the consensus in the discussions in all three of these scientific sub-disciplines was that the development of new techniques along these lines could be one of the most important impacts of the existence of new kinds of soft x-ray light sources. The quest for nonlinear x-ray spectroscopies is just beginning.

(5) Exploration of Nanoscale Dynamics and Complexity. The challenge in this area is understand the structure and dynamics of materials at the nanoscale and to be able to tailor new materials for nanotechnology and energy applications. To extend the study of

dynamics (of magnetic systems, for example) to the ultrafast time scale, one needs suitably short pulses. High spatial resolution is required (often in 3D) to study heterogeneous, porous, or complex materials with structure on the 1-to-50-nm scale. The approach can involve real-space imaging using zone-plate optics or reciprocal-space techniques such as diffraction microscopy and soft x-ray photon correlation spectroscopy (SXPCS)

Implications for Future Facilities

No light source in existence, under construction, or on the drawing board can deliver the beams required for the cutting edge science described in this document. Thus, we are led to ask what kind of light source would be able to conduct the next-generation experiments required to address these scientific challenges? During the decade or longer before the completion of the first of the new class of light sources contemplated in this workshop, the free electron laser (FEL) technology on which large-scale user facilities in this domain might be built will evolve and be refined far beyond the currently existing examples. At the same time, at the individual laboratory scale, high-harmonic generation (HHG) based on intense short-pulse optical laser technology will also continue to evolve. The discussions at this workshop took place explicitly in the context of these certainly complementary and potentially competing technologies for producing soft x-ray pulses. The case for the deployment of flexible user facilities based on FELs is being made, in part, by the initial applications of HHG sources at the bench scale. The boundary between the science that can be addressed only with large-scale facilities and that accessible in the laboratory is not entirely clear, but there was no doubt left by the workshop discussions that the large-scale facilities will be necessary.

The experiments addressing new scientific opportunities at a future soft x-ray light source will be very diverse, and therefore a multi-user facility would be of great interest. For example, some parts of the BES community must have much higher temporal resolution and repetition rates than are now available. Other parts require higher intensity and spectral resolution in order to make the progress that would justify the cost of such facilities. Correspondingly, the requirements for any new soft x-ray facility to address the majority of the science will be demanding. Such a light source should

- Cover an energy range of approximately 13.6 eV to 3000 eV (resonant edges of elements from hydrogen to argon), thereby enabling both x-ray spectroscopies and imaging
- Be capable of operating with a very high repetition rate—100 kHz or greater is desirable.
- Provide both pump and probe pulses in the XUV or x-ray, or multi-color sequences, for example to actively align molecules in three dimensions, and synchronization between optical and x-ray pulses.
- Have independently tunable beamlines.
- Allow individual control over the pulse length and shape at each beamline.

- Generate very stable photon beams of high brightness and peak intensity.
- Include control of polarization, linear and circular, which is essential for dichroism spectroscopy and microscopies.

Moreover, future experiments will involve a level of complexity that is a generation beyond that of experiments are routinely performed at today's light sources, resulting in additional infrastructure requirements for the facility: sample-preparation facilities, staging areas, accessibility for custom-made end-stations, integrated and synchronized optical and x-ray laser systems, temperature- and vibration-controlled environments, and sufficient time allocations to successfully mount complex and challenging experiments.

I. Introduction

A. Purpose of this Report

The workshop “Science for a New Class of Soft X-Ray Light Sources,” (see Section C below) on which this report is based was organized in the fall of 2007 as an extension of earlier discussions at the Lawrence Berkeley National Laboratory about the increasingly evident need of the U.S. scientific community for a new class of soft x-ray light sources. From an analysis of the most compelling scientific questions that could be identified and the experimental requirements for answering them, we set out to derive the capabilities that such light sources must deliver in order to dramatically advance the state of research in the areas represented in the programs of the Office of Basic Energy Sciences (BES) in the Department of Energy. The fundamental intent of this workshop and this report is to help drive the planning and design of such facilities by the science that will depend on them.

This entire exercise has been informed by the recent “Grand Science Challenges Report” of the Basic Energy Sciences Advisory Committee (BESAC) entitled *Directing Matter and Energy: Five Challenges for Science and the Imagination* [1]. The scope of those challenges is breathtaking:

- Quantum Control of Electrons in Atoms, Molecules, and Materials
- The Basic Architecture of Matter: Directed Assemblies, Structure, and Properties
- Emergence of Collective Phenomena: Strongly Correlated Multiparticle Systems
- Realizing the Dream of Nanoscience: Energy and Information on the Nanoscale
- Matter Far Beyond Equilibrium

It proved easy to see from the outset that soft x-ray experimental methods will have to play a role in addressing central aspects of all of them; however, capabilities far beyond those available today will be necessary for such experiments. Because the range of disciplines in the Basic Energy Sciences portfolio is broad, it is not surprising that the individual requirements of those scientific fields are sometimes disparate. Therefore this report emphasizes the range of capabilities and flexibility that new soft x-ray facilities must have if they are to support the broad community. For example, some parts of the BES community must have much higher temporal resolution and repetition rates than are now available. Other parts require higher intensity and spectral resolution in order to make the progress that would justify the cost of such facilities.

The central purpose of this report is to describe the most pressing scientific questions identified in the workshop discussions that we will be unable to answer without new kinds of soft x-ray experiments. Scientific areas in the Basic Energy Sciences range from materials science to atomic physics, and it would seem that the most important questions in those disciplines might have little similarity. However, the same themes emerged repeatedly from the workshop discussions in different disciplines. The attosecond manipulation of electronic motion was one of those, as was the breakdown of the separation of the timescales of electronic and atomic motion when light is absorbed by a

molecule or solid (non-Born–Oppenheimer dynamics). These ideas appeared frequently in our discussions of chemical physics, atomic physics, and correlated materials. The observation, control, and imaging of magnetic phenomena formed another set of common threads in the discussions of the workshop.

Sections II through VI of this document report on aspects of the discussions and presentations at the workshop concerning these scientific challenges and themes, and form a large portion of the “science case” that has emerged for the creation of new light sources to serve the disciplines in the BES programs. Those sections of this report also identify key requirements for those facilities, without regard to the specific technologies upon which they might be based.

The potential to design individual facilities that can serve the entire array of disciplines in BES arises from a combination of the new technological developments on which they might be based and the commonalities that can be found in the scientific themes emerging from the workshop discussions. For example, many areas of inquiry require femtosecond or attosecond scale pulses at energies ranging from a few hundred electron volts to three kilovolts. Those capabilities would serve condensed matter investigations as well as gas phase chemical or atomic and molecular physics. Other areas, including inelastic scattering experiments that probe electronic structure in condensed matter and imaging at the nanoscale will both be served by high resolution and coherence in the soft x-ray region.

B. New Technologies and the Context of the Workshop

The context of the workshop also involved an underlying tension between technologies for producing short pulses in the soft x-ray. There is a worldwide effort that is currently developing and refining the capabilities of free electron lasers (FELs) to produce such pulses at photon energies from tens of eV to tens of keV. At the laboratory scale, in contrast to large user facilities, the phenomenon of high-harmonic generation (HHG) based on high-average-power optical lasers is being exploited to produce short extreme-ultraviolet (XUV) and x-ray pulses.

So what fraction of the scientific questions we identify here will be answerable at the laboratory scale, without national facilities? Are large-scale FEL facilities needed in the soft x-ray, or will they be obviated by developments in high-harmonic generation? The answers to these questions are not yet clear. While the limits of applicability of HHG are not yet known, a consensus has arisen in our discussions that many of the most pressing questions will require intensities at energies near the x-ray edges of the first row elements that HHG seems unlikely to provide. These two technologies are therefore complementary—and radically different in cost, scale, and number of users served.

The technologies for FELs in this regime, if they are to provide the high repetition rates, tunability, short pulses, and intensities that are needed by the scientific community, need further development. An important observation made during our discussions is that research and development of high-average-power lasers is necessary for both FELs and

HHG, because such lasers are needed to drive the photocathodes for FELs as well as for the electron-bunch manipulation that will allow ultrashort pulses.

Sections VII and VIII of this report turn to some of those questions. They cannot be completely resolved here, because this report is primarily about the science that will depend on these technologies. However the discussion about those scientific questions cannot take place outside of this context.

C. The Workshop and Its Organization

Nearly 80 scientists from around the world attended the workshop “Science for a New Class of Soft X-Ray Light Sources,” held in Berkeley on October 8-10, 2007. At the outset the purpose and boundaries of the workshop were clearly stated by the organizers:

- To consider the science that might be done and that will drive the design of new soft x-ray light sources.
- To help develop a scientific basis for those decisions and to influence the design of those facilities—not to justify an existing proposal for any of them.
- To help guide the design of new facilities so as to ensure that they will be capable of addressing the most important outstanding scientific questions.

The working definition of soft x-rays was the energy range below 3 keV. The workshop opened with a summary of the BES Grand Scientific Challenges report by Graham Fleming, followed by a brief summary of light source projects around the world and the tension between competing technologies for producing short pulses in this spectral region.

Eleven plenary lectures set the scientific tone of the discussions, and each afternoon there were many short talks given in parallel breakout sessions that were divided into five broad scientific categories:

- Chemical Physics
- Atomic, Molecular and Optical Physics
- Magnetization and Spin Dynamics
- Correlated Materials
- Exploration of Nanoscale Dynamics and Complexity

The workshop agenda and discussion leaders are included in the Appendix.

In each of these areas we discussed both the scientific challenges and the requirements of a soft x-ray source to meet them. Clearly there was more said than we have been able to reproduce in detail in a report of this size, but in Sections II through VI of this report, the authors have attempted to include most of the essential aspects of the relevant science in each of these areas.

D. References

1. *Directing Matter and Energy: Five Challenges for Science and the Imagination.* Basic Energy Sciences Advisory Committee, U.S. Department of Energy, December 20, 2007. Available online at www.sc.doe.gov/bes/reports/list.html.

II. Chemical Physics

A. The Frontier: Attosecond Manipulation of Electronic Motion

Many chemical and physical systems exhibit temporal dynamics on ultrafast timescales. In recent decades, femtosecond laser experiments have played an ever-increasing role in extracting key information about fundamental atomic and molecular mechanisms. Examples of atomic and molecular science that are markedly influenced by ultrafast technology include chemical transition-state dynamics, cluster and liquid-state caging dynamics, photoprocesses in photosynthetic systems and visual pigments, as well as coherent phenomena such as wave-packet dynamics and quantum information. With the advent of Ti:sapphire lasers, femtosecond time dynamics has reached a high state-of-the-art. Relentless improvements in this laser technology now offer tunable radiation typically down to tens of femtoseconds, and sometimes less. The femtosecond timescale is well matched to the timescales for the motions of atoms or nuclei in molecules, such as vibrations and rotations. If an electronic transition is detected, such as an electronic state change or curve crossing, it usually exhibits a timescale governed by the nuclear motion.

Beyond the femtosecond domain, the scientific world is now approaching a new frontier centered on ultrafast processes occurring on an attosecond time scale [1, 2, 3]. With attosecond resolution, one can control and monitor matter via manipulation of electronic rather than nuclear dynamics. The attosecond time domain can directly address the timescales for dynamics induced by electron correlation effects in atoms and molecules, one of the most important interactions in chemistry and atomic/molecular physics. Many of the concepts developed for nuclear dynamics, such as vibrational wave packets comprising coherent superpositions of vibrational eigenstates, can, in principle, be translated into the electronic time domain.

There have been major recent breakthroughs in attosecond science, based on the technology in which an intense 800-nm femtosecond laser pulse interacts with a gas jet to generate either an attosecond pulse train or isolated attosecond pulses in the soft x-ray regime. This scheme has enabled new atomic-physics experiments in which time scales for Auger emission and electron tunneling through Coulomb barriers have been determined for the first time. However, the low intensity of laser-based attosecond sources ($\sim 10^7$ photons/sec) severely limits the types of experiments that can be performed. The attosecond capabilities of the class of light sources considered in this workshop, on the other hand, will make it possible to fulfill the dreams and aspirations of attosecond science.

In the following sections, we identify two research directions in attosecond science that offer new conceptual paradigms in chemical physics: extreme non-Born–Oppenheimer dynamics, in which the broad bandwidth associated with attosecond light sources is used to create a coherent superposition of electronic states of a molecule, and coherent core-hole correlation spectroscopy, the x-ray analogue of multidimensional NMR or IR spectroscopy. In addition, we discuss two specific examples, catalysis and dynamics of aqueous systems, where attosecond and femtosecond capabilities will open new doors.

B. Extreme Non-Born–Oppenheimer Chemical Dynamics

In order to appreciate extreme non-Born–Oppenheimer dynamics, we refer to Figure 1, showing the typical situation in photochemistry using excitation pulses with femtosecond or longer duration. Under these circumstances, only a single excited electronic state is accessed, and the subsequent dynamics involving some combination of energy relaxation, isomerization, and dissociation are determined by evolution on Born–Oppenheimer potential energy surfaces that are coupled by radiationless transitions and conical intersections at nuclear configurations where two (or more) surfaces approach one another. In principle, it is possible to control the outcome of this excitation process by designing the excitation pulse to create a wave-packet that can steer the initial dynamics in a specified direction; this is the basis of some of the “coherent control” schemes that have been implemented in recent years. However, even a 10-fs pulse has a bandwidth of only 65 meV, generally limiting the initially prepared state to a vibrational wave-packet largely associated with a single electronic state, and control of the dynamics subsequent to excitation is limited.

In contrast, a 300-as pulse has a bandwidth of 6 eV, sufficient to create a novel type of initial wave function, comprising a superposition of multiple electronic states, that lies totally outside the realm of the Born–Oppenheimer approximation. The subsequent dynamics will then involve simultaneous wave-packet motion on this multitude of electronic states. These wave-packets will interfere with one another at conical intersections, and this interference has the potential to control the branching between electronic states at each intersection. By adjusting the energy, chirp, and duration of the

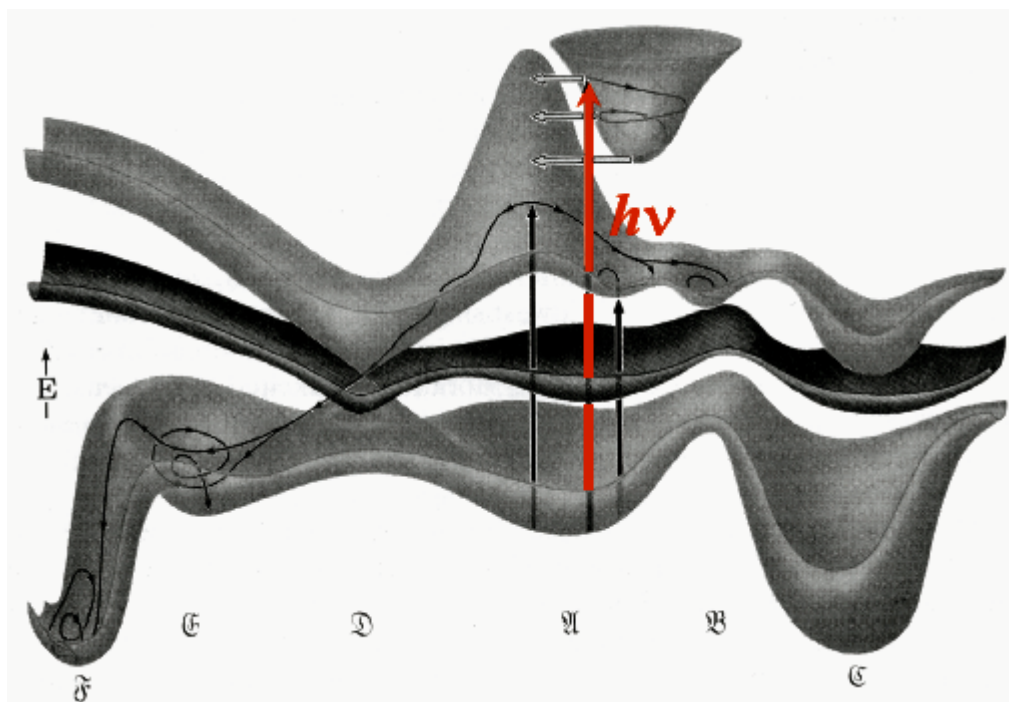


Figure 1. Schematic diagram of multiple conical intersections between several potential surfaces.

initial attosecond excitation pulse, one can in principle create vastly different initial conditions leading to different reaction products. The dynamics could be followed, for example, by pump–probe photoelectron spectroscopy techniques in a novel class of experiments that will be enabled by new light sources with attosecond capabilities.

Further control over the dynamics can be achieved by pre-alignment of the molecules with a femtosecond laser pulse. This will ensure that the attosecond pulse excites not just a randomly oriented ensemble of molecules but instead an ensemble preferentially aligned relative to the electric field of the attosecond pulse, and provide another “knob” governing the electronic composition of the initially created wave-function, since different electronic states within the pulse bandwidth will be excited with different probabilities depending on the alignment direction.

C. Ultrafast Core-Hole Correlation Spectroscopy

Coherent ultrafast core-hole correlation spectroscopy is essentially two-dimensional electronic spectroscopy performed in the soft x-ray regime. It is designed to probe correlation effects between pairs of excited electrons excited from different atomic sites in a molecule, based on nonlinear interactions with coherent, attosecond x-ray pulses. It is conceptually similar to 2D NMR, which probes correlated spin-dynamics, and perhaps even more similar to 2D infrared spectroscopy, which probes the interactions between vibrational modes in a molecule. While these ideas are still speculative at x-ray energies [4], several variants of them are receiving wide attention currently. Such experiments would require pulses of only a few femtoseconds (or less) in duration, but they would represent a revolutionary capability for the study of correlation effects in complex molecules. The electron correlation effects probed in this proposed experiment are ubiquitous in chemistry; they are comparable in magnitude to chemical-bonding energies and are thus crucial for predicting molecular geometries, reaction barriers, and reaction rates with chemical accuracy. They are also critical in semiconductors and artificial nanostructures.

The theoretical basis for this experiment is outlined in Figure 2 (taken from [4]). Here, an aminophenol molecule interacts with two attosecond pulses, one centered at 400 eV (ω_N) and the other at 535 eV (ω_O), coinciding with $1s$ core excitations in N and O atoms, respectively. The proposed experiment is a coherent four-wave mixing process in which the target interacts with three x-ray pulses separated by times t_1 and t_2 and emits a fourth pulse with temporal profile $S(t_3, t_2, t_1)$. The two-dimensional Fourier transform of this signal with respect to t_1 and t_3 yields a two-dimensional electronic spectrum in frequency space. Off-diagonal features in this 2D spectrum are present only when there is correlation between the two excited electrons on the N and O atoms; no signal should be seen in the Hartree-Fock limit of independent orbitals. Calculations show that the extent of this correlation depends not only on molecular structure (i.e., it differs in ortho- and para-aminophenol, but also on the nature of the molecular orbitals excited within the energy envelopes (~ 10 eV) of ω_N and ω_O .

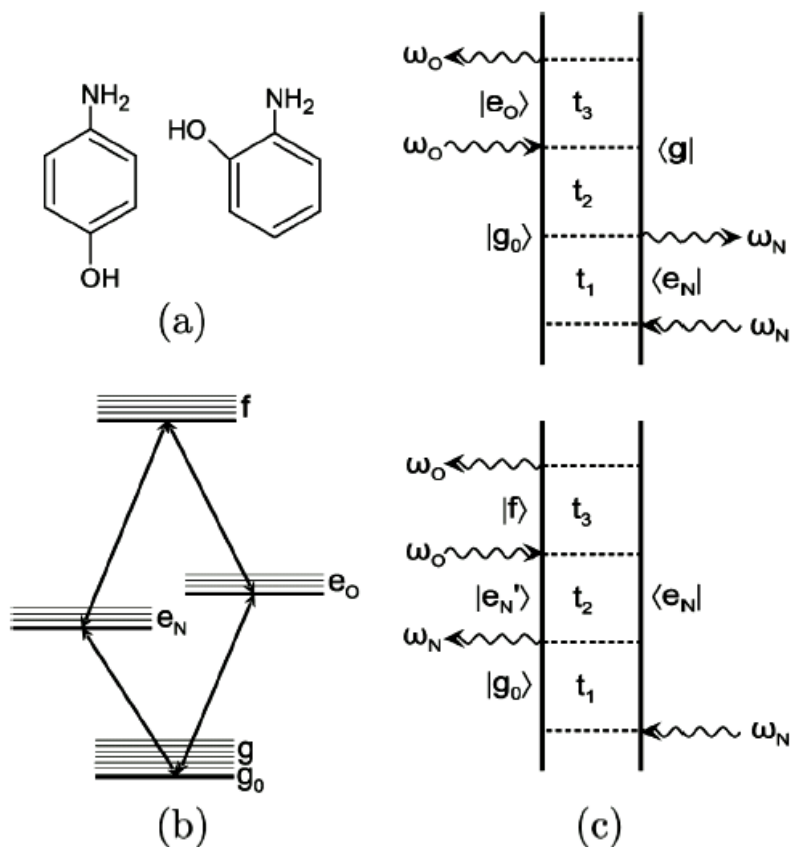


Figure 2. (a) Para and ortho isomers of aminophenol. (b) Valence and core-excited states of aminophenols. (c) Double-side Feynman diagrams representing the two contributions to the predicted cross-peak 2D x-ray correlation spectroscopy signal [4].

D. Catalysis and Surface Chemistry

There are a vast number of societal and economically important processes that rely on reactions at surface and interfaces, such as catalysis in chemical and energy production. The 2007 Nobel Prize in Chemistry was given for the fundamental understanding of surface chemistry and catalysis related to the identification of the various reaction pathways and the energetics of different intermediates for the ammonia synthesis and carbon monoxide reactions. Could it be possible to go much deeper into the fundamental problem and observe catalysis in real time?

The microscopic understanding of heterogeneous catalysis requires a detailed understanding of the dynamics of elementary processes at surfaces, such as charge and energy transfer between molecular adsorbates and catalytic substrates and the appearance of different reaction intermediates [5]. Figure 3 illustrates a surface reaction including adsorption, formation of different intermediates, and desorption. The number and complexity of theoretical calculations of model catalytic reactions continues to grow at an enormously fast rate, but the field of surface chemistry lacks the necessary time-resolved tools with which to investigate surface-reaction dynamics [5]. Owing to the low concentration of reactants, large substrate absorption, and extremely short lifetimes

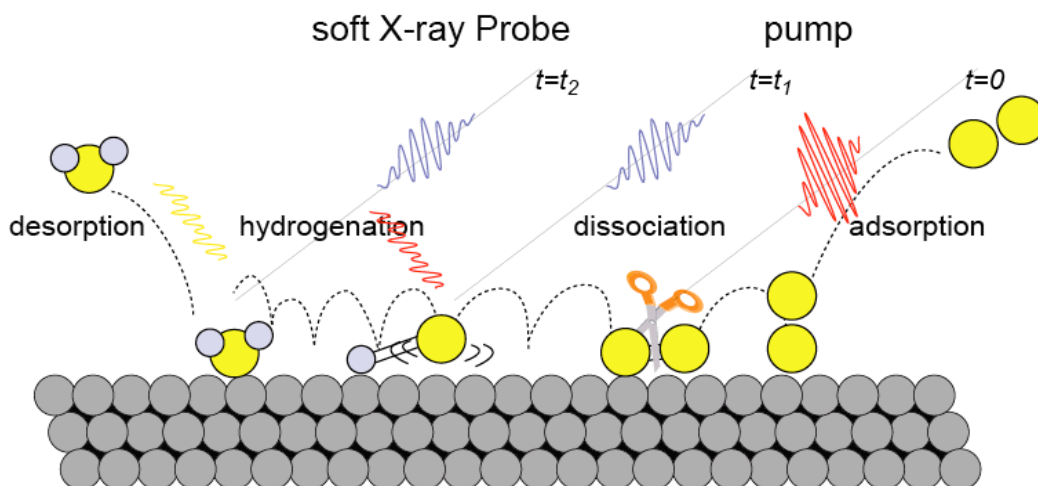


Figure 3. Elementary steps in a catalytic reaction involving molecular oxygen and hydrogen. The reaction can be stimulated by THz radiation or optical lasers and probed with XES or XPS using a soft x-ray pulse from an FEL.

of electronic excited states, the tools of ultrafast spectroscopy developed for studies in bulk media have not been generally applicable to metal surfaces, thus making the new development of comparable surface-sensitive tools critical to advancing our understanding of catalysis. With a time resolved x-ray spectroscopy probe, we have the potential to experimentally resolve the elementary steps during a surface reaction and thereby reach an atomic-scale mechanistic understanding that can be compared with theory.

One of the most important challenges to the field of surface chemistry is the need to develop a fundamental understanding of reactions at surfaces beyond the Born–Oppenheimer approximation (see Figure 4) [6, 7, 8]. Furthermore, such advances that go beyond the Born–Oppenheimer approximation will enable predictive control of other solid-state processes that involve excited electronic states. These include photocatalysis, electro-chemical sensing, and photoconductivity in solids.

(1) Ultrafast pump–probe experiments

We envision using ultrafast THz and optical-laser pumps and free-electron-laser (FEL) probes to conduct x-ray emission spectroscopy (XES) or x-ray photoelectron spectroscopy (XPS) experiments in order to identify short-lived reaction intermediates, charge and energy transfer, and the ways they evolve on a femtosecond timescale. We would need a soft x-ray source with a 20-fs time resolution and 100-kHz repetition rate. From knowledge of the details of the electronic structure, we can derive how the electrons have flowed between the substrate and reactants and relate this to changes in the nuclear coordinates. A detailed understanding of the time-dependent evolution of reactants, products, and intermediates will allow for the construction of detailed kinetic models and estimates of the various activation barriers in catalytic and other surface reactions.

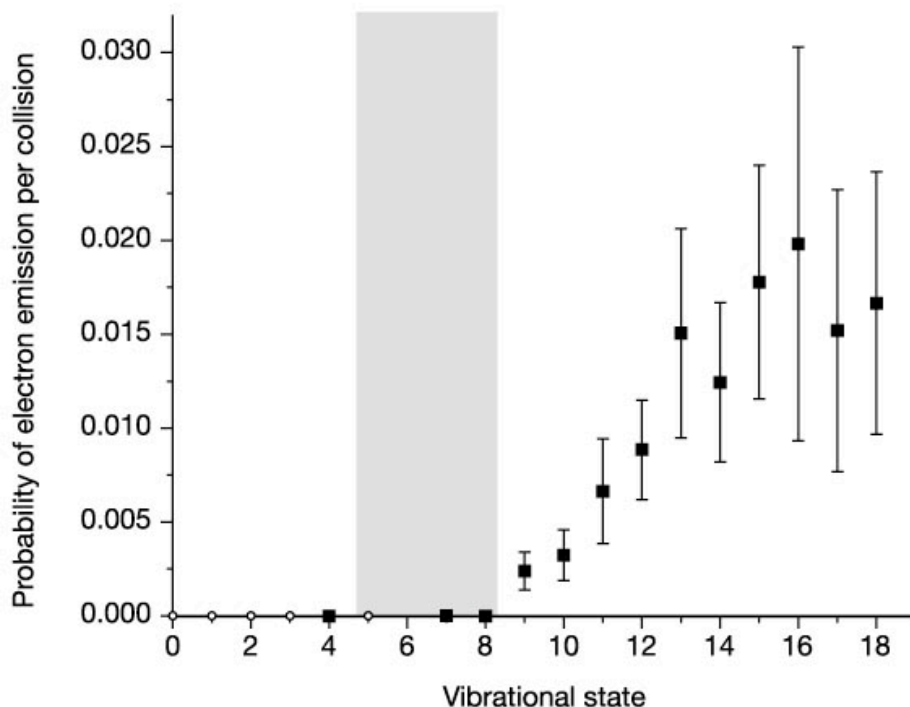


Figure 4. The experimental evidence of Born–Oppenheimer breakdown in molecule–surface interactions is now compelling. Here we show, an experimental demonstration of Born–Oppenheimer breakdown in molecule surface interactions. NO molecules are prepared in specific vibrational states with energies up to two-thirds of the NO bond energy. The probability of electron emission when a molecule collides with a metal surface is determined by the vibrational motion. When the vibrational excitation exceeds the work function (gray bar indicates the vibrational equivalent of the work function), electron emission to the vacuum is observed. This is some of the most direct evidence that large-amplitude vibrational motion, similar to what occurs in bond dissociation, efficiently excites electrons to large energies. From [6].

Both XES and XPS have the unique ability to provide an atom-specific probe of the electronic structure [9, 10] and their application to ultrafast spectroscopy would open entirely new windows into the realm of atomic motion, electronic structure rearrangements and thereby chemical dynamics. In XES the atomic sensitivity arises from the creation of a core hole during the absorption process and the fact that this core hole can only be filled by valence electrons in the proximity of the excited atom, see Figure 5 [10]. The final state of the x-ray emission process is a valence-hole state similar to the final state in valence-band photoemission, but here the valence electronic structure is projected onto a specific atom. Another essential aspect of the spectroscopy is that the polarization of the incident radiation and the direction of the emitted radiation allow directional sensitivity, providing a direct measure of the molecular orbital symmetry. In XPS the core electron is ionized and the binding energy provides a direct measure of the local chemical surrounding [9].

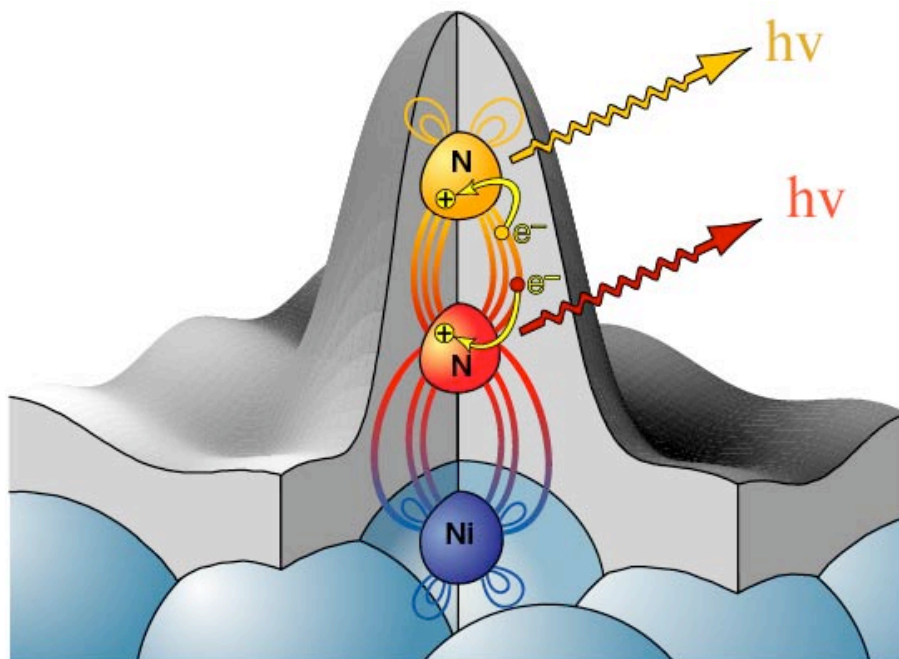


Figure 5. Schematic picture illustrating the local probe character in XES for N_2 adsorbed on a Ni surface. From the total charge density (gray envelope) valence electrons with p angular momentum (contour lines) decay into the N 1s core hole.

We show as an example how we can follow the dissociation process of N_2 that has been initiated by laser-pulse-induced electron heating on a stepped Ru surface. The dissociation of N_2 is the rate-limiting step in the Haber–Bosch process that produces ammonia from nitrogen and hydrogen over an Fe or Ru catalyst [11]. It has been shown that the active sites are steps on catalyst particles [11]. Figure 6 shows a large number of possible intermediates based on density functional theory (DFT) calculations together with simulated XES spectra. The angular-resolved spectral changes between the species are relatively large and can be further enhanced by imposing polarization control of the incoming ultrashort x-ray pulses. Depending on the orientation of the incident E-vector and specific photon energy, different resonances in the x-ray absorption (XAS)-mediated excitation process will enhance the contrast of certain species over others. We can in that sense follow different species as they evolve over time. From the projected spectra in the three different directions, one can see that the rather large changes are due to σ – π rehybridization when both N atoms start to interact with the surface.

(2) The combination of THz and x-ray spectroscopy—a unique opportunity

The increased reactivity at a catalyst surface is due to lowered reaction barriers, which provide more favorable reaction paths. Accordingly, typical catalytic reactions are triggered thermally by the reactants coupling to a hot substrate. In the past, thermal heating has been mimicked in the laboratory by using an ultrashort laser pulse to heat the sample at a well-defined time in order to provide a reference time for the reaction. Surface photoreactions driven by a visible or near-infrared pulse typically proceed via the

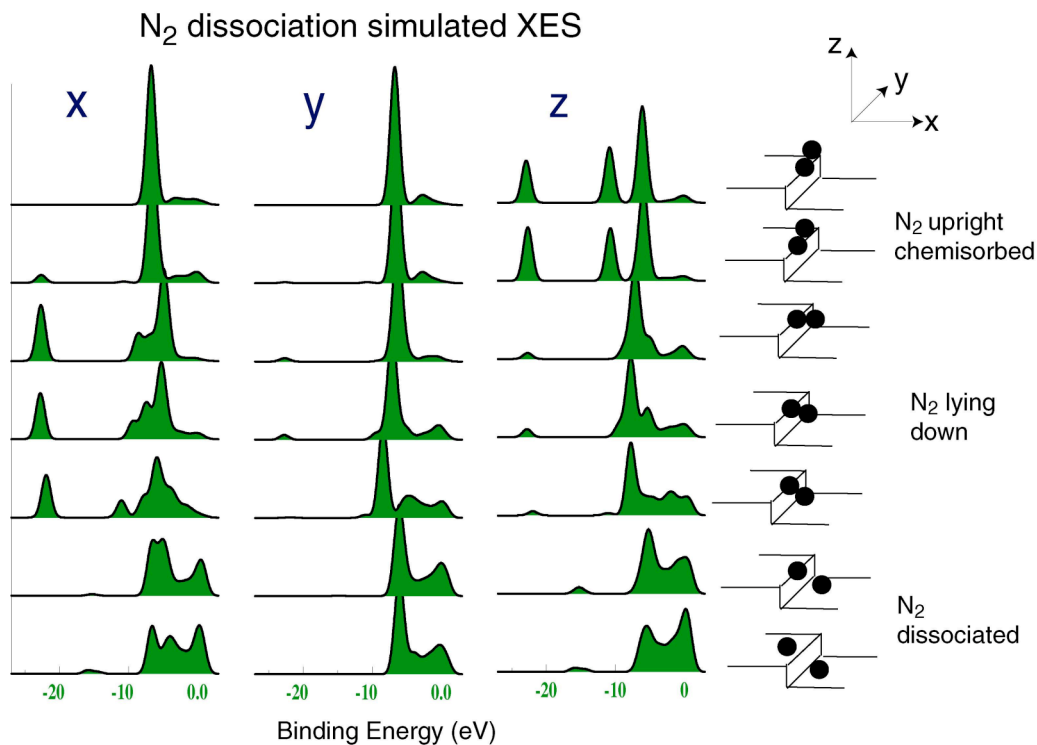


Figure 6. Simulated XES spectra for both nitrogen atoms in the dissociation of N_2 at steps. The spectra have been projected in the three high-symmetry directions.

substrate, since the absorption cross-section of a single adsorbate monolayer is too small to efficiently drive a reaction. Instead, hot electrons are excited in the substrate, which may thermalize and couple to the adsorbate within the first picosecond. Alternatively, the hot electron bath excites phonons within a few picoseconds and these phonons, in turn, can couple to the adsorbate and initiate a reaction. This non-equilibrium between electron and phonon temperatures within the first few picoseconds allows the determination of energy coupling mechanisms and has triggered a body of experimental [12] and theoretical [13] work to determine the potential energy surfaces and degree of non-adiabaticity in surface reactions.

Excitation of phonons, frustrated rotational and translational motions of molecular adsorbates, plays an important role in processes at surfaces that are driven by kT , i.e., temperature. At the moment, there exists no direct way to pump surface reactions by exciting the motion of the nuclei of an adsorbed molecule on an ultrafast timescale. However, the ultrashort electron pulse obtained in the linear accelerator to feed the x-ray FEL can also be employed for generation of coherent synchrotron radiation in the low-energy THz regime to be used as a pump. The coherent THz radiation provides an electric-field pulse with a certain direction that can collectively manipulate atoms or molecules on surfaces. In this respect, a chemical reaction can be initiated by collective atomic motion along a specific reaction coordinate. Assuming an electron pulse width of 100 fs, broadband radiation will be obtained with a high frequency cut-off at 10 THz, which is close to blackbody radiation at room temperature; the frustrated vibrational motions of adsorbates are detected in the far infrared/THz regime. Thus, a temperature

jump on an ultrashort time scale is possible by exciting frustrated vibrational motions using the ultrashort electron bunch. If the coherent THz radiation is generated from the same source as the soft x-ray FEL radiation, the full synchronization required for pump–probe experiments would be possible. The combination of THz and x-ray spectroscopy could be a unique opportunity for FEL facilities to conduct ultrafast chemistry studies at surfaces.

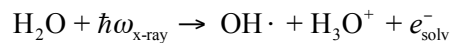
E. Excitation Dynamics in Aqueous Systems

The critical role that the aqueous environment plays in the many chemical and biological processes that are essential in maintaining the balance of the ecosystem and hence to sustain life on Earth is the driving force behind the need for the understanding of its properties across a wide range of environments and conditions. Of particular importance to the role of water in life are the physical and chemical transformations that high-energy radiation is known to induce to aqueous environments. Typical sources of high-energy irradiation include nuclear waste, where radiolysis in aqueous solutions leads to the production of hydrogen gas; nuclear reactors, where deterioration is accelerated when irradiated materials come into contact with aqueous environments; and high-energy electromagnetic radiation used to destroy waste, to process materials, to probe functionality in biological system (diagnostics), or to destroy specific targets (e.g., cancer cells). These processes occur under a wide variety of conditions, ranging from ambient temperatures and pressures in biological systems to high temperatures and pressures in nuclear reactors and waste destruction processes.

(1) *X-ray pump–probe experiments to study radiolysis of water*

Over the last few decades there have been tremendous advances in the study of the radiolysis of water [14, 15] in an effort to gain understanding about processes driven by electrons in aqueous environments. Although the cascade of events following the impact of high-energy radiation on liquid water and in homogeneous, dilute aqueous solutions have been characterized during the last 30 years, their complexity and the fact that they occur over multiple length and time scales have made it difficult to develop predictive models of the underlying physical and chemical processes at the molecular level.

Figure 7 provides a pictorial presentation of the range of chemical phenomena initiated by ionizing radiation in water. Prior experimental studies indicate that the initial ionization leads, via a cluster of low-energy electrons (spur) that proceed to ionize and excite nearby water molecules, to solvated electron formation and the dissociation of a water molecules into hydroxyl radicals and protons, which quickly solvate and participate in the hydrogen bonding network [15, 16, 17, 18]



The core excited oxygen decays in a few femtoseconds via the Auger process (near unity probability), leaving a two-hole final state and an Auger electron of ~ 500 -eV energy. This Auger electron and the initial photoelectron will undergo numerous inelastic

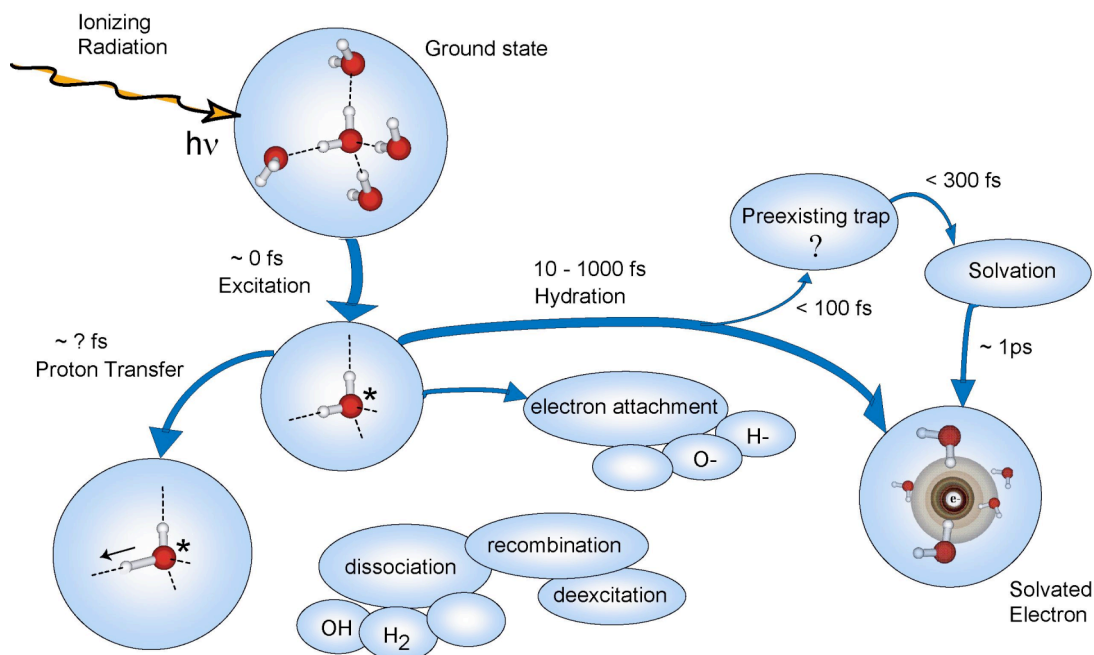


Figure 7. A schematic of elementary processes and their timescales occurring in water as a result of ionizing radiation.

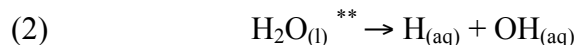
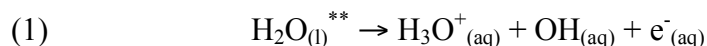
scattering events, producing a secondary cascade of ionization and dissociation events [19, 20]. Simulations indicate that the majority of the secondary-electron cascade also occurs in a few femtoseconds [20]. Any experiment to probe these processes must have sufficient time resolution to observe the inelastic electron scattering events and primary molecular dissociations on an attosecond time scale, while a time resolution of 10-20 fs will be sufficient to determine the yield and products of the electron cascade and molecular dissociations, as well as the solvation of the electrons, protons, and hydroxyl radicals. Determining these aspects of the radiolysis dynamics for water will be of extreme importance for the field of excited-state chemistry in aqueous systems.

We can anticipate novel x-ray pump–probe experiments using x-ray emission spectroscopy. With two-color experiments, one with a wavelength below the O K edge to pump the system and the other at a wavelength above the O K edge and an appropriate delay line that spans from attoseconds to nanoseconds x-ray-induced dynamics could be followed in detail. X-ray emission spectroscopy has the unique ability to provide an atom-specific local probe of the electronic structure [21]. The emission spectrum provides access to the occupied valence-electron density scaled by the (dipole operator) overlap with the excited core hole, e.g., K-edge emission for low- Z elements probes the local electronic structure of 2p character. In particular, the oxygen K-edge emission shows sensitivity to the hydrogen-bonding environment, making this technique, in principle, very sensitive to radiation chemistry. Recent high-resolution O K-edge spectra of liquid water reveal fine structure of the lone-pair, interpreted as due to specific structural motifs that change population as a function of temperature [22]. We estimate that detectable concentrations of solvated electrons and hydroxyl radicals can be generated by the x-ray pump. The solvated electron resides in the band gap of liquid

water and should appear in the O1s XE spectrum at low binding energy well separated from the valence molecular orbitals and the signature of the hydroxyl radical at energies below the water lone-pair orbital state. We can follow the spectral evolution as a function of delay between pump–probe pulses and of the intensity of the pump pulse. These experiments can be extended to probe various aqueous solutions containing ions, molecules and also water at interfaces and in confinement.

(2) *VUV or EUV excitation of excited-state dynamics*

All photochemical reactions originate from the reactivity of excited states. In radiation chemistry, the trickle down of energy results in the production of a cornucopia of super-excited states (similar to those produced via photo-excitation). Despite their importance in water radiolysis, the excited-state dynamics of liquid water are poorly understood. The initial super-excited-state dynamics play an important role because the reactive species that form when a water molecule decomposes are responsible for the subsequent chemistry of the system. Radiolysis produces a broad distribution of energies that makes it difficult to determine the role of specific excited states. Access to an ultrafast source of VUV to EUV laser excitation allows one to selectively tune the energy and explore the electronic states in detail. Probing in the visible (electrons and radical species) and EUV [aqueous holes (H_2O^+)] can be used to follow the chemistry of the water excited states. The excitation energy and the character of these states determine whether a molecule relaxes back to the ground state, ionizes (1), or dissociates (2).



Competition among the relaxation, ionization and dissociation channels provide important clues about the excited states, and how the liquid environment changes the character of those states relative to the gas phase.

The excitation of water has a number of possible outcomes including electron ejection into the conduction band (CB) of the bulk liquid. By measuring the geminate recombination dynamics, precise information on the ejection (thermalization) distances of the electrons and the survival probability for hydrated electrons can be determined. From these, ionization mechanisms can be deduced. Figure 8 demonstrates how the ejection path of the electron increases with the total excitation energy. Two regimes for water ionization (low- and high- energy) are clearly seen. Yet what causes such a drastic change in the behavior that is indicative of switchover between competing ionization mechanisms is not fully understood. Only above the threshold for vertical electron ejection (~ 11 eV) is it possible to directly ionize liquid water to produce $\text{H}_2\text{O}_{(aq)}^+$ and a “quasifree” electron, followed by rapid proton transfer from the $\text{H}_2\text{O}_{(aq)}^+$ species to a neighboring solvent molecule (reaction 1).

At high excitation energy, the water can undergo direct (vertical) ionization with ejection of a CB electron. The exact onset of this band and the character of electron states in this band are not known. Recent liquid-jet and water-cluster anion photoelectron spectroscopy

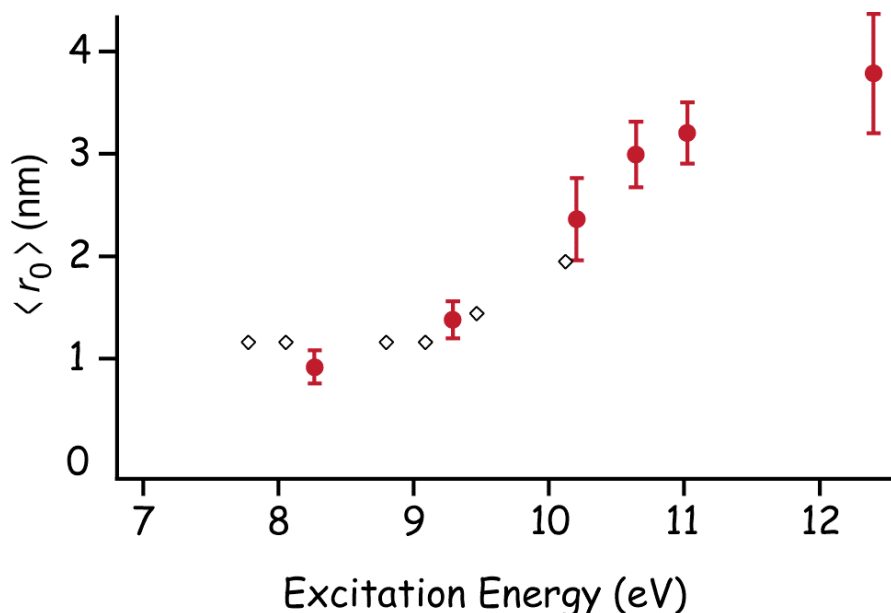


Figure 8. Variation of ejection path of electrons in water with the total excitation energy, showing that the ejection path of the electron increases with energy. Two regimes for water ionization (low- and high-energy) are clearly seen. From [23, 24].

measurements combined with newer estimates of the magnitude of the solvent stabilization energy (-0.12 to 0.0 eV) gives a most probable transition energy between 11.1 and 11.2 eV for promotion of an electron from the valence band directly to the bottom of the CB. Recent studies are consistent with these estimates.

However, it is known that photoionization also occurs for much lower energies, down to the onset of optical absorption of liquid water at about 6.5 eV. Reorganization of the excited molecule and its surroundings is necessary for the system to attain a favorable geometry for electron ejection in this low energy regime, where concerted nuclear motions play a central role. Despite many speculations as to the exact mechanism for this low-energy ionization pathway the exact way in which this mechanism operates has not been addressed, either experimentally or theoretically. Unraveling this mechanism is one of the most important tasks before radiation chemists. Significantly, similar low-energy channels exist in other molecular liquids (e.g., alcohols): the problem is general.

For aqueous anions, it has been shown that one-photon excitation may lead to qualitatively different outcomes of electron photodetachment as compared to two-photon excitation of equal total energy (e.g., for hydroxide). Contrary to commonly made assumptions, selection rules appear to have a large effect on energetic photoreactions in condensed matter systems. Similar observations have been made for liquid water. Recent work shows that for the one- and two-photon absorption spectra the relative intensities are distinctly different for excitation of the first and second excited states. In contrast to the one-photon spectrum that has a strong absorption maximum at 8.2 eV, this band is much weaker in the two-photon spectrum, decreasing by about an order of magnitude in

this region. The nature of this difference is not understood, but may indicate that there are different selection rules for accessing the lower lying excited states.

To resolve these problems it becomes necessary to directly excite the lower-lying states using VUV radiation. Such one-photon studies will eliminate the controversies introduced from previous multiphoton ionization studies and provide means of comparing the experimental and theoretical studies of water excitation; furthermore, with this approach we could study the branching ratios (ionization, fragmentation, relaxation) of water excited states that realistically occur in radiolytic spurs (tight clusters of excited and ionized molecules).

F. Requirements of a New Soft X-Ray Source to Meet These Challenges

The requirements are summarized briefly in the table below. The experiments proposed here that involve the combination of laser pump or probe with x-ray pump or probe, as well as those that involve pump–probe pulses both in the XUV or x-ray, will involve a level of complexity a generation beyond that of experiments that are routinely performed at today’s light sources. The scientific output of new facilities in the soft x-ray region can only be insured by the availability of appropriate staging areas and reasonable data-taking time for each experiment associated with one of the multiple simultaneously operating beamlines and by the time necessary to successfully mount experiments in which a substantial challenge will be to operate state-of-the-art short pulsed lasers systems synchronized to the x-ray pulses.

Table 1. Chemical Physics Requirements for a New Soft X-Ray Source

Property	Chemical Physics Requirements	Comments
Energy range (eV)	10 – 1000	Tunability is essential.
Repetition rate (kHz)	100 or higher	High repetition rates for coincidence experiments.
Power (W/cm ²)	10 ¹⁴ –10 ¹⁸	High power for dilute targets (0.3 GW peak power for attosecond pulses). Otherwise: 1 Ionization event per shot for coincidence.
Pulse length	picosecond femtosecond (10-100) attosecond (100)	Electron dynamics requires attosecond pulses.
Harmonics	< 0.1 %	As low as possible (third higher harmonic is a problem for low energies): Filter elements needed.
Spot size (μm)	~10	Tunable from 100 to 1.
Energy stability (eV)	0.1 eV	High resolution not needed but some is required.
Background signal	<0.1 %	Pure beams: any background hurts. Contrast 1:1000 desirable.

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III. Atomic, Molecular, and Optical Physics

A. The Frontier: Electron Dynamics at the Time Scales of Atomic and Electronic Motion in Highly Excited Atoms and Molecules

Third-generation light sources have provided unparalleled tools in terms of photon intensity, energy resolution, tunability, and repetition rate to study fundamental processes that govern the interaction of photons, electrons, atoms, and molecules. These atomic, molecular, and optical sciences (AMOS) studies have shaped our understanding of photoionization, single-photon multiple ionization, electron correlation, and Auger processes, as well as the importance symmetry plays in their interference, core-hole relaxation, photodissociation dynamics, and other processes, all of which are fundamentally important and occur in complex chemical and biological systems. A common aspect of almost all experimental studies at these light sources across the broad portfolio of AMOS studies at these light sources is the use of targets that are in their ground state prior to the interaction with x rays. Next-generation light sources provide a unique opportunity to extend AMOS studies from the interaction of x rays with ground-state targets to the interaction of x rays with targets in excited or even highly excited states, thus enabling new research that could dramatically move the field from probing electron and nuclear dynamics to controlling it.

Two themes recur repeatedly in discussions of the new science that will become possible in AMOS as more intense, short-pulse soft x-ray and XUV sources become available: (1) The manipulation of electron dynamics and (2) the breakdown of the Born–Oppenheimer separation of the time scales of nuclear and electronic motion in highly excited molecules. Many of the long list of specific opportunities for new science in AMO physics with next-generation light sources that became apparent in the workshop discussions and presentations are joined by these two themes.

(1) *Opening the experimental frontier at the timescale of electronic dynamics*

In the valence shells of atoms and molecules, where bonding forces are created, the natural timescale of the motion of electrons responsible for generating the most important properties of molecules is of the order of a few hundred attoseconds. The advent of sub-femtosecond pulses in the soft x-ray regime is opening the possibility for direct study and manipulation of electronic motion on that timescale. The experiments that will do so are dramatically more challenging than those being undertaken today, both in terms of detection and combinations of multiple radiation pulses, and will rely on the robust detection of signals for effects that are almost undetectable today. To be successful, they will require flexible and intense soft x-ray sources that provide those signals and that will allow multicolor x-ray experiments.

The first experiments to hint at this new frontier are being done at the FLASH facility in Hamburg, Germany, where, for example, studies of two photon double ionization of atoms (He and Ne) have been done by A. A. Sorokin et al. [1] and by a collaboration of the Heidelberg and Frankfurt AMO groups described by Joachim Ulrich at the workshop.

(2) *The breakdown of the Born–Oppenheimer separation of the timescales of electronic and atomic motion*

Even in molecules containing only a few atoms there is increasing evidence that the breakdown of the Born–Oppenheimer picture plays an essential role in determining the products of photodissociation or dissociative ionization of molecules. In AMO sciences, the ability to detect all the products of a reaction of a small molecule, like acetylene or ethylene, following core-hole ionization has provided strong evidence that the dynamics associated with conical intersections determines the fragmentation patterns of the breakup of the molecular ion. The prospect of completely characterizing the dynamics of reactions that occur through conical intersections will open up with the advent of intense femtosecond and sub-femtosecond light sources.

This theme connects strongly with a principal thrust of the Chemical Physics part of the workshop, discussed in Section II, called extreme non-Born–Oppenheimer dynamics there. It appears that in excited large polyatomic molecules, dozens of conical intersections may determine dynamics and that they are the critical feature for understanding the photochemistry of vision and photosynthesis. However, only in small molecules is it now imaginable that polyatomic non-Born–Oppenheimer dynamics could be understood experimentally in complete detail. The complete experimental characterization of these processes in small molecules is a prerequisite if we are to understand this critical and ubiquitous aspect of photo-induced reactions, and develop the theoretical language to describe it correctly. We expect that the AMO science community will lay the groundwork for understanding these key issues in chemical physics in general.

B. Key Types of Experiments Not within Our Current Reach

Fourth-generation light sources with their very short and intense photon pulses will open the door to investigate (1) attosecond and femtosecond time-resolved probing of excitation, ionization, relaxation, and molecular dissociation, (2) multiphoton-driven processes and nonlinear x-ray optics, and (3) dilute targets. While hard x rays are well suited for probing atomic positions and structure, soft x rays are better tools for investigating the dynamics of the driving processes and thus the function of each participating particle in atomic and molecular reactions.

(1) *Femtosecond and attosecond dynamics—the need for short pulses*

Only the first tentative steps towards probing electronic motion on its own time scale are being taken experimentally at this time, mostly with high-harmonic-generation techniques [2,3,4]. However, there is a growing theoretical literature in AMO physics that is suggesting novel experiments to both probe and manipulate correlated electrons that are currently beyond practical reach. For example, Hu and Collins [5] have proposed a class of attosecond pump–probe experiments, the simplest case of which is shown in Figure 1. A UV pump pulse places a target atom or molecule in an oscillating wave-packet of excited states and an intense, 250-as XUV probe is used to doubly ionize the

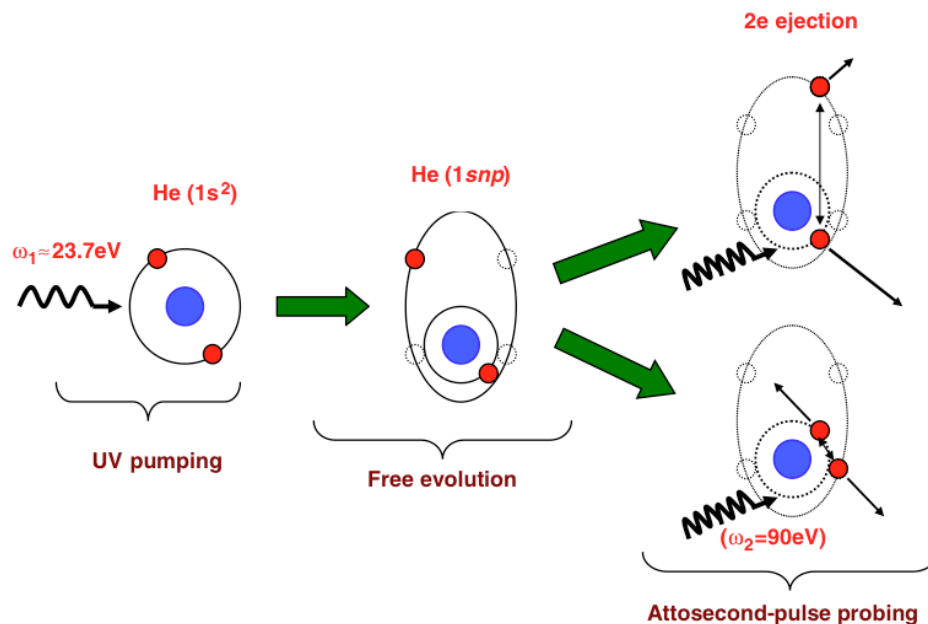


Figure 1. UV pump followed by XUV attosecond probe that preferentially doubly ionizes the excited target when the correlated pair of electrons is in closest proximity. From [5].

excited atom. Since one-photon double ionization is sensitive almost exclusively to electron correlation, the atom preferentially ionizes when the target electrons are closest together, and the variation in the double-ionization signal over a few-femtosecond delay maps out the oscillations of the excited target wave-packet.

At the workshop C. D. Lin argued that experiments on the simplest test case for highly correlated electrons, namely the doubly excited states of helium, must measure the momentum distributions of pairs of electrons ejected by attosecond pulses in order to directly reveal the correlated motion of the electrons [6]. Figure 2 shows such a pump-probe scheme. With the new class of light sources under discussion at this workshop, such experiments could be performed more easily with intense, attosecond soft x-ray probes, which would also address other, more complex, targets.

The initial steps of molecular dynamics following the excitation of a polyatomic molecule to a high-lying electronic state have to be very fast to compete with fast quenching processes, such as inter-shell relaxation, autoionization or dissipative processes related to the environment. In most cases, the electronic and molecular degrees of freedom are coupled and the molecular dynamics is non-adiabatic. As an example, photoinduced cis-trans isomerization represents one of the simplest means for converting photon energy to mechanical motion, and such processes are ubiquitous in biological systems. Ethylene is one of the smallest molecules in which this process can be studied both experimentally and theoretically in detail, and it may serve as a paradigm within which the isomerization photochemistry and photophysics of larger unsaturated hydrocarbons can be understood. The possible experiment on this prototypical system is to excite a substituted ethylene molecule to the V or Z-states with an intense

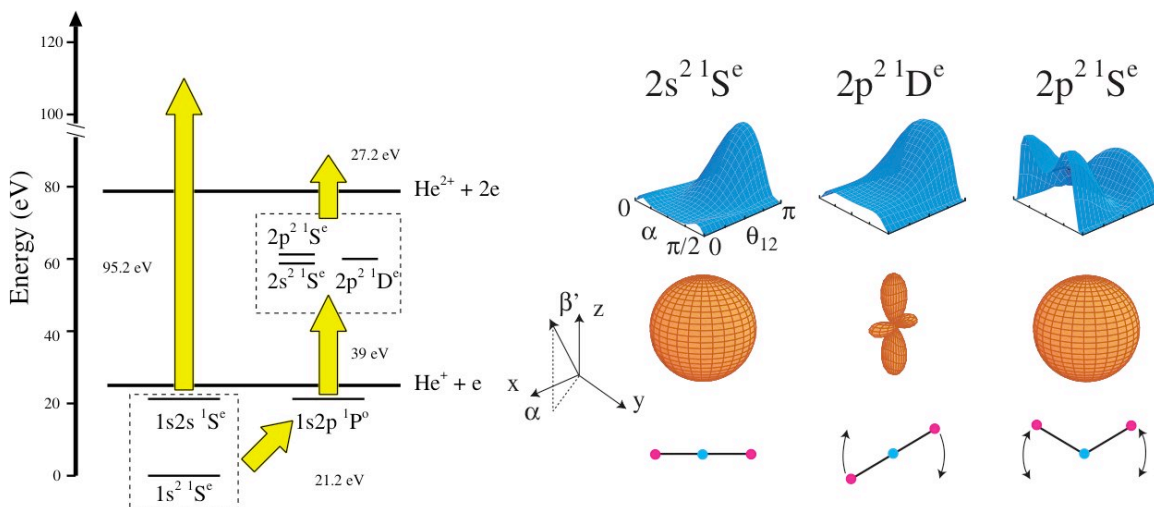


Figure 2. Pump–probe scheme for mapping the correlated motion of the doubly excited states of helium.

femtosecond UV source and use a femtosecond soft x-ray pulse to probe the coupled electronic and nuclear motions as a function of the time delay between the UV/VUV pump and soft x-ray probe. A variety of tools developed by the AMOS community, such as high resolution photoelectron spectroscopy, momentum imaging, COLTRIMS, and core-hole probing, can be used to completely characterize coupled electronic and nuclear motions, especially in the vicinity of the passage through conical intersections shown in Figure 3, taken from [7]. Similar studies can be extended to the highly excited cationic states of small molecules, such as cyanide, acetylene and ethylene, where a manifold of states can be coherently excited with an attosecond XUV pulse and probed with soft x rays.

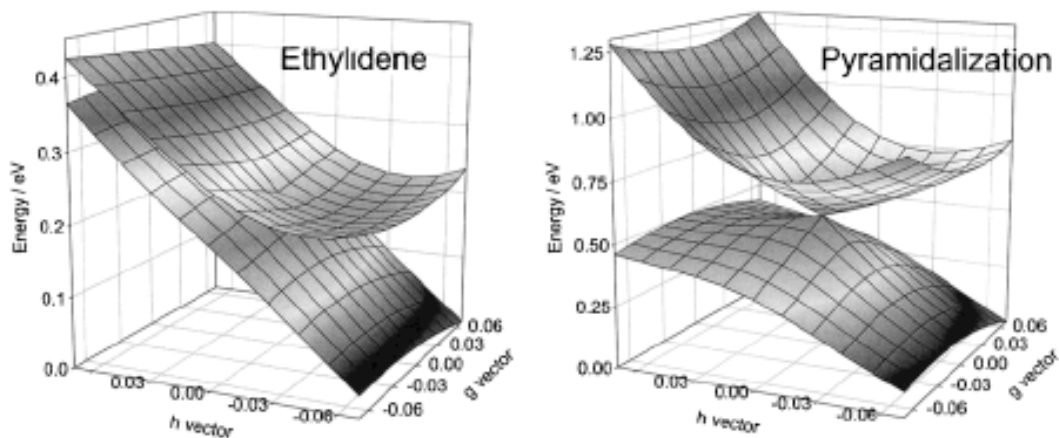


Figure 3. The ground and first excited electronic states of ethylene, computed using the SA-2-CAS(4/7) wave function as a function of displacement along the g and h vectors. All other coordinates are kept at their values at the ethyldene (left) or pyramidalized (right) conical intersections. The ethyldene conical intersection has a sloped topology, while the pyramidalization conical intersection is more strongly peaked. From [7].

(2) *Multiphoton experiments in the soft x-ray—the need for high peak intensity*

Light sources with high peak brightness will open a pathway to study, for the first time, nonlinear processes in the x-ray regime. Multiphoton physics in the short wavelength regime will differ considerably from the optical high intensity regime. One of the major differences is that in the optical regime, multiple ionization (by an intense IR source, for example) removes the most weakly bound electrons first, followed by more tightly bound ones. By contrast, in the x-ray regime the largest cross sections are for ionization of the inner-shell electrons, and more weakly bound electrons are ejected by other processes, like Auger decay. With high peak power, one can access a regime where Auger processes and x-ray absorption start competing. A natural question to ask is whether that leads to enhanced double-core-hole formation? A typical experiment will use an atomic target such as neon or a two-center target such as N_2 to investigate double core-hole creation.

Also in this intensity regime, the competition of sequential and non-sequential multiphoton double ionization may yield unique information on electron-correlation that is not accessible through single-photon double ionization.

Two-dimensional x-ray spectroscopy was discussed in Section II in the context of its potential application, were it to become a reality, to complicated polyatomic targets [8]. A principle difficulty with the premise of these proposed experiments is that they involve the creation of core holes, which have a lifetime determined by the time scale of Auger decay, typically of the order of 8 fs. Even with the fastest sequence of four pulses that one might imagine, shown schematically in Figure 4, such experiments would be difficult to realize. However, variants of this idea, involving stimulated inelastic x-ray scattering, are being considered that might not suffer from these intrinsic limitations. Those discussions started at the workshop and are ongoing [9]. It will be in small molecules, in the context of AMO gas-phase experiments that these techniques will be first developed, if they are to be realized at all. The search for useful nonlinear x-ray spectroscopies in the soft x-ray region is an ongoing effort, and if it is successful, they will play a central role at new light source facilities.

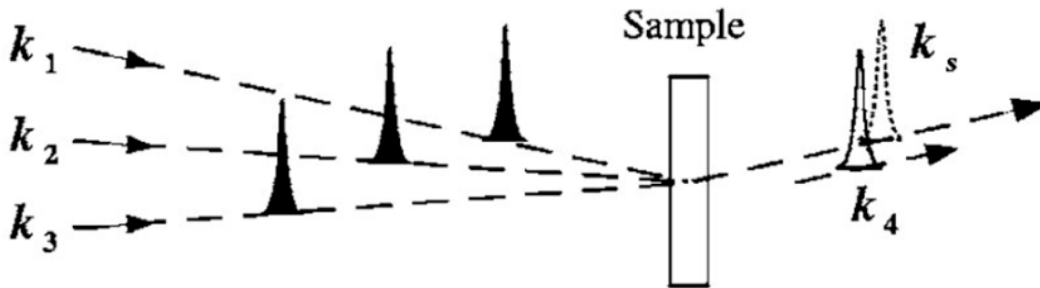


Figure 4. Schematic of an x-ray four-wave-mixing experiment to realize two-dimensional x-ray spectroscopy.

(3) ***Dilute samples and small cross-sections—the need for high integrated flux***

Photoionization studies of some of the most abundant species in the universe such as cations or chemically important species such as anions are very scarce because of the low densities associated with these species. High integrated flux coupled with high resolution will open a complete new field of detailed studies that can parallel work done with neutral species. Kinematically complete experiments and photoelectron spectroscopy studies can be performed on a variety of anions and cations with a level of detail never before thought achievable. A typical set-up will couple an ion trap with state-of-the-art multi-parameter detection and momentum-imaging techniques. These will open a complete new field where new benchmarks can be set and new theories tested.

C. Requirements of a New Soft X-Ray Source to Meet These Challenges

(1) ***Source requirements***

To achieve the stated scientific goals, the AMOS community envisions the following capabilities for a fourth generation light source.

- **Pulse length and brightness.** To meet the scientific goals mentioned above very stable short-pulse photon beams of high brightness and peak intensities are indispensable; for instance a photon intensity of $>>10^{17}$ W/cm² will be needed to study strong nonlinear effects. In the attosecond-pulse range, $>>10^{13}$ photons/s are needed, while in the picosecond-pulse range a much higher flux ($>>10^{17}$ photons/s) is needed to study very dilute targets.
- **Energy range and purity.** The new light source should cover an energy range from 13.6 eV (hydrogen) to about 1000 eV (neon) and has to operate with a very high repetition rate (>100 kHz) in order to make coincidence experiments feasible. A good spectral purity is essential, since the cross sections for multiphoton absorption is on the order of a few percent and thus contributions of high harmonics in the photon beam can be detrimental.
- **Focus.** The foci should be as small as $1\ \mu\text{m}^2$, while the focal points are expected to be 1.5 to 2 m after the last beamline valve (not closer since differential pumping stages in front of the experimental apparatus will be an important part of any setup).
- **Pulse shape and pump–probe capability.** The experimenters hope for individual control over the pulse length and shape as well as the polarization of the beam (linear and circular). Two color pump–probe pulses x-ray/x-ray and IR/x-ray on an attosecond-time range or IR/IR/x-ray sequences to actively align molecules in three dimensions are needed.

Table 1. AMO Science Requirements for a New Soft X-Ray Source.

Property	AMO Requirements	Comments
Energy range (eV)	10 – 1000	Emphasis on tunable up to 1000 eV.
Repetition rate (kHz)	100 or higher	Coincidence measurements require high rep rate.
Power (W/cm ²)	10 ¹⁶ –10 ²¹	High power for dilute targets (0.3 GW peak power for attosecond pulses). Otherwise 1 Ionization event per shot for coincidence.
Intensity stability	5%	Intensity should be recorded shot by shot.
Pulse length	picosecond femtosecond (10-100) attosecond (100)	The shorter, the better. Attosecond pulses need at least >10 ¹⁰ photons/s.
Harmonics	< 0.1 %	As low as possible (third higher harmonic is a problem for low energies): Filter elements needed.
Spot size (μm)	~1	Tunable from 50 to 0.05.
Polarization	variable, linear/circular	Having the choice is desirable.
Energy stability (eV)	0.1 eV	High resolution not needed but some required.
Background signal	<0.1 %	Pure beams: any background hurts. Contrast 1:1000 desirable.

(2) Facility requirements

- **Number of end-stations.** Based on the experience with third-generation light sources and the FEL test facility FLASH in Hamburg/Germany, the beamlines should have open ports to host researchers with their custom made end-stations. Two to three ports or beamlines per undulator are desirable to allow longer setup-times and ensure that always two to three groups are ready to make use of the beam at any time. Stacking experiments in sequence should be possible as well, thus enough space for the experimental set-ups should be reserved.
- **Space issues.** Since the photon energy can be low (under 100 eV) beam dumps will be needed to avoid reflecting photons. They have to be at least 2 to 3 m away from the experiment.
- **Controls.** The FEL beamlines will need continuous attenuation (gas cell) and controllable apertures of different sizes to give the user control of the intensity of the photon beam.
- **Building requirements.** It is crucial that the experimental hall have a high stability in temperature (less than 0.3 F) and motion.
- **Position of the lasers.** The pump or probe laser should be fed-in toward the front of the beamline (not near the user end-station), and an alignment laser should be available for any beamline.

- **Safety concerns.** Enough space for moveable laser hutches/tents to cover the experimental end-station and fulfill laser safety requirements has to be ensured.

D. References

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IV. Magnetization and Spin Dynamics

A. The Frontier: Magnetism at Fundamental Length and Time Scales

Magnetism as one of the oldest scientific discipline is not only at the forefront of the emerging nanotechnology era [1], but within the current discussions about the “Grand Challenges for Science” to control matter and energy, the magnetic properties in solid-state materials play a major role.

While the very fundamental concepts of magnetism and the development of novel magnetic materials with unique characteristics are subject to intense research today, numerous technological applications, such as permanent magnets in electricity generation and use, hard drives, and read heads in information-storage technology as well as medical applications such as MRI, have become part of everyday life.

Only state-of-the-art synthesis capabilities, theoretical modeling and new analytical and characterization tools will ensure that basic scientific discoveries will continue to be made and developed into applications and devices in the future. For example, the giant magnetoresistance (GMR) effect—a large resistance change in metallic multilayers upon application of an external magnetic field—first observed by Gruenberg and Fert in 1988 was already used in commercially available hard drives fabricated by IBM less than 10 years later. The importance of the GMR discovery was recognized with the Nobel Prize in Physics in 2007.

Magnetism is of quantum mechanical origin and therefore experiments at fundamental length and time scales are needed to achieve a complete understanding. While fundamental length scales, such as magnetic-exchange length in magnetism can already be accessed to a large extent both experimentally and theoretically with a variety of techniques, the corresponding fundamental time scales down to the femtosecond regime can be approached only by means of optical-laser techniques; however, only very limited spatial sensitivity has been achievable. The underlying question—how magnetism behaves when both the fundamental magnetic length and time scales are approached—cannot be addressed today. This limitation prevents us at the moment from achieving a thorough understanding of basic magnetic behavior, such as the nature and origin of the exchange interaction.

(1) *Magnetic interactions*

Essential questions in magnetism can be addressed once fundamental magnetic length and time scales can be approached. This can be qualitatively understood by looking closely in the underlying magnetic interactions, which occur at various energy scales.

Magnetic behavior in matter is established by a number of competing fundamental interactions [2]. At the high-energy end (several eV), the Pauli principle, intra-atomic exchange, and Hund’s rules establish the atomic magnetic moment. The development of quantum mechanics at the beginning of the twentieth century contributed significantly to

their knowledge and understanding, and their general features have been established in great detail by atomic spectroscopy.

At a lower energy scale—the 100-meV range or (in units of magnetic field) the 100-T range—comes the inter-atomic exchange interaction Γ , which is also of quantum mechanical origin. It is short ranged and favors, in some particular circumstances, a parallel alignment of neighboring magnetic moments even against the Pauli principle which would generally prefer anti-parallel alignment.

Additional fundamental interactions relevant for determining the magnetic state of matter are the quantum mechanical spin-orbit coupling-induced magnetic anisotropy λ and the classical dipolar interaction Ω , which is already included in the classical Maxwell equations of magnetostatics. These two interactions are much weaker—of the order of the 1 meV (about 1 T)—but are in competition with Γ and therefore relevant at suitable spatial and time scales. More precisely, $\sqrt{\Gamma/\lambda}$ is the spatial length scale (in units of the lattice constant) at which a magnetic domain wall is established, typically around 10 nm. The dipolar length determines the size of magnetic domains and depends on the geometry of the sample [e.g., in thin films, it is of the order of Γ/Ω (some 100 nm)]. Dipolar fields therefore dominate spin motion occurring on spatial scales that are comparable to the domain size—including the motion of the domain wall, which is driven by a tiny imbalance of dipolar fields within the wall itself. To connect to characteristic times associated with this motion one has to multiply these dipolar fields with the gyromagnetic ratio and thereby arrive at a few hundred picoseconds.

The theoretical description of these experiments is generally done within a continuum theory of micromagnetism, e.g., applying the Landau–Lifshitz–Gilbert equation of motion. However, a femtosecond excitation brings the magnetic system in a highly non-equilibrium state, where thermodynamic continuum approaches are not expected to work. At these time and energy (few eV) scales, new theoretical developments are direly needed.

It is important to stress the likely importance of new theoretical efforts that complement the experimental results probed by the new machine. For example, it is desirable to use the new femtosecond measurements of magnetic systems to push fundamental theories of magnetism to the next level. Moreover the development of predictive tools that probe the time-dependent response will be important both in analyzing the data and in interpreting femtosecond-scale phenomena.

(2) *The importance of soft x rays*

Currently, only the length and time scales associated with low-energy interactions can be accessed by state-of-the-art time-resolved soft x-ray microscopies with sub-100-nm spatial and sub-100-ps temporal resolution available at today's synchrotron facilities. However, the limited flux of current synchrotron facilities poses a severe limitation on these experiments: They can only be performed in a stroboscopic pump–probe scheme,

which requires that the spin-dynamics process has to be perfectly reproducible or else one can detect only the time- and space-averaged component of the spin dynamics.

A future femtosecond soft x-ray source will enable us for the first time to

- observe
- understand, and
- control

magnetism and magnetic response with both femtosecond temporal and nanometer spatial resolution simultaneously.

The importance of soft x rays for magnetization dynamics studies arises from the fact that experiments at the transition metal L edges and rare-earth M edges probe the dipole-allowed $2p \rightarrow 3d$ and $3d \rightarrow 4f$ transitions of the $3d$ and $4f$ valence states that largely determine the magnetic properties of transition metals and rare earths, respectively. The difference between the absorption of left and right circularly polarized x rays can be up to 100%, rendering this technique extremely sensitive to even subtle changes in magnetic moments. Element specificity and chemical-site sensitivity are intrinsic to x ray absorption spectroscopies and allow separating the contributions of multiple magnetic species in complex magnetic systems. Most importantly, theoretically derived sum rules link dichroism intensities to spin and orbital magnetic moments as well as magnetocrystalline anisotropy energies, i.e., sum rules make the use of x rays for quantitative magnetometry possible. It is the uniqueness of these simultaneously accessible features when using soft x rays that give them advantages over any competing technique such as neutron scattering.

B. Key Types of Experiments Not within Our Current Reach

(1) *Non-deterministic magnetization processes on sub-100-nm spatial and sub-100-ps time scales*

At the mesoscopic spatial scales and the corresponding times described above, where quantum mechanics meets classical physics, a string of spectacular recent pump-probe experiments, which to a large extent have been pioneered at the ALS by various groups (e.g., J. Stöhr [3], A. Scholl [4], P. Fischer [5], and many others), have produced a very accurate picture of the spin motion. Our knowledge of magnetism is therefore well advanced on these scales.

However, on these spatial and temporal scales, there are further classes of phenomena that do not exhibit a deterministic behavior, such as the motion of a domain walls (e.g., after spin injection [6]) and the dynamics of other types of topological excitations and magnetic singularities [7, 8]. Non-deterministic processes also appear when the magnetic probe is subject to the extremely strong magnetic fields required to reduce the precessional switching time [9]. Yet it is just such kinds of phenomena that are really happening in practical situations related to magnetic recording or to magnetic logical

applications. The understanding of this kind of processes on a 10-ps time scale and with 100-nm resolution is potentially crucial for real applications and requires the single-shot or near-single-shot experiments that are envisaged with the new class of soft x-ray light sources discussed here.

(2) *Dynamics of spin structures requiring few-picoseconds time and sub-10-nm spatial resolution*

A scientifically challenging but experimentally completely unresolved problem is the evolution of the internal spin structure of domain walls or similar topological singularities during their motion. This is an intricate problem that depends on the actual driving force (Oersted field versus spin torque) and whose resolution would clarify in detail the relevance of both mechanisms during the motion. Imaging of these processes requires a few-picoseconds temporal resolution and about 10-nm spatial resolution, again in a single-shot mode.

(3) *Magnetism at the time and length scale of exchange interaction—few nanometers and sub-picosecond*

Length and time scales related to the interatomic exchange interaction Γ are completely unavailable at present synchrotron sources. Here, nanometer length scales and—most important—a time scale of the order of \hbar / Γ in the sub-picosecond regime is required [10]. Magnetism in these ranges of space and time is completely unknown and its study represents the most important challenge of future experiments with the new class of soft x-ray light sources. It will lead to fundamentally new insights into pure quantum mechanical phenomena, which might revolutionize the physics of today.

It is known, for example, that electrons passing through a magnetic materials change their spin polarization in analogy to the Faraday effect of optics [11]. It is speculated that this is made possible by transferring some spin torque to the target electrons via the exchange interaction. Similar experiments where spin torque is relevant must work with the same rules. Unfortunately, it is not at all known how this angular momentum is transferred and in particular how this transfer evolves with time. It is obvious that the transfer has to be related to the exchange time scale. It can be anticipated that the next class of soft x-ray sources might be able to go beyond the exchange time scale, thereby providing a new tool to probe the time evolution of the exchange process itself.

C. Observation and Control in Magnetization and Spin Dynamics

(1) *All-optical control of spin and magnetization dynamics—few nanometer and subpicosecond*

The control of magnetism by light is one of the most spectacular developments in ultrafast magnetization dynamics. As the essence of magnetism is angular momentum, using circularly polarized light, which also carries angular momentum, might lead to direct optical control of spins. Recently it was indeed shown that, owing to the inverse, opto-magnetic Faraday effect, circularly polarized femtosecond laser pulses can excite and coherently control the spins in magnets [12]. Although previously believed to be

impossible, even the reversal of magnetization by a single 40-fs circularly polarized laser pulse was achieved without any applied magnetic field [13]. The direction of this opto-magnetic switching was unambiguously set by the helicity of light. In all these experiments the effect of a circularly polarized ultrashort optical pulse on a magnetic system was found to be equivalent to the effect of an equally short magnetic field pulse with strengths up to 1 T, thus demonstrating that an opto-magnetic pulse can be used as a fundamentally new stimulus of magnetism with a huge potential to bring the control of magnetization down to femtoseconds.

Nevertheless, there are still many fundamentally intriguing issues to be answered on the way to real applications of opto-magnetic phenomena and a “THz opto-magnetic revolution” in magnetic recording and information processing (see Figure 1). Particularly,

- Laser control of magnets whose sizes are smaller than the wavelength of light raises many intriguing questions at the junction of nano-photonics, magneto-optics and nano-magnetism. Future magnetic recording bits should be at most $300 \text{ nm} \times 300 \text{ nm}$. How will light interact with spins in such nano-magnets and what will be the distribution of the laser-induced magnetic field at the nanoscale?

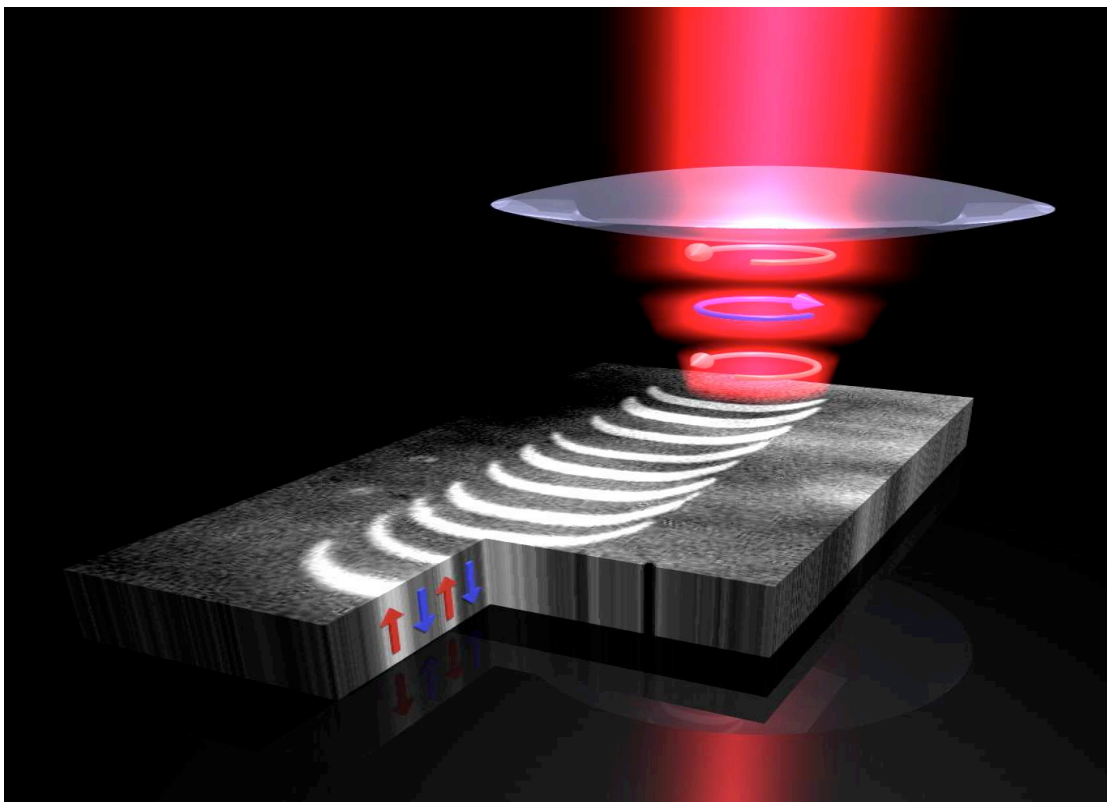


Figure 1. All-optical magnetic recording with 40-fs circularly polarized laser pulses [13]. Recording was achieved by scanning a circularly polarized laser beam across the sample and simultaneously modulating the polarization of the beam between left- and right circular. The size of the recorded domain is $5 \mu\text{m}$. Can such an all-optical switching operate at the nanoscale?

- The excitation with femtosecond laser pulses puts a medium in a highly non-equilibrium state, where a conventional description of magnetic phenomena in terms of thermodynamics is no longer valid. Therefore the phenomenon of ultrafast magnetization reversal is poorly understood.

In order to address these basic questions that are also highly relevant for possible future applications, new experiments and theory are needed. The new-generation light sources may provide the ideal combination of necessary time resolution (femtosecond), spatial resolution (nanometer), and atomic and spin sensitivity.

(2) Terahertz radiation and magnetism

Very recently, it has been recognized that terahertz radiation is an ideal tool for the study of spin dynamics, essential for the basic understanding of magnetism and its technological applications [14, 15, 16]. Ultrafast changes of the magnetization induced, e.g., by a laser pulse, will lead to the emission of terahertz radiation that probes the time dependence of the spontaneous magnetization [16, 17]. Moreover, terahertz radiation can also be used to induce changes in the magnetic structure and electronic properties of a magnetic sample. In experiments at the SLAC FFTB facility, Gamble et al. have shown that the terahertz radiation accompanying compressed highly relativistic electron bunches can be used to insert large electric and magnetic fields into metals [18]. Their yet unpublished results testify to the truly unique possibilities that open up for the study of solid materials probed with short x-ray pulses after excitation with terahertz radiation. This stunningly simple experiment yielded the first clear evidence of a new type of magnetic anisotropy, generated by an **E**-field-induced distortion of the valence states. More generally, the electromagnetic field led to multiple ultrafast switching of the magnetization and, moreover, modified the electronic structure.

Applications of magnetic materials are based on the control of magnetic anisotropies, in particular the creation of suitable atomic arrangements to manipulate the magnetic anisotropy energy. It is safe to predict that in future applications, pulses from terahertz lasers can replace the relativistic electron bunches and thus terahertz radiation will be one of the primary tools for the study and application of ultrafast magnetization switching and spin dynamics. X-ray circular magnetic dichroism, on the other hand, is the most powerful tool to dynamically probe the changes of the electronic and magnetic structure induced by terahertz radiation [19].

The SLAC experiment

As shown in Figure 2, a powerful electric and magnetic field pulse rivaling the field acting on valence electrons is created in a thin film of magnetic metal by a relativistic electron beam traversing the sample. The **E**-field penetrates into the metal because relativistic contraction has forced the field into a flat disk parallel to the surface. Such electromagnetic field pulses of 100-fs to 2-ps duration are very similar to half-cycle pulses of terahertz photons [14]. In this case, it is equivalent to a pulse of terahertz radiation of frequency ~ 10 THz.

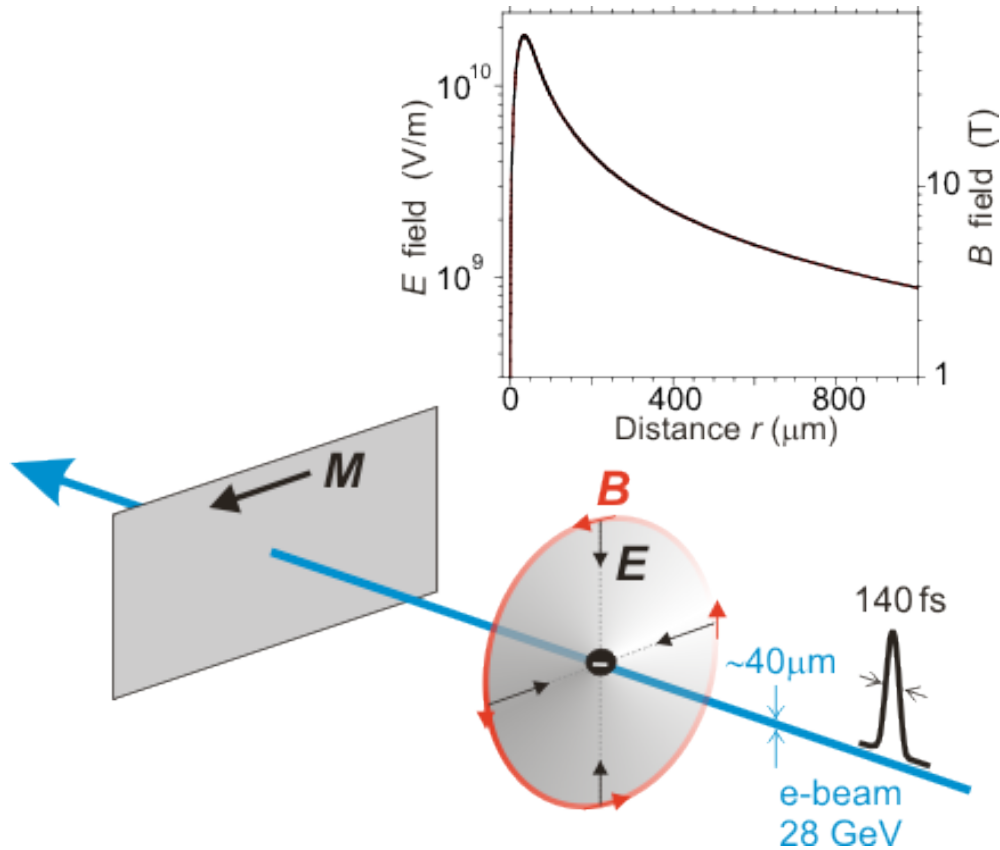


Figure 2. Injecting an electric field into a metal is possible with a pulse of terahertz radiation or here equivalently with an electron bunch. One electron bunch of 28-GeV energy per electron traverses a thin metallic ferromagnetic film perpendicular to the surface. The magnetization M is initially set uniformly as shown. The electron bunch of Gaussian half width τ (standard deviation) has a duration of $\tau = 70$ fs in the laboratory frame. The electric field E and the magnetic field B are perpendicular to each other and are relativistically contracted to a flat disk perpendicular to the beam as shown. The inset shows the E - and B -field strengths versus distance from the beam center using the longitudinal, $\tau = 70$ fs, and transverse, $\sigma_r = 20 \mu\text{m}$, Gaussian standard deviations corresponding to the conditions of the experiment with the compressed pulse.

Using spin precession as a diagnostic tool, the experiments observed the generation of a large new type of magneto-electronic anisotropy in a ferromagnetic thin film subjected to such ultrafast (70 femtoseconds) and ultrastrong ($\geq 10^9$ V/m) electric field pulses (see Figure 3). The E -field induced anisotropy can lead to switching of the magnetization in a thin film. In the experiment, the resulting anisotropy field led to a spin precession (in addition to the one introduced by the magnetic field alone) that was detected in the magnetic switching pattern. This pattern was recorded in the film and could be read out long after the bunch had passed with a magnetic-imaging technique.

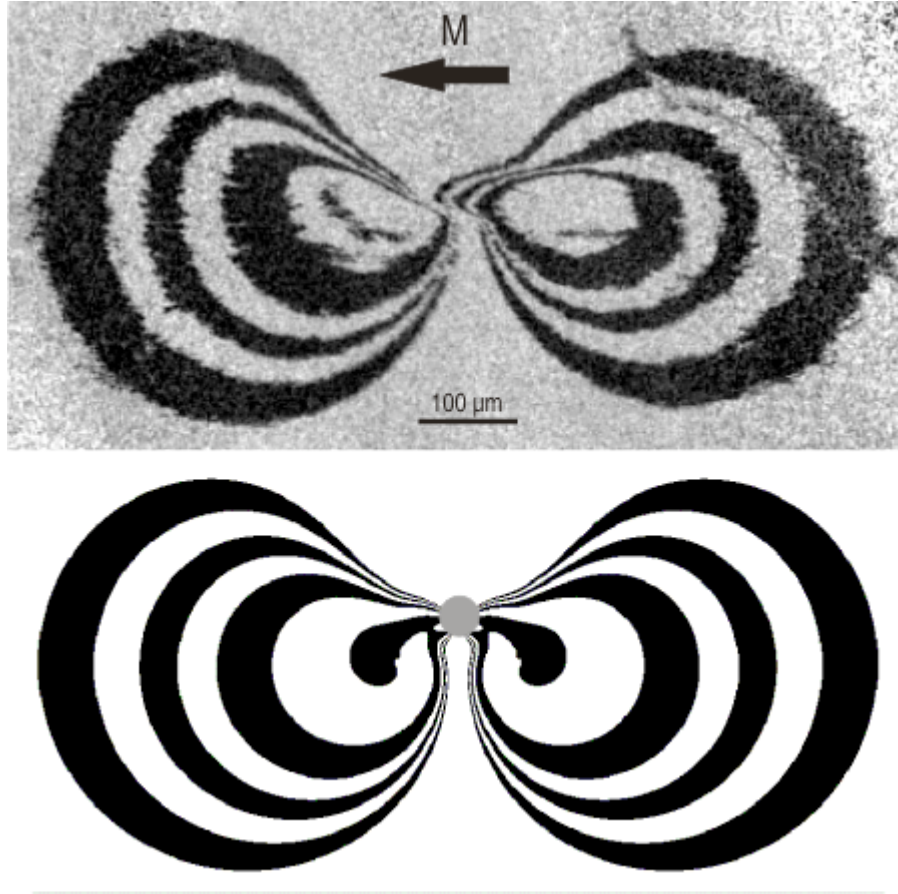


Figure 3. Experimental (top) and calculated (bottom) magnetic patterns for a single compressed electron bunch of $\tau = 70$ fs that traverses the thin film sample along the surface normal. The experimental pattern was recorded by spin sensitive scanning electron microscopy (SEMPA). In the light gray regions, M points into the preset direction as shown, while in the dark regions M has switched into the opposite direction. The lower pattern is calculated with the Landau-Lifshitz-Gilbert (LLG) equation, including the torque generated by the anisotropy field induced by the E-field of the bunch. This pattern reveals the characteristic flattening of the upper switching boundaries, created by the presence of the E-field inside the metallic sample. The location of beam impact and width of the bunch is indicated in gray.

The experimenters also observed the ultra-fast manipulation of the electronic and magnetic structure of a metal by electric-field pulses created in the scheme shown in Figure 2. Analysis of the magnetic and topographic images of exposed samples revealed the absence of heating in a ferromagnetic thin film subjected to the ultrafast and ultra-strong electric fields. For this experiment two different temporal pulse lengths were used: $\tau_1 = 2.3$ picoseconds and $\tau_2 = 70$ femtoseconds. The pattern produced by the longer pulse clearly heated and damaged the sample, as shown in parts A and B of Figure 4, while the pattern produced by the shorter pulse left the sample remarkably damage free, as shown in parts C and D of Figure 4.

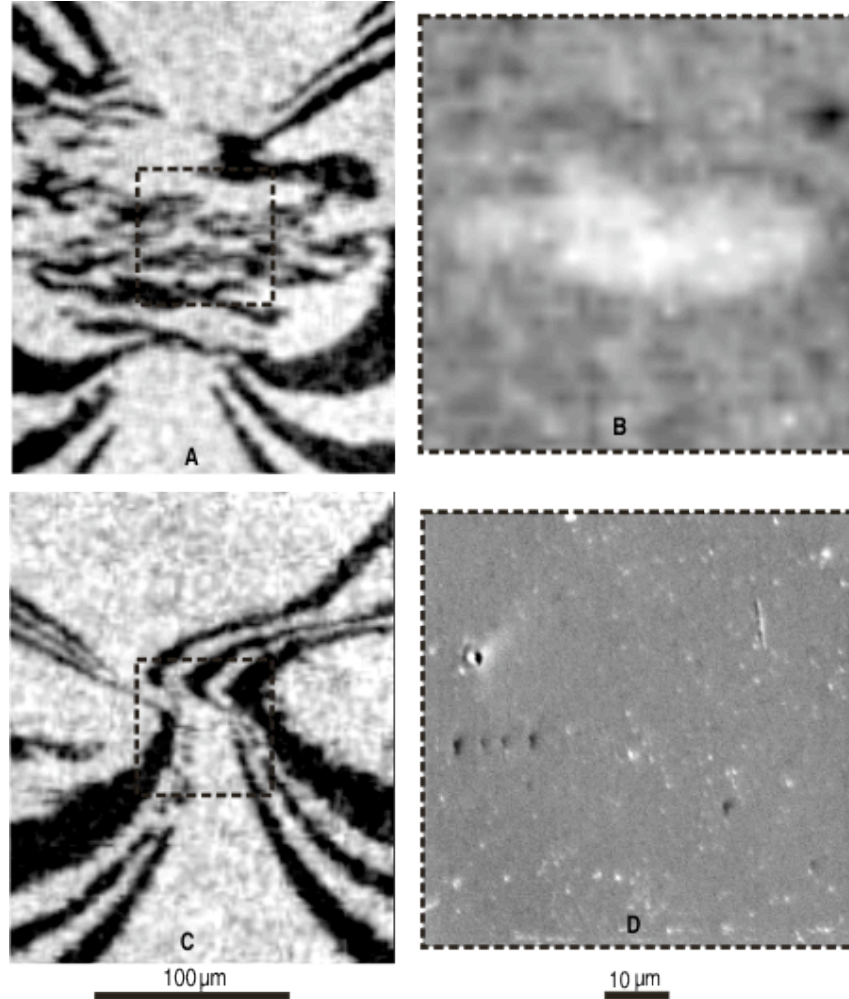


Figure 4. Magnetic (A, C) and magnified topographic (B, D) images of the sample close to the beam impact point for the longer τ_1 (A, B) and shorter τ_2 (C, D) electron bunches. The images are taken with a scanning electron microscope with spin polarization analysis (SEMPA), which can be operated for magnetic or topographic contrast. With the τ_1 electron bunch, irregular magnetic domains indicate that the sample has been heated to $T \geq T_C$ (where T_C is the Curie temperature) in a region of $200 \mu\text{m}$ at the point of beam impact, and the topographic image reveals ablation of the sample within the beam impact area. With the τ_2 bunch (C, D), no random domains indicative of heating are observed, and there is no topographic modification of the sample. The topographic images (B, D) cover the marked region of the magnetic images.

The heating in the case of the longer τ_1 bunch is due to electron–phonon collisions, while the absence of heating with the τ_2 bunch must be due to the lack of energy transfer from the electron gas to the lattice due to the short duration of the electric-field pulse compared to the electron–lattice equilibration time. By probing the electronic structure with short bursts of circularly polarized x rays (XMCD) as demonstrated in [20], it will be possible to observe and understand the transient electronic structure induced by the terahertz fields.

(3) Utilizing new experimental capabilities: x-ray/optical pump with x-ray/optical probe

Optical and x-ray spectroscopic methods are characterized by different sensitivity to spin and orbital degrees of freedom and different time and spatial resolution. Therefore, a combination of these techniques should provide complementary information about the ultrafast laser-induced changes in magnetic systems. In particular, many of the magnetic systems of interest are alloys or complex oxides containing a variety of both rare earth and transition metal elements [21]. X-ray probing of femtosecond optical excitation will provide both elemental selectivity as well as a means to separate spin and angular contributions to the magnetic moments.

(4) Response of localized vs. itinerant magnetism

All-optical control and even switching of magnetization has been observed in a variety of systems, including ferromagnets, ferrimagnets, and anti-ferromagnetic systems [12, 13, 21, 22, 23, 24]. However all these systems contained a certain percentage of rare earths. It has been demonstrated that despite their very deep-lying energy levels, the Gd 5f electrons for example play an important role in the optical manipulation of the magnetization in GdFeCo. But it is unclear how this works. Also, it is not known whether optical control can only be achieved via localized moments or do the itinerant transition metal electrons also play a role. Finally, can optical control be achieved in itinerant magnets?

(5) Experiments targeting magnetization far from equilibrium

The fundamental relaxation processes between electrons, phonons, and magnons in solids are still unresolved. Their understanding would represent a major achievement in solid-state physics and would help to clarify the fundamental limits in thermally assisted data-writing processes.

When a short laser pulse hits a solid, its energy is absorbed initially by the electrons in the solid. This first excitation step drives the electronic system out of equilibrium with respect to the other subsystems of the sample. Figure 5 shows the measured evolution of the electronic temperature following a 50-fs laser pulse excitation for two different initial sample temperatures [25]. The dashed lines represent the evolution of the lattice temperature. Electron and lattice equilibrate only 400 fs after laser excitation and are different for shorter time delays.

For intense laser-pulse heating it might even become difficult to assign a fixed temperature to the different subsystems of the solid, since non-thermal energy distributions can occur during the excitation process [26]. Magnetic properties depend on temperature as well, and the magnetisation of a magnetic solid vanishes at its Curie temperature. The open question is whether the temperature driving the magnetic behavior follows the lattice temperature or the electronic temperature or whether magnetism has its own dynamics. Early experiments suggested that the magnetization follows its own dynamics [27]. Later it was observed that fast demagnetization is possible [28] but that its

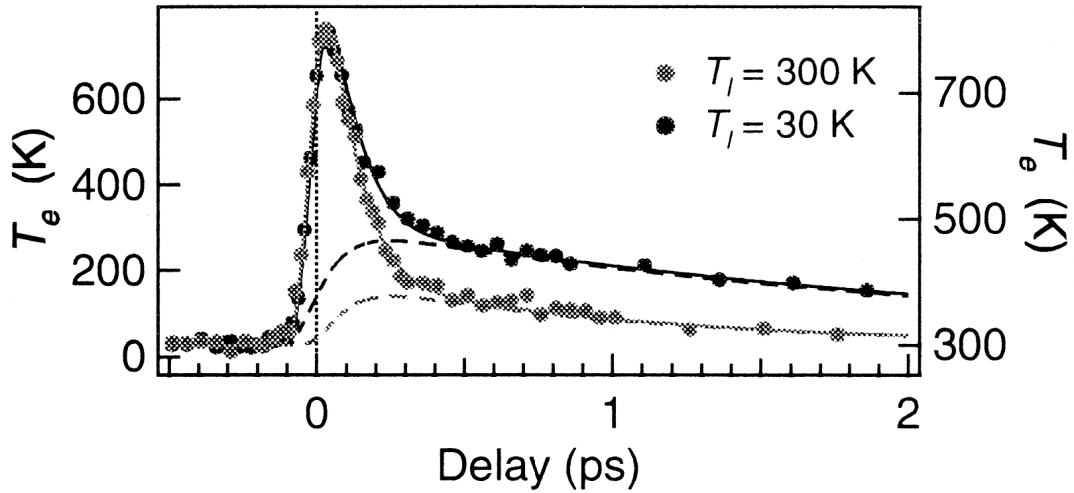


Figure 5. Time evolution of the electronic temperature for two different initial lattice temperatures T_l . (black marks, left axis; grey marks, right axis) [25].

recovery (cooling down) is slow compared to the electronic system and the lattice [26]. Figure 6 shows this fast demagnetization followed by the slow recovery through the binding energy shift of the majority spin states in Ni. The fast upward shift of the binding energy suggests the decay of magnetic order through the loss of exchange

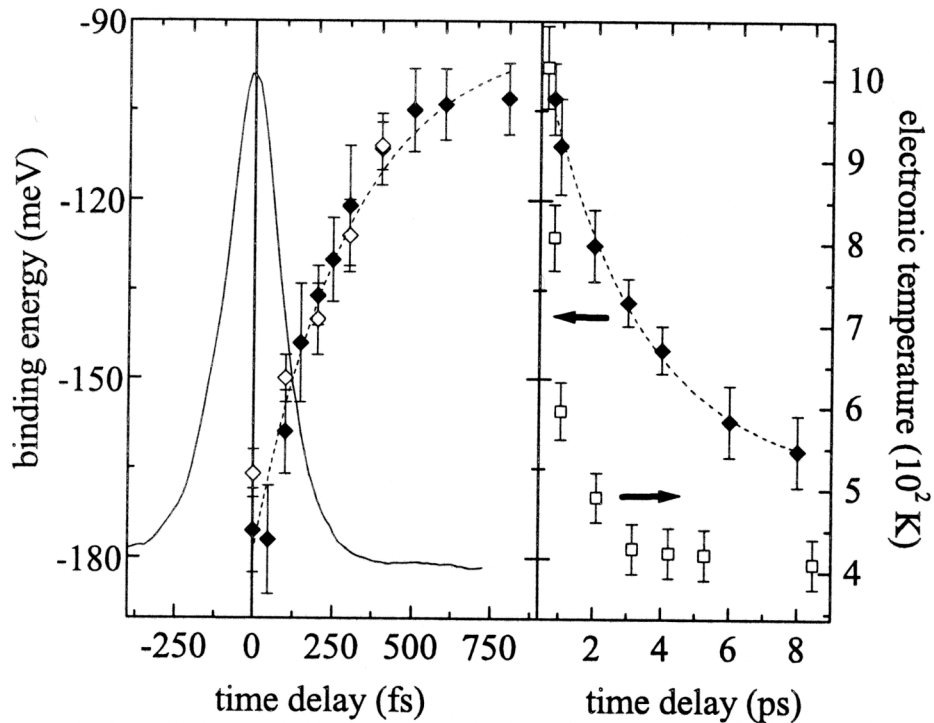


Figure 6. Temporal evolution of the binding energy of the majority spin states in Ni (diamonds) and of the electronic temperature (open squares) after laser pulse excitation [26].

splitting. This measurement is however not spin sensitive and probes only a very small fraction of the states in the band structure. Therefore it was not possible to pin down the cause of the change in exchange splitting.

Up to now we have had no way to follow the evolution of delocalized and localized electronic states on a short time scale. So far, optical methods [28], which depend on the band structure, and threshold photoemission [26], which detects only electrons close to the Fermi energy, were used to follow the effects of laser excitation. With short x-ray pulses it would become possible to probe band structure and total spin polarization during the excitation process. The combination of energy resolution and spin sensitivity would allow a complete tracking of the electronic and magnetic subsystems of a sample, thus opening the way to an unprecedented view of non equilibrium thermodynamics.

(6) Ultrafast dynamics of internal spin structures

Internal spin structure such as domain walls or topological singularities such as vortices in magnetic nanoelements are both scientifically challenging, but offer also technologically new perspectives. Domain walls are considered as elementary units (e.g., in advanced magnetic storage) or as a trapping device, owing to their spin structure. Vortex structures in nanoelements and their dynamics are interesting alternatives for THz storage devices. Studies of the domain wall and vortex dynamics currently are of great interest [3, 4, 5, 6, 7, 8]. Relevant length scales are in the sub-10-nm regime and the current (limited) approach by stroboscopic pump–probe can only provide information on the repetitive part of the process. A femtosecond, high-intensity soft x-ray source will allow imaging of these processes with sub-picosecond temporal resolution, sufficient photon intensity for single-shot mode, and less than 10-nm spatial resolution.

D. Requirements of a New Soft X-Ray Source to Meet These Challenges

The experiments that will utilize the new opportunities at a femtosecond soft x-ray laser source can be very diverse and therefore a multi-user facility would be of great interest.

With respect to the requirements of a new source the following key parameters for the new facilities are.

- **High intensity per pulse.** This will enable single-shot experiment to study, for example, non-deterministic processes of spin dynamics
- **Repetition rate.** Pump–probe experiments to study, for example, magnetism far from equilibrium will utilize high -power laser systems, and for these studies the repetition rate of the new facility should match the laser-excitation frequency. Synchronization between laser and x-ray pulses will be required.
- **Time resolution.** As outlined in the previous sections, spin dynamics at the new facility will explore many time scales ranging from a few tens of femtoseconds to picoseconds. The attosecond regime is probably at the moment of minor interest, since the core-hole lifetime in spectroscopies is the limiting time scale.

- **Detector development.** The opportunity of having a femtosecond soft x-ray source in combination with <10-nm spatial-resolution capabilities for advanced imaging techniques will require fast readout 2D detector. The current initiatives focused on detector development will be of high importance to the planned experiments at the next-generation facility.
- **Variable polarization.** The x-ray dichroism effect will be the essential contrast mechanism to study spin dynamics. Full control of the polarization characteristics at the femtosecond source will be crucial.

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V. Correlated Materials

A. The Frontier: Emergent Phenomena Due to Collective Behavior in Complex Materials

The next generation of soft x-ray light sources (NGLSs) will present an exceptional opportunity to address a grand challenge in condensed-matter physics: understanding, exploiting, and ultimately controlling emergent phenomena in complex materials. Meeting this grand challenge will have tremendous potential impact across wide areas of human endeavor ranging from: energy conversion, transport, and utilization; to information processing, storage and communication; to materials and nanostructures with engineered thermal, mechanical and electrical properties with myriad applications. One need only consider the remarkable impact of semiconductor technology on society over the past 60 years to get a sense of the even greater technological potential and importance that the broad class of complex materials will have for society.

At a fundamental level, emergent phenomena in complex materials are a consequence of collective behavior reflecting strong interaction among charges, and between charge, spin, orbital, and vibrational (lattice) degrees of freedom (Figure 1). Such phenomena challenge existing paradigms of condensed matter, two pillars of which are single-electron band structure models of crystalline solids, and the Landau theory for Fermi liquids. Furthermore, collective behavior gives rise to unique, unexpected, and technologically relevant properties, the two most prominent examples of which are unconventional superconductivity and colossal magnetoresistance.

By providing new quantitative probes of valence charge structure, atomic structure, material properties and correlated many-body excitations on fundamental time and length

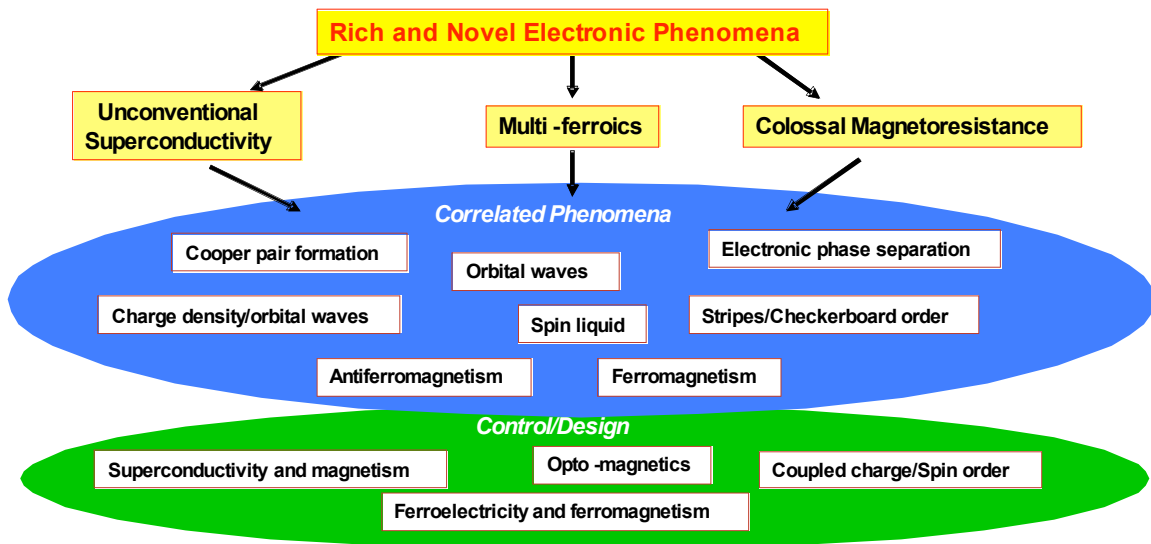


Figure 1. Strongly correlated electron materials are often realized in transition-metal-oxide and rare-earth compounds. Strong correlation often leads to enhanced properties such as superconductivity at high temperatures or a dramatic change of magnetic state.

scales, under non-equilibrium conditions, and through transient phase transitions [1, 2, 3, 4, 5], the next generation of x-ray light sources promises to revolutionize our understanding of complex materials and emergent phenomena. The powerful combination of atomic spatial resolution, elemental specificity, momentum resolution, meV energy resolution, coherence, and ultrafast time resolution will drive dramatic advances in our understanding, predictive capability, and technical control of the interplay between atomic and electronic structure in complex materials, including those incorporated into nanostructures and those under non-equilibrium conditions.

Among the multiple new approaches empowered by new sources that are essential to advancing our understanding of novel physical processes occurring in complex materials, workshop discussions covered both advanced time-resolved x-ray spectroscopic and scattering techniques and novel (for x rays) multidimensional and photon correlation spectroscopies.

B. Ultrafast Time-Resolved Spectroscopy and Scattering

The development of electronic correlations and their interplay with atomic structure is necessarily dynamic, ranging from the picosecond time scale characteristic of electron-phonon interactions, to the attosecond frontier that characterizes electron-electron correlation times. The importance of ultrafast time-resolved measurements in understanding these systems lies in the capability to drive them out of correlated equilibrium on time-scales shorter than the underlying correlations, and then disentangle the interactions by probing their time response as the correlation develops. Such studies are an important expansion beyond static (or time-averaged) measurements of material properties as a function of temperature, pressure, doping, magnetic field, isotope substitution etc. Moreover, the very nature of complex materials, where there is a delicate balance among various order parameters, means that perturbations from equilibrium can give rise to dramatic changes in material properties—an exciting prospect for effective manipulation and control of relevant properties.

An essential premise for scientifically relevant ultrafast studies of correlated materials is that the excitation be tailored (e.g., time scale, photon energy, pulse shape, coherence, vibrational coupling, charge-transfer excitation etc.) to drive systems out of equilibrium in a controlled and perturbative manner. This is critical in order to derive meaningful scientific information from dynamic experiments. To date, the study of ultrafast dynamics in complex materials has focused on transient changes in optical properties following perturbative, ultrafast optical excitation. Interpretation of the relaxation kinetics provides limited physical insight, since optical properties are only indirect indicators of the underlying structural dynamics. The next generation of soft x-ray light sources will enable advanced ultrafast techniques in x-ray range to achieve direct measurement sensitivity to changes in atomic structure and valence electronic structure.

Direct quantitative measurements of the atomic structure and electronic structure on the ultrafast time scale of the underlying correlations are indispensable for achieving new insight onto the physics of complex materials, nanostructures, and novel states of matter. It is also an instrumental step toward addressing the grand challenges: (i) to understand

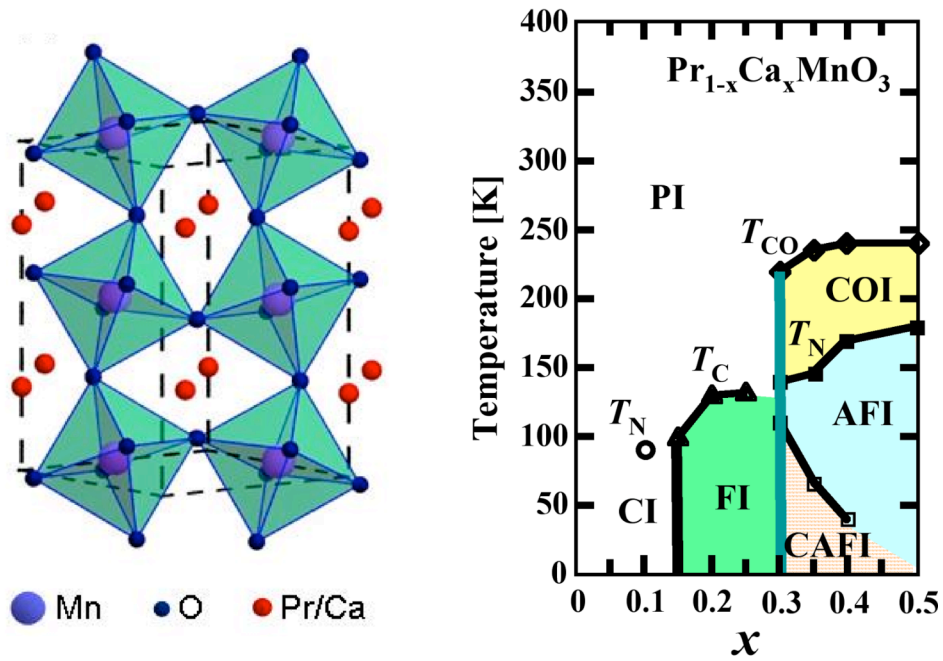
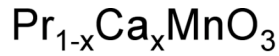
complex material systems out of equilibrium, and (ii) to ultimately use tailored excitation to control emergent behavior in complex correlated systems to achieve desired properties.

(1) Time-resolved x-ray absorption spectroscopy of complex materials

Ultrafast soft x-ray spectroscopy is an important emerging field of research for studying the evolution of valence electronic structure (bonding, charge distribution, spin/magnetic moment, orbital hybridization, etc.) in complex materials. Soft x-ray absorption probes valence states via transitions from localized core levels with well-defined symmetry, energy, and element specificity and is thus an essential complement to visible probes that measure the joint density of extended electronic states. Detailed information about dynamics of the valence charge structure in the vicinity of specific atomic species is provided by time-resolved XANES (x-ray absorption near-edge structure). Correlated phenomena in complex materials will be clarified both by separation in the time domain and by direct measurements of the essential material properties on a time scale short compared to the underlying correlations. Moreover, tailored excitations (e.g., charge-transfer, coherent vibrational pumping, and transient spin-waves) will be employed to provide substantially more insight to the physics underlying specific materials.

Time-resolved studies of the phase-transition dynamics in manganese oxides are one important illustrative example of the power of this approach. Manganites represent a compelling class of complex materials in which the transition-metal d electrons experience the competing forces of Coulomb repulsion (leading to localization and ordering) [6] and hybridization (delocalization) [7] that are ubiquitous in complex materials. The strong interplay between charge, spin, and subtle lattice distortions give rise to a rich phase diagram (see for example Figure 2), with dramatic changes in the structural, magnetic, and transport properties associated with striking correlation effects including charge and orbital ordering, stripe formation, spin-polarized half-metallicity, phase separation etc. [8]. In addition to the potential technological relevance of colossal magnetoresistance (CMR) [9], these systems represent an important and convenient testing ground for studying and understanding correlation phenomena relevant for a variety of related correlated materials, including high- T_c superconductors.

Important recent experiments demonstrate that in this regime, a first-order insulator–metal phase transition can be induced on the sub-picosecond time scale by: (i) coherent vibrational excitation of the Mn–O stretch and perturbation of the perovskite-structure tolerance factor [10, 11] in the electronic ground state [12] and by (ii) optical photoinjection of carriers into the COI state [10, 13, 14, 15]. Fundamental new insight to the underlying physics will emerge by using x rays to follow the electronic properties as they evolve during the course of the phase transition. The importance of time-resolved XANES in this context is illustrated in Figure 3, which shows preliminary measurements of the photo-induced insulator–metal phase transition (IMT) in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ at the O K edge, using picosecond x-ray pulses. The broadening of the pre-edge absorption and dynamic shift of spectral weight is attributed to the competition between the tetragonal lattice distortion and the charge dynamics, consistent with static XANES measurements



COI - charge ordered insulator
 PI – paramagnetic insulator
 AFI – antiferromagnetic insulator
 CA – canted antiferromagnetic

Figure 2. The crystal structure and complex electronic phase diagram [16] of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ where, at $x = 0.3$, a hidden ferromagnetic metal phase is accessed by a relatively modest magnetic field (CMR effect).

of the insulator and metallic phases of the related bi-layer manganite LSMO [17]. Present experimental capabilities illustrated here are clearly inadequate for revealing the details of this competition as it develops, owing to limitations of current ultrafast soft x-ray sources. The unprecedented average flux, tunability, and temporal resolution of next-generation sources will have a dramatic impact on our understanding of manganites and complex materials in general by enabling such studies with <100 -fs temporal resolution and <100 -meV energy resolution.

(2) *Time-resolved x-ray dichroism in complex materials*

The application of x-ray dichroism spectroscopy on the ultrafast time scale will be essential to understanding magnetic-ordering phenomena that often play a central role in the physics of complex materials, including CMR manganites, high- T_c superconductors, multiferroics, dilute magnetic semiconductors, nanostructures, and many others.

Following magnetic phase transitions, magnetization dynamics, and the flow of angular momentum in real time will lead to new insight into multi-critical emergent phenomena.

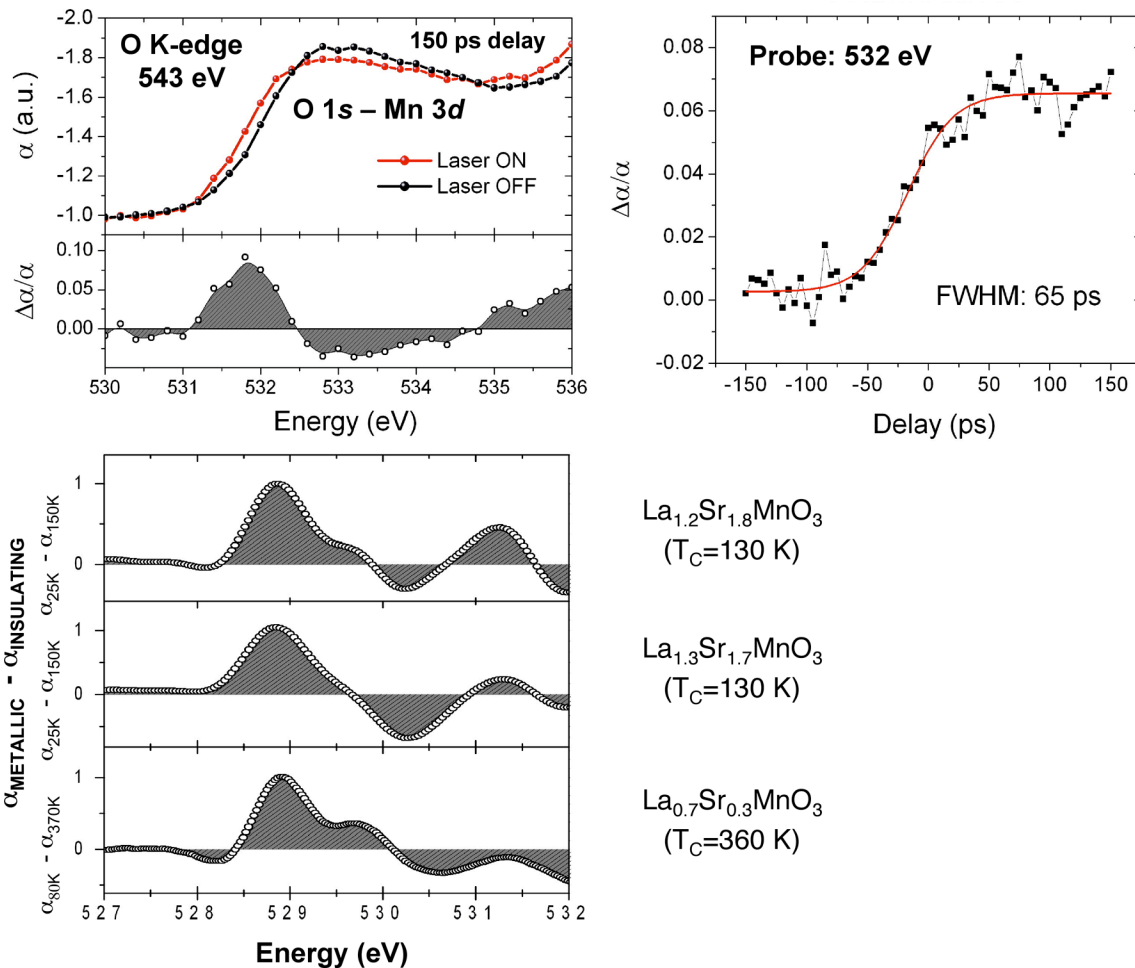


Figure 3. Top Left: XANES spectra $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ without laser excitation (black) and ~ 150 ps following femtosecond excitation at 800 nm (red); below is the differential absorption spectra. Top Right: Transient differential absorption in the pre-edge region of the O K edge at 532 eV. Bottom Left: For comparison, static differential absorption spectra at temperatures above and below T_C , for related manganite compounds exhibiting a temperature-dependent insulator/metal transition [17].

As discussed in Section IV, x-ray dichroism techniques offer a tremendous advantage for probing complex magnetic materials by combining elemental specificity with strong magnetic contrast (many orders of magnitude stronger than the Faraday effect at visible wavelengths). In contrast to visible techniques, x-ray dichroism techniques are sensitive to both ferro- and antiferromagnetism, facilitating the study of important ferro-, ferri- and antiferromagnet materials. Element specificity is particularly useful for studies of transition-metal oxides, magnetic semiconductors, exchange-coupled multilayers, and exchange-bias systems. In further contrast with visible techniques, x-ray magnetic circular dichroism separates the orbital and spin components of the total moment and is insensitive to the complications of optical bleaching and state-filling effects.

At present, the only tunable femtosecond x-ray source in the world with complete polarization control is the slicing beamline at BESSY. Recent BESSY results on

ferromagnetic Ni have unambiguously determined the quenching of both spin angular momentum and its transfer to the lattice on a times scale of ~ 120 fs [18]. An unexpected increase in valence-electron localization is suggested as a driving mechanism for the remarkably fast spin–lattice relaxation. This addresses a decade-long controversy prompted by the first observation of ultrafast demagnetization [19] that defied conventional models for of spin–lattice relaxation [20, 21]. While promising, such measurements are severely limited by the available flux, which is 10^{-7} that of non-time-resolved synchrotron beamlines and further limited in temporal resolution. New light sources will provide dramatically enhanced capability for dichroism spectroscopy, with full polarization control, average flux exceeding present synchrotron sources, and 10^3 – 10^5 enhancement in temporal resolution.

Beyond conventional ferromagnetic metals, there is a strong need to understand magnetic phenomena in complex materials such as transition-metal oxides where the magnetic ordering originates via super exchange and double exchange across the oxygen bonds (in contrast with $3d$ metallic band ferromagnets). Time-resolved circular and linear x-ray dichroism will be indispensable for understanding the dependence of the magnetization dynamics on charge ordering, orbital ordering, electron-electron correlations, and subtle lattice distortions in these systems. From a fundamental point of view, such studies will be directly relevant to understanding ultrafast photo-induced transitions near critical points in the phase diagram, and will be an important complement to the x-ray absorption spectroscopy studies described previously. One illustrative example is the challenge to understand the magnetic character of the photo-induced metallic phase in CMR manganites. According to current theories based on double-exchange, the transition between insulating and metallic behavior in manganites results from the competition between ferromagnetic and antiferromagnetic spin arrangements. Following the magnetic dynamics in response to optical and/or vibrational excitation will provide new insight into the nature of the insulating state and how the optical interaction perturbs the charge localization/delocalization mechanisms (Jahn–Teller distortion and double exchange). Such studies may shed new light on this crucial, yet poorly understood aspect of the physics of manganites: the cause–effect relationship between ferromagnetism and metallicity, which cannot be elucidated by conventional adiabatic means.

Finally, the strong coupling between spin, charge, and orbital degrees of freedom in complex materials may be exploited to devise new strategies for ultrafast control of magnetization. In most studies to date [19, 20, 21, 22], laser-induced demagnetization results from a rapid temperature increase of the spin system due to optical absorption. The thermal origin of such an effect sets fundamental limits for possible high-speed applications. More recently, non-thermal mechanisms for coherent magnetization control have emerged, including the enhancement of ferromagnetic order by photo-generated carriers in semiconductor heterostructures based on III-V elements [23, 24] and opto-magnetic phenomena induced by circularly polarized femtosecond pulses via the inverse Faraday effect [25]. Correlated electron solids offer compelling new approaches for non-thermal magnetization control, as recently demonstrated in the perovskite manganite $\text{Gd}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ [26]. In such systems, the magnetic properties may be manipulated via cooperative effects triggered by optical excitation, utilizing the antiferromagnetic–ferromagnetic phase transition accompanying the photo-induced melting of the charge-

ordered insulating phase. Time-resolved x-ray dichroism techniques will be the most direct probe for studying ultrafast photo-magnetic phenomena in these systems; providing new fundamental understanding and underpinning important technological applications. Ultrafast x-ray dichroism studies will be highly relevant for a large class of complex materials, including multiferroics synthesized at the nano-scale for manipulation and ultrafast control of electronic properties and for understanding the controversial relationship between magnetism and superconductivity.

(3) *Multiferroics: Manipulation of correlation effects via nanoscale synthesis*

Multiferroic materials combining magnetic and ferroelectric properties are a central theme of modern condensed-matter research [27]. Systems exhibiting simultaneous ferroelectric and magnetic behavior hold tremendous promise for technological applications based on novel, low-cost, and energy-efficient devices with improved performance and multiple functionalities. However, understanding and controlling coupled ferroelectric and magnetic ordering phenomena is a tremendous scientific challenge. Theoretical studies suggest that the most common mechanisms for ferromagnetism and ferroelectricity are mutually exclusive, since they require partially filled and empty transition metal orbitals, respectively. This explains in part the rarity of natural multiferroic materials, and has prompted the search for non- d electron mechanisms for ferromagnetism as well as ferroelectric order that do not require d^0 configurations [28]. X-ray spectroscopy and scattering techniques are uniquely suited to aid this search by providing detailed electronic, magnetic, and structural information on multiferroics in an element-, valence- and site-specific way.

An important approach, beyond natural multiferroics, is the nanoscale synthesis of two-phase materials, e.g., with ferroelectric and a ferromagnetic order [29]. The lattice-matched coupling between the two correlated materials leads to the emergence of new properties and new physics in the interface region, and is a powerful approach for tailoring the magnetoelectric properties by varying the composition and structure at the nanoscale. The study of magnetoelectric nanostructures with soft x-ray scattering and spectroscopy providing interface sensitivity and nanometer spatial resolution will elucidate crucial coupling mechanisms and allow targeted optimization of the composites.

Probing the dynamic properties of multiferroics on fundamental time scales will be critical for understanding the emergent properties and for characterization of materials for technological applications. Measuring the speeds of polarization and magnetization domain wall motion will be possible employing time-resolved microscopy techniques using soft x rays. Moreover, studying the time evolution of ferromagnetism and ferroelectricity as well as their coupling on ultrafast time scales following magnetic, electric, and heat pulses will become feasible for the first time with the improved performance of next-generation light sources.

(4) ***Ultrafast time- and angle-resolved photoemission spectroscopy of complex materials***

Modern high-resolution angle-resolved photoemission spectroscopy (ARPES) provides unprecedented insight into the electronic structure of solids. ARPES measures the single-particle spectral density function $A(\mathbf{k}, \omega)$ by probing the occupied valence electronic states directly as a function of energy and momentum. This information, generally unavailable from other techniques, is essential for understanding the novel states of matter underlying complex materials. It is an important complement to absorption spectroscopy, which probes *unoccupied* states, and to inelastic scattering, which probes the charge-density correlation, as discussed in the following section.

The next generation of soft x-ray light sources will drive dramatic advances in ARPES capabilities for probing complex materials by enabling time-resolved ARPES at high photon energies. Present ARPES techniques are highly surface-sensitive, owing to the photon energies typically used (~ 10 to 100 eV), and the corresponding electron mean-free path (~ 1 nm or less). The surface sensitivity significantly restricts the range of samples for which ARPES is applicable; for example, of the high T_c superconductors, only very specific cuprates are amenable to ARPES studies. Although the mean-free path increases at lower photoelectron energies (< 10 eV), final-state effects significantly complicate ARPES measurements in this energy range.

Initial studies employing high-energy photoemission to achieve bulk sensitivity have demonstrated the feasibility of angle-integrated core-level spectroscopy with resolution on the order of 50 meV ($\Delta E/E > 10,000$ at 6 keV) using photon fluxes of 10^9 ph/s/0/1%BW and count rates of 10^4 sec $^{-1}$. However the capabilities of present hard x-ray sources severely limit the development of hard x-ray valence-band (VB) photoemission, owing to the decrease in VB cross-section. Even at relaxed resolution (70 – 200 meV) and with long acquisition times, hard x-ray photoemission is still not competitive with lower-energy, surface-sensitive, angle-resolved techniques.

Extending ARPES capabilities to the few keV range (> 50 Å mean-free path) while maintaining meV energy resolution will be a major advance by providing truly bulk sensitivity. This will become possible at next-generation soft x-ray light sources, e.g., using the third harmonic in the 2 – 3 keV range, where both the flux per pulse and high repetition rate are very well suited for ARPES. The unprecedented average flux will further enable spin resolution and nanometer spatial resolution (spin-ARPES, and nano-ARPES).

Equally significant, ARPES research at next-generation soft-x-ray sources will combine bulk, spin, and nanoscale sensitivity with access to fundamental time scales, from sub-femtosecond (characteristic of electron correlation) to picoseconds (characteristic of electron–phonon coupling), with an ability to optimize the time/energy resolution for each experiment—without a monochromator. Time-resolved ARPES provides the important advantages of momentum-resolving non-equilibrium carrier distributions, and following the evolution of the electronic band structure in response to specific tailored perturbations. This is a powerful means of unraveling the underlying correlation

phenomena and will provide completely new insight into the electronic structure of complex materials. For example, such materials can exhibit a “non-rigid” band structure, where the dispersion and spectral weight of electronic states depend critically on the carrier occupation. The evolution of the band structure following transient photo-doping of low-energy excitations, charge-transfer states, or similar perturbations of the valence charge distribution can then be directly measured. Moreover, in the electronic ground state, it will be possible to directly measure changes in the electronic dispersion correlated to specific vibrational modes coherently excited via femtosecond resonant mid-infrared absorption or impulsive Raman processes.

(5) Elastic scattering: Time-resolved resonant x-ray diffraction in complex materials

Charge ordering, orbital ordering, stripe formation and related phenomena are a hallmark of correlated materials. Time-resolved resonant diffraction will be an important new approach to extract more direct information about the dynamics of charge ordering (Figure 5), as well as coupling of photo-excited carriers to the spin, charge, and crystal lattice. Static resonant x-ray diffraction has already been shown to be an effective probe of charge and orbital ordering in manganites [6, 30, 31] and other systems. Superlattice ordering breaks the lattice unit-cell symmetry, as prominently observed at absorption resonances [30, 32]—even distinguishing charge ordering from orbital ordering [31].

As one example, time-resolved resonant diffraction measurements in manganites will allow us to understand for the first time the role of charge ordering, and order-melting

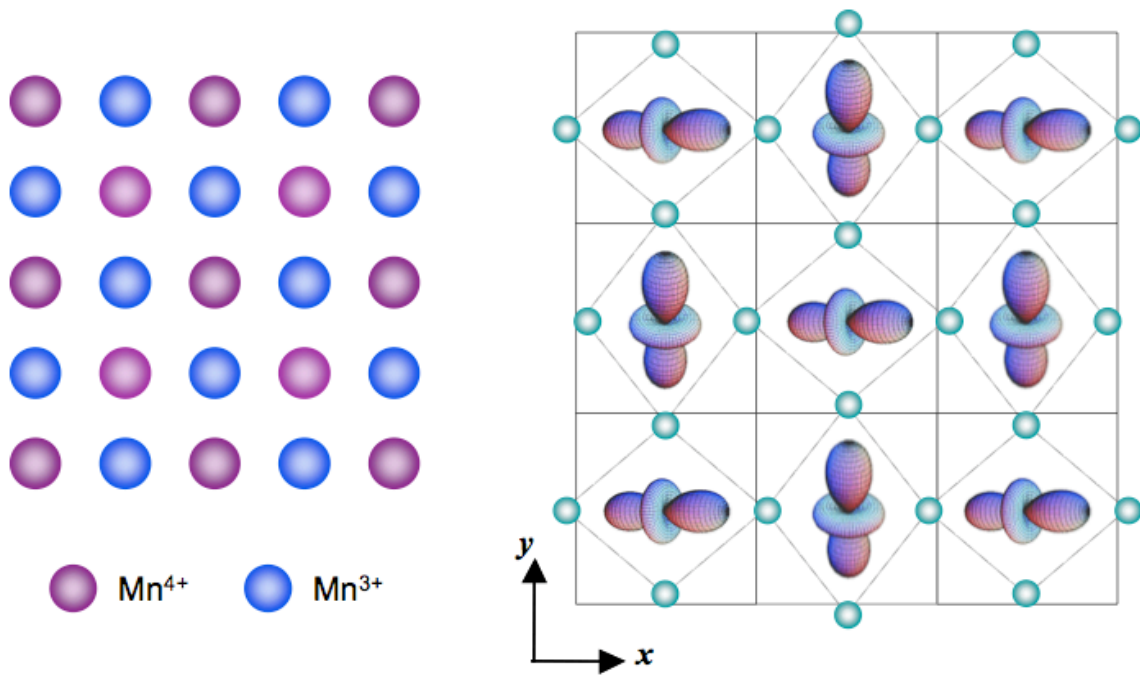


Figure 5. Illustration of charge ordering (left) and Mn *d*-orbital ordering (right), and associated long-range Jahn-Teller distortion of oxygen octahedra in doped manganites.

dynamics in the ultrafast insulator–metal transition. The capabilities of next generation sources will make it possible to distinguish the more subtle dynamics of orbital-ordering and Jahn–Teller effects from the dominant charge-ordering. Such studies will be widely applicable and extremely relevant to broad classes of complex materials (e.g., unconventional superconductors, organics, multiferroics, mixed-valence compounds etc.) where charge-density waves, orbital waves, and similar ordering phenomena underlie their exotic properties.

(6) Inelastic x-ray scattering studies of correlated phenomena

One of the most fundamental attributes of emergence is that an interacting quantum system must exhibit charged collective modes. The dispersion, scaling, and polarization behavior of such modes are fundamental characteristics of the interacting system itself that cannot be obtained from independent single-particle measurements. In fact, the nature of these characteristics determines whether a Landau description or a single-particle band description is valid or not. Charged collective modes are characterized by the dynamic density–density correlation function $N(\mathbf{q},\omega)$, or $N(\mathbf{q},t)$, which contains the full details of the electron-electron correlation. More importantly many new phases of correlated systems are characterized by spectral evolution that is well defined only in the $N(\mathbf{q},\omega)$, or $N(\mathbf{q},t)$ channel, owing to the emergence of charge collective modes [2–5, 33, 34].

Direct measurements of the density–density correlation function is an essential complement to ARPES and inelastic neutron scattering (INS), which measures the magnetic state given by the spin fluctuation spectral density, $S(\mathbf{q},\omega)$. For inelastic x-ray scattering (IXS) studies of correlated materials, energy scales (time scales) of important excitations include ~ 10 meV (~ 182 fs) for a typical superconducting gap, ~ 20 meV (91 fs) for optical phonons or magnons, ~ 100 meV (18 fs) for pseudogaps, and 1 eV or greater (< 2 fs) for d - d excitations, charge-transfer gaps, or Mott gaps [35]. Additional features that distinguish IXS from presently available probes of electronic structure include: bulk sensitivity; suitability for probing insulating samples (organics, bio-materials etc.); compatibility with external fields (magnetic, electric), pressure, and optical excitation; and sensitivity to symmetry-forbidden optical transitions. Finally, resonant IXS (RIXS) provides signal enhancements from 10^2 to 10^3 , is element specific and sensitive to buried interfaces, and probes spin and orbital ordering, e.g., via $2p \rightarrow 3d$ transitions in transition-metal complexes.

The limited impact to date of inelastic x-ray scattering (IXS) on correlated materials is a direct consequence of the restricted capabilities of current x-ray sources, specifically low throughput (low average photon flux) and low energy resolution. These limitations are related, since present approaches for improving energy resolution (based on monochromators) also reduce the available photon flux for a given source bandwidth – often by orders of magnitude in order to reach energy scales of interest. Thus, most IXS studies of collective charge modes have been largely limited to energy scales of d - d excitations and Mott gaps [36–39].

Next-generation light sources will provide many orders of magnitude more flux in a nearly transform-limited bandwidth from a controlled FEL beam with full transverse coherence. Following are only a few key scientific challenges in correlated electron materials that can be addressed for the first time with such a source:

Collective charge dynamics in the vicinity of ubiquitous Mott transition in correlated matter

The evolution of a strongly correlated material, as a function of doping, from a Mott-insulator to a conducting metal, is one of the most intensively studied issues in current condensed matter physics. This evolution has revealed numerous surprises, including high-temperature superconductivity, colossal magnetoresistance, non-Fermi liquid behavior, and nanoscale phase separation [1–5]. In the vicinity of the metallic phase, insulators exhibit softening of charge, spin or lattice collective modes (Figure 6).

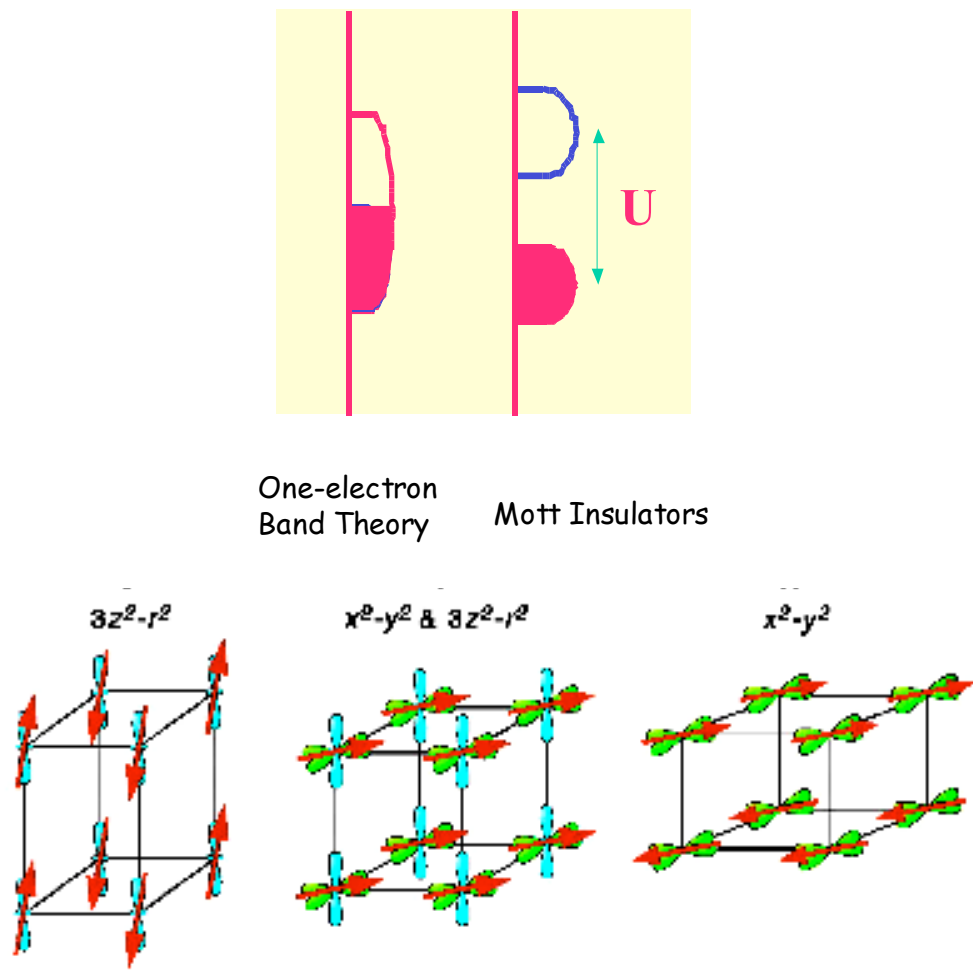


Figure 6. Top: Strong electron-electron correlation leads to Mott insulating behavior, which requires a many-body theoretical description beyond one-electron effective-band theories. Bottom: Mott insulators often exhibit charge, spin, and orbital order or Coulomb localization. The full spectrum of collective modes associated with such order is not typically probed in present day scattering/spectroscopic methods (5).

Although the behavior of spin and lattice collective modes in this regime has been studied extensively via neutron scattering, the critical behavior of charge collective modes (throughout the Brillouin zone) near a phase transition is still not experimentally accessible.

In a conventional band-insulator, the collective exciton mode softens to zero in approaching the transition, and a sharp valence plasmon emerges in the metallic phase. In contrast, for doped Mott insulators, the evolution of charge collective modes is not known, particularly near critical points of the phase diagram. The experimental difficulty arises from the fact that frequency softening of the collective modes cannot be followed down to the zero-mode energy, as the scattering cross-section drops dramatically in this region. Current spectroscopic capabilities do not allow probing the details of charge dynamics (e.g., self-energy or lifetime effects) below the Mott-gap edge where the most exciting emergent and critical behaviors are to be observed at the energy scales of charge pairing and exchange. The all-important charge-fluctuation spectrum of correlated materials at these energy scales can be achieved using novel spectrographs that match the brilliance and coherence of anticipated new light sources.

A comprehensive understanding of emergence of enhanced collective properties of matter cannot be achieved without a microscopic investigation of the dynamic interplay of multiple degrees of freedom – namely charge, spin, orbital and lattice exhibited by correlated materials. Non-degenerate Mott insulators such as copper oxides order antiferromagnetically at low temperatures, hence only charge and spin degrees of freedom are directly relevant to their physics. However, unlike cuprates, the majority of transition metal oxides exhibit orbital degrees of freedom which to date remain largely unexplored [1, 5]. The tensorial character of orbital dynamics naturally couple to the lattice degrees of freedom, and this dynamic interplay is a prominent factor in determining the balance between competing ground states and the underlying physics of most transition-metal oxides, an important example of which is the class of colossal magnetoresistive (CMR) compounds. A complete understanding of magneto-transport properties of these correlated oxides remains elusive. Orbital degrees of freedom play a major role in determining the magneto-transport behavior. IXS represents a powerful technique for studying orbital fluctuations, lattice fluctuations, and their coupling in a systematic manner. Collective processes and associated charge modes are in the range of 1 to 500 meV and orbital fluctuations are in the range of 0-0.1 eV. Here the resolution and average flux from next-generation sources will elucidate these modes for the first time over the full wavelength range of crystals.

Collective pairing in high- T_c superconductors

The existence of novel charged collective modes or charge oscillations in the range of 1–100 meV in high-temperature superconductors has been suggested by numerous theories, including gauge theories, high-symmetry-group-based unification schemes of high-temperature superconductivity and quantum anti-ferromagnetism, and one-dimensional self-organized fluctuating charge objects (Figure 7) [3, 4, 33]. Such collective excitations are not directly observable in single-particle excitation spectroscopies like ARPES.

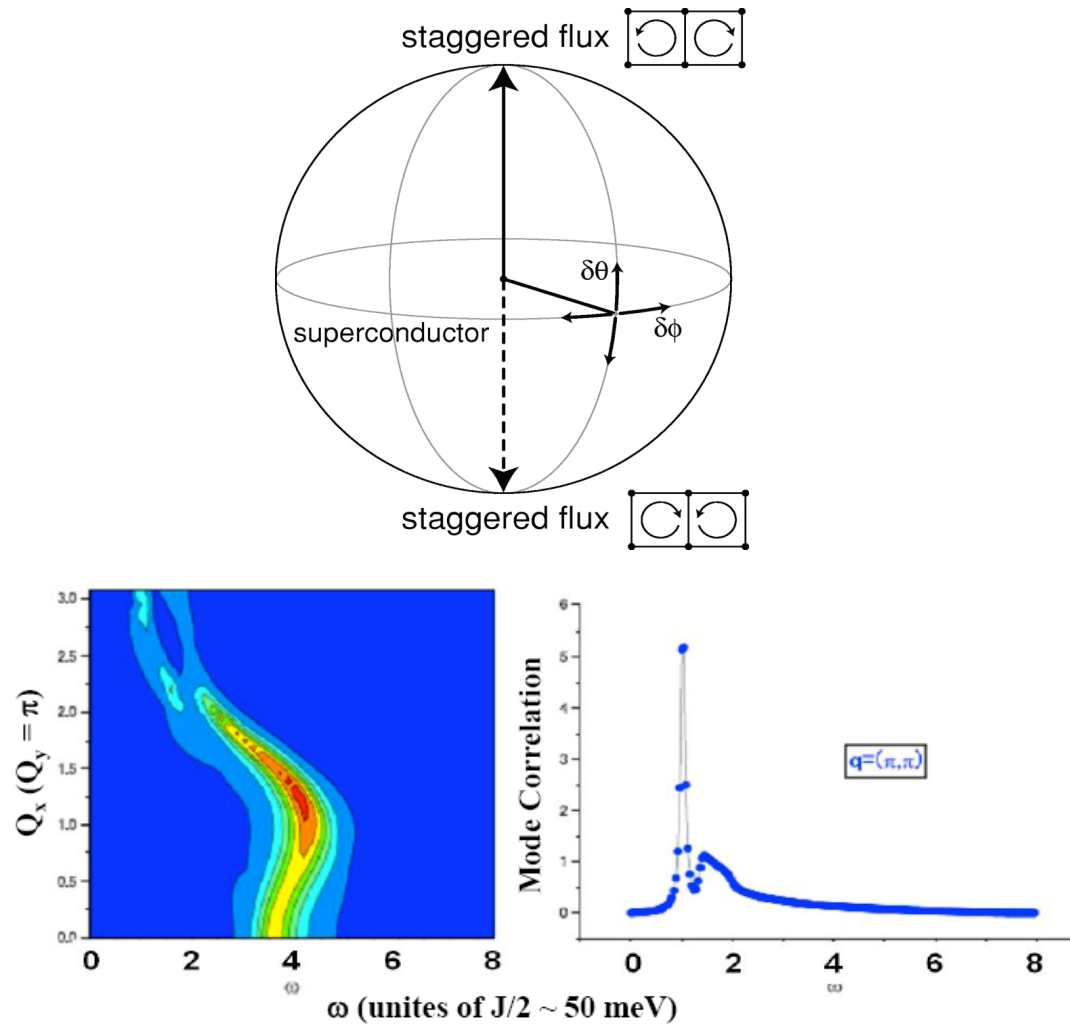


Figure 7. Existence of charge collective modes in cuprate superconductors has been predicted in many theories that propose microscopic mechanisms for electron pairing and phase coherence [33]. In certain classes of gauge theories, a duality is proposed between a superconductor and a staggered flux state so that the resulting charge collective modes gain large amplitudes at finite Q . Only high-resolution finite- Q measurements can reveal the charge-mode spectrum. (Figure Courtesy P.A. Lee).

Inelastic scattering or time-resolved x-ray studies are thus vital for their detection. The scattering cross-section for these charge excitations is about 3 to 4 orders of magnitude below present detectability thresholds using third-generation synchrotron sources. The scattering cross-sections are enhanced substantially by operating at absorption resonances, which further enhances the sensitivity to electronic excitations, allowing them to be readily distinguished from phonon scattering. While meV energy resolution for hard x-ray scattering can be achieved over a limited range using present sources, the resolution is not always achievable at resonances of interest, and the available flux is less than 10^{11} photons/sec, which is substantially below what is required for sensitive measurements.

Field-induced transformation of density waves in correlated matter

Many correlated electron systems exhibit dramatic responses with respect to magnetic or electric fields (Figure 8). Even under a modest field certain doped Mott insulators undergo metal–insulator transitions (MIT). Such phase transitions lead to a dramatic rearrangement of charge dynamical spectral weight. For example, many MITs are known to open a gap at the Fermi level, pushing spectral weight to very high energies. The spectral weight is often redistributed over the entire Brillouin zone, and therefore it is critical to study $N(\mathbf{q},\omega)$ over a large \mathbf{q} -range to map out the electronic modes that are affected by the correlated MIT. This mode map establishes a fingerprint of the underlying nature of the phase transition. Such experiments are currently not possible—even without magnetic fields. Novel spectroscopies at the new light sources will open up possibilities for carrying out a map of mode distributions that are affected by a particular MIT, shedding light on the MIT process itself.

The spectral mapping of even a conventional metal to a Fermi surface nesting charge density wave (CDW) has never been carried out (Figure 9). The application of a magnetic field while preserving significant signal/noise for $N(\mathbf{q},\omega)$ opens up many new possibilities for understanding correlated electron systems.

Low-temperature, high-field phase transitions

Quantum phase transitions take place when electronic matter becomes unstable to a new, ordered ground state at low temperatures where vacuum fluctuations dominate. A growing body of experimental work on such phase transitions (e.g., highly correlated

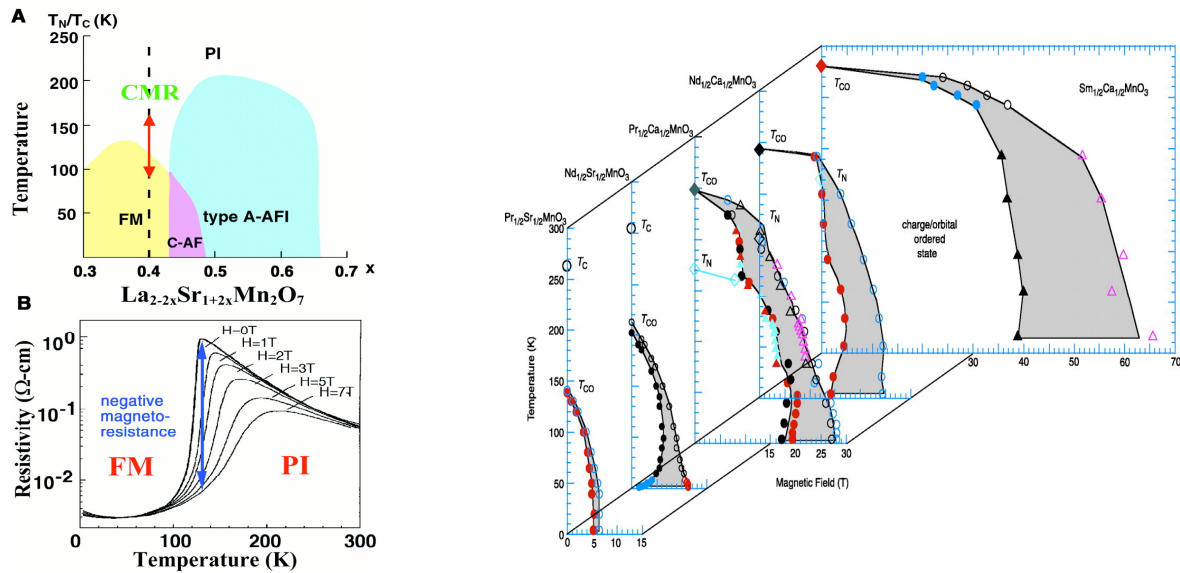


Figure 8. In many transition-metal-oxide correlated materials, pronounced changes in the electronic structure are often observed. Top: Magnetic field leads to metal–insulator transition whose microscopic details and or mechanisms are largely unknown. Spectroscopic tools that operate in the presence of fields are quite critical.

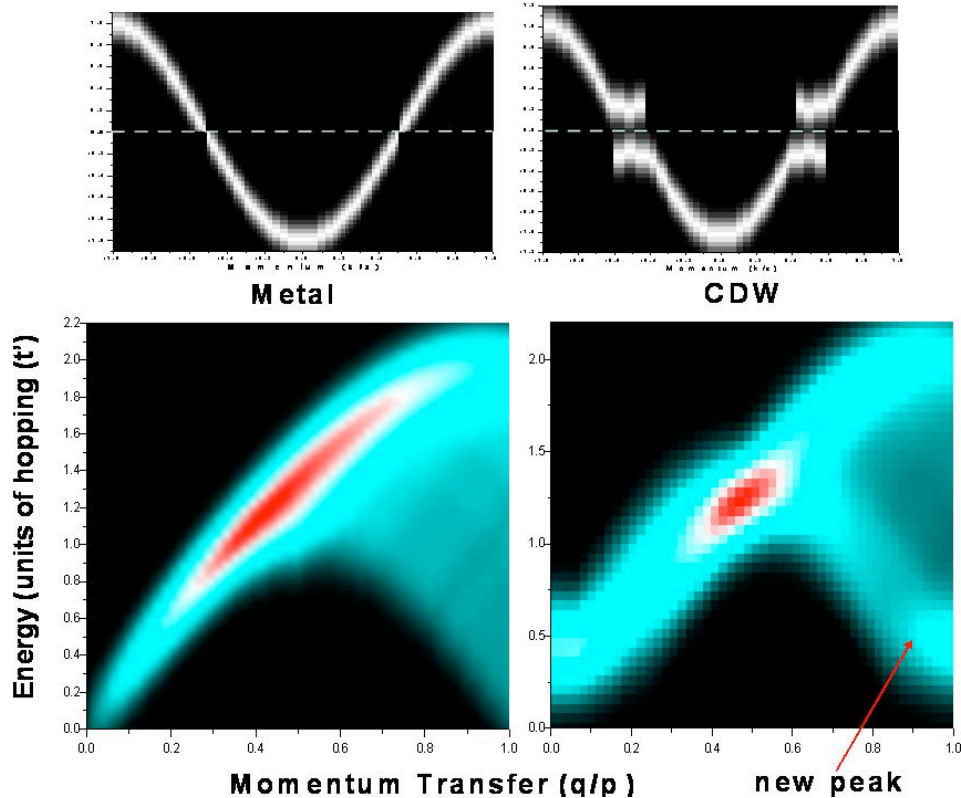


Figure 9. Even the field behavior of Fermi-surface-driven CDW phase transitions have not been within experimental range, owing to the lack of a high-resolution, high-flux spectroscopic facility. Resonant inelastic x-ray scattering with ultra-high resolution (≤ 10 meV) can allow us to study charge-, orbital-, and lattice-coupled excitations and resolve the interaction energy scales and relevant processes in correlated electronic materials.

metals, quantum magnets, and Bose-Einstein fluids) indicates that fundamentally new physics can develop in the vicinity of quantum phase transitions. Second-order quantum phase transitions lead to the phenomenon of “quantum criticality.” Although a quantum critical point (QCP) lies at absolute zero, it forms a kind of bare singularity in the material phase diagram. Thus, a wide region of the finite-temperature phase diagram develops novel properties that can be probed with finite-resolution spectroscopies. Quantum critical metals develop transport and thermodynamic properties that deviate fundamentally from the properties of conventional metals and exhibit spectral weight redistributions over a large energy scale.

Photon-in/electron-out and photon-in/photon-out spectroscopies are essential for understanding the complex electron behavior in quantum matter in the vicinity of QCP. Thus, pushing the limits of high-energy-resolution x-ray scattering will provide fundamental new insights into the charge and spin transport mechanisms in such systems (Figure 10). For example, in URu_2Si_2 and $\text{Sr}_3\text{Ru}_2\text{O}_7$ the existence of magnetic-field-driven phase transitions have been identified by thermodynamic and transport measurements. However, the nature of the transitions remains mysterious. For URu_2Si_2 , the phase is completely unknown, thus termed “hidden order.” For $\text{Sr}_3\text{Ru}_2\text{O}_7$, the critical point is thought to be related to some form of Pomeranchuk Fermi surface instability.

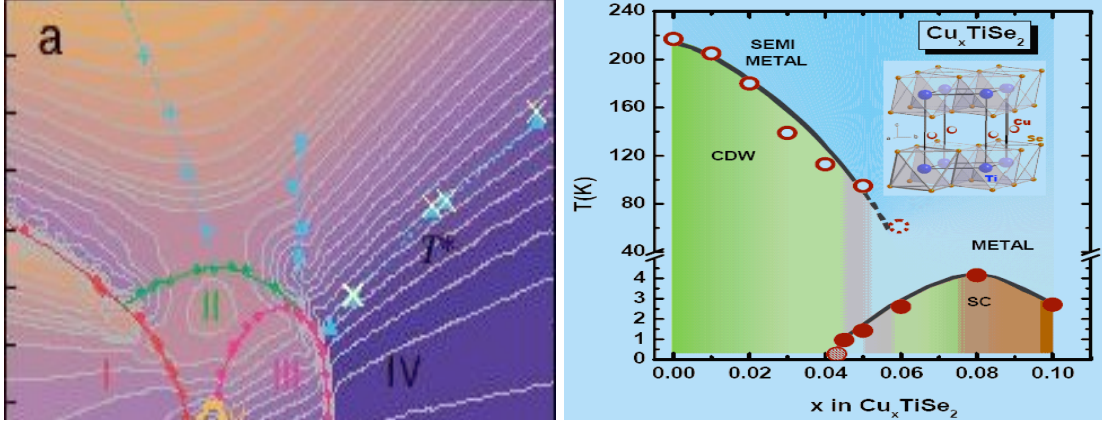


Figure 10. Left: Magnetic field vs temperature phase diagram in YbRh₂Si₂. Right: Doping vs. temperature phase diagram in Cu_xTiSe₂ outline a phase composition where an electronic CDW competes and co-exists with superconductivity [40].

D. Multi-Dimensional X-Ray Spectroscopy Studies of Correlated Phenomena

Inelastic x-ray scattering, as discussed above, is spontaneous Raman scattering (SRS) in the x-ray regime. Since its discovery nearly eight decades ago, SRS has exploited primarily optical fields (visible to IR) to probe lower-frequency vibrational resonances in matter, whereas SRS in the x-ray regime probes valence optical excitations. A powerful extension of SRS, coherent Raman scattering (CRS) or stimulated Raman scattering, which is a third-order, $\chi^{(3)}$, four-wave mixing process whereby three incident fields: $E_n(k_n, \omega_n)|_{n=1,2,3}$, generate a stimulated signal, e.g., $E_{\text{sig}}(-\omega\omega_1 + \omega_2 + \omega_3)$, in the momentum-matched direction, $k_{\text{sig}} = -k_1 + k_2 + k_3$.

In the past decade, ultrafast multi-dimensional electronic spectroscopy based on CRS (using three- and four-pulse sequences) has emerged as a powerful tool for understanding coupled electronic excitations in condensed-matter molecular systems and crystalline solids [41–43]. Multi-dimensional electronic spectroscopy is an optical analogue of 2D NMR whereby coherent sequences of ultrashort laser pulses directly probe (via time-ordering and momentum-matching) specific Liouville-space pathways that describe coupled quantum systems.

The next generation of soft x-ray light sources will make it possible to extend CRS and multi-dimensional spectroscopy to the x-ray regime. This development will be a major breakthrough for understanding the correlation effects and many-body processes that underlie the properties of complex materials [44, 45]. X-ray CRS is a direct (though non-trivial) extension of IXS/RIXS, providing crucial missing phase information and the capability to resolve correlated states (density correlation function) in time as they evolve in response to specific perturbations. Following is a broader description of the compelling advantages of investigating correlated phenomena via multi-dimensional x-ray spectroscopy:

- ***Time (or phase) information.*** Such information is unavailable from conventional IXS/RIXS measurements, which probe $N(\mathbf{q},\omega)$ in the frequency domain but without phase information. Two examples of the power of time-domain (equivalently, frequency and phase) measurements are (i) the capability to distinguish different contributions to the density-correlation spectral distribution (e.g., homogeneous vs. inhomogeneous distributions of correlated states), (ii) the capability to follow emergent properties as they evolve from non-equilibrium conditions created by specific electronic or vibrational excitations (e.g., modulation or manipulation of correlated states via coherent vibrational modes or charge-transfer excitations).
- ***Element specificity.*** Specificity is essential for understanding the correlation between valence states associated with particular atomic or molecular orbitals. For the first time it will be possible to directly follow the coherent energy transfer between different atomic sites in time, energy, and space. This ability will be extremely powerful for understanding mixed-valence complexes, dilute-magnetic semiconductors, multiferroics, charge-transfer complexes, cuprates (states coupled to Cu orbitals vs. O orbitals), etc. Although conventional RIXS is element specific, it is not able to distinguish coherences across different atoms.
- ***Symmetry selectivity.*** Transitions originating from core levels of well-defined symmetry provide sensitivity to specific valence states (e.g., $3d$ vs. $2p$) and the capability to distinguish spin and orbital moments via powerful x-ray dichroism effects.
- ***Access to the entire manifold of electronic transitions.*** Since the excitation wavelength is comparable to the unit-cell/molecular size (\mathbf{k} vector large compared to the Brillouin zone), the strict dipole selection rules that mediate optical transitions are substantially relaxed. Thus, nearly the entire electronic manifold of valence momentum states is directly accessible.
- ***Quantum selectivity.*** Specific terms of the contributing Liouville-space pathways that describe coupled quantum systems can be isolated via momentum matching, and time sequencing of pulses. For example, coherent coupling of quantum states can be isolated from incoherent population transfer or relaxation, excited-state absorption, ground-state bleaching, etc. In combination with element specificity and ultrafast time resolution, this capability will be a major breakthrough for understanding correlated systems.

The potential impact of multi-dimensional x-ray spectroscopy is illustrated in Figure 11, which shows a generalized four-wave mixing geometry. Here, the signal of interest is the nonlinear polarization, $P^{(3)}_{\text{sig}}$, which is resolved in amplitude and phase via heterodyne detection with a local-oscillator field, E_{LO} . Note that simple x-ray pump-probe is formally a four-wave mixing process with self-heterodyne detection (i.e., pulses k_1 and k_2 are degenerate, and k_3 and E_{LO} are degenerate—with identical \mathbf{k} vectors exactly overlapped in time).

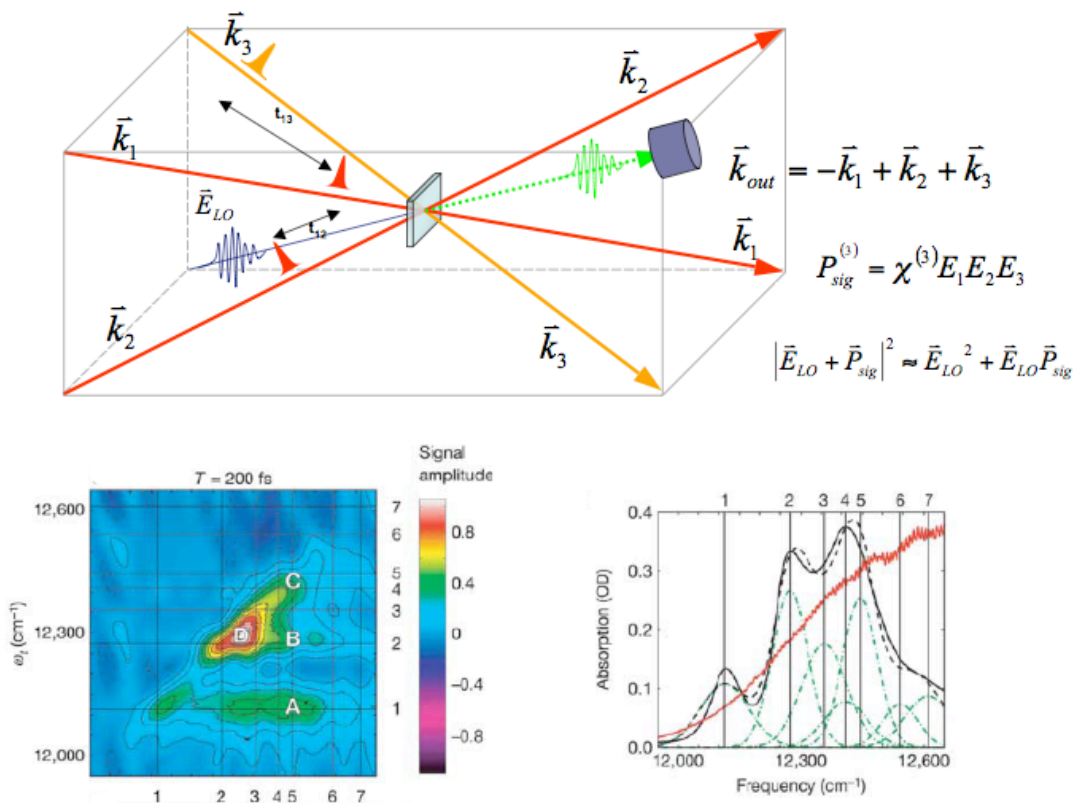


Figure 11. Top: Generalized schematic of multi-dimensional electronic spectroscopy using a four-wave mixing geometry with a three-pulse sequence (k_1, k_2, k_3). The signal of interest is the nonlinear polarization $P_{sig}^{(3)}$ —shown here resolved in phase and amplitude via heterodyne detection with a local-oscillator field E_{LO} . Bottom: 2D electronic spectra snapshot (at 200 fs delay, t_{13}) of bacteriochlorophyll photosynthetic reaction center [42] which consists of seven coherently-coupled exciton states (lower right). The two (energy/frequency) axes of the 2D spectrogram are the Fourier variables corresponding to the delay t_{12} , and the delay between k_3 and E_{LO} .

In this example, multi-dimensional spectroscopy (in the visible regime) is applied to the bacteriochlorophyll photosynthetic reaction center, which consists of seven coherently coupled exciton states (responsible for the primary collection of solar energy). The upper-right panel is a snapshot of the 2D spectra taken at a delay of $t_{13}=200$ fs. The presence of off-diagonal signals, A and B, directly show the coherent transfer of electronic energy between excitons [42]. Extending these multi-dimensional electronic studies to the x-ray regime will have profound consequences for understanding complex materials by providing critical information unavailable from any present approach.

The advantages of multidimensional x-ray spectroscopy are a consequence of core-hole excitations, which impose the additional requirement that the time duration (or more accurately the coherence length/duration) of the excitation pulses be less than the core-hole lifetime. Generating broadly tunable coherent x-ray pulses of sub-femtosecond duration is one of the remarkable attributes and most ambitious goals of next-generation light sources. This will truly revolutionize our understanding of complex materials by enabling the full implementation of multi-dimensional x-ray spectroscopy as a probe of

many-body correlations. In advance of the technical development of coherent sub-femtosecond pulses, such sources in the initial stages will readily provide pulses with ultrashort coherence lengths (with unprecedented average flux and peak intensities) that will be an important starting point with significant scientific impact.

E. Ordering Phenomena in Complex Materials via X-Ray Photon Correlation Spectroscopy

Ubiquitous ordering phenomena in complex materials (charge ordering, orbital ordering, stripe formation etc.) lead to nanoscale inhomogeneities, phase separation, self-organization, percolation, and related macroscopic phenomena. Next-generation sources offer a new opportunity to directly probe these spatial correlations via x-ray photon correlation spectroscopy (XPCS), which measures the speckle pattern created by scattering of a spatial coherent x-ray beam from complex matter. This spectro-holographic technique [46] is substantially more powerful (and significantly more demanding of the x-ray source) than the simple resonant diffraction techniques described earlier. XPCS (discussed in more detail in Section VI) leverages the full spatial coherence of the new sources combined with high average flux to access regions of reciprocal space, \mathbf{q} -vectors, that are well beyond any present approach, and will open a new window of understanding for complex matter. Moreover, XPCS on future light sources will employ pairs of scattering pulses, delayed in time, to access to an incredible range of correlation/fluctuation time scales. Finally, combining XPCS with pump-probe techniques, we will be able for the first time to observe the evolution of nanoscale inhomogeneities, phase separation, and self-organization phenomena as they evolve in response to specific electronic and/or vibrational excitation on time scales from a few femtoseconds and ranging upward over 15 orders of magnitude.

F. Requirements of a New Soft X-Ray Source to Meet these Challenges

Table 1. Condensed Matter Physics Requirements for a New Soft X-Ray Source

Property	Value	Comments
Energy range (eV)	10–1200 (also third harmonic)	Resonance edges of C, O and transition metals.
Repetition rate (kHz)	10 KHz to 1 MHz	Limited flux/pulse—damage, nonlinear effects, require high average flux.
Average Flux	>3 rd generation sources	High average flux required (e.g., IXS, XPCS).
Peak Power (GW)	<1	High peak power required for four-wave mixing.
Intensity stability	5%	
Timing stability (fs)	5 or lower	Synchronization for pump–probe experiments.
pulse length (fs)	1-100 fs, psec	Control of Δt and ΔE .
Bandwidth	transform limit (2–3x OK)	Use mono (pin hole) to get 100% transform limit when necessary.
Harmonics	need 3 rd	The availability of 3 rd harmonic at lower flux/pulse will be very useful.
Source position stability	<10% source size	
Pointing stability (μ rad)	<10	
Spot size (μ)	5-100	Focus down to 5 micron (vertical)x 100 micron (horizontal).
Polarization	variable, linear/circular	Having the choice is desirable.
Energy stability (eV)	0.01 eV	Will use monochromator to get further energy stability and resolution.
Background signal	<0.1 %	Pure beams: any background hurts. Contrast 1:1000 desirable.

Possible additional requirements for CMP experiments

- Two color pump–probe experiments will require femtosecond THz–UV pump lasers.
- Need to develop <10-meV-resolution emission spectrograph operating at 500–1000 eV.
- Split multilayer mirrors for four-wave mixing experiments.
- Ample space for sample preparation and movable (**q**-resolved) emission spectrographs.

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VI. Exploration of Nanoscale Dynamics and Complexity

A. The Frontier: X-Ray Imaging and X-Ray Photon Correlation Spectroscopy with Soft and Medium-Energy X Rays

The DOE's 2008 "Grand Challenges" report (see Section I) on opportunities for basic research in energy science repeatedly stresses the need to "enhance our current capabilities of time-resolution and imaging" and to "image materials and devices with atomic resolution, chemical specificity, and electronic- and magnetic-state sensitivity" in order to meet these challenges. Here, we describe the contribution that diffraction microscopy, full-field x-ray imaging, and soft x-ray photon correlation spectroscopy (SXPCS—the analog of dynamic laser-light scattering, but now using a free-electron laser) will make to these goals. Diffraction microscopy will provide tomographic images of microstructure at the nanoscale in materials science and biology; full-field imaging will explore ultrafast dynamics; while SXPCS allows study of the time-dependent fluctuations in complex condensed-matter systems. The addition of pump-probe possibilities and femtosecond pulses adds many new possibilities to these recently developed capabilities, which we present below. We also suggest some more speculative experiments for the future, and finally indicate the machine-design requirements for such advanced x-ray imaging techniques.

Soft and medium energy x rays provide access for chemical imaging to the spectroscopy of the first few rows of the periodic table, important for biology, semiconductor devices, ceramics, oxides and transition metal systems. In addition, since the scattering cross-section depends inversely on wavelength squared and coherent flux is higher at longer wavelengths, the resulting energy dependence of scattered intensity gives the soft x-ray region a powerful advantage over hard x-ray methods.

B. Diffractive Imaging

Dramatic advances in recent years [1, 2, 3] have demonstrated the ability to perform diffraction-limited, tomographic "lensless imaging" of non-periodic samples in which a computer is used to replace the lens normally used for image reconstruction. The numerical algorithms that solve the phase problem iteratively thus make possible aberration-free imaging at a resolution approaching five times the wavelength (the current resolution is about 10 nm). An FEL will have a dramatic impact on this work, since its predicted minimum five-orders-of-magnitude increase in peak flux will reduce an existing 24-hour exposure to a few seconds.

Other major advantages of an FEL for diffractive imaging will include

1. Spatially coherent illumination, avoiding the need for collimating devices, which currently introduce severe background.
2. Nearly transform-limited longitudinal coherence, which eliminates the need for monochromators.

3. Using the third harmonic of the FEL at 3 keV (0.4-nm wavelength), a variety of crucial structural features become visible, including dislocations, surface growth steps, and stacking faults in materials and the spatial arrangement of alpha-helices in proteins.

We emphasize, however, that the exciting field of diffractive (lensless) imaging is rapidly evolving, and no consensus has emerged on the optimum modality, which currently includes Fourier transform holography, in-line divergent-beam holography and ptychography, in addition to iterative phasing of Fraunhofer diffraction patterns.

The possibility of pump-probe diffractive imaging experiments has also recently been demonstrated [4]. Here images of an excited state can be obtained if many identical orientated particles are available. A variety of methods of particle or molecule orientation are under investigation, including the use of applied fields, lasers and the detection of fragments from the coulomb explosion.

(1) *Beating radiation damage with ultrafast pulses*

Radiation damage caused by any imaging probe has previously been considered a “fundamental” limitation for high-resolution imaging in biology. Evidence is rapidly mounting, however, that sufficiently short and intense pulses, before completely destroying a sample, provide a useful diffraction pattern [5] because a pulse shorter than the Auger relaxation time terminates before any damage occurs (Figure 1). In this sense, femtosecond x-ray diffraction promises to solve the oldest and hitherto most important limitation in high-resolution biological imaging. It does so by providing an additional degree of freedom (pulse duration) with which to escape the trade-offs between dose, damage, and resolution that have been mapped out in past decades [6]. In late 2007, images of sucrose-encapsulated DNA particles about 80 nm in diameter were obtained by diffractive imaging with 13.5-nm-wavelength soft x rays at the FLASH FEL in Hamburg [7]. A single 10-fs pulse was used, containing about 10^{12} photons. That the particles were initially hydrated and were caught “on the fly” as they passed across the x-ray beam from an electrospray source opens the way to biological applications of free-electron lasers. Since that time, in unpublished work, images have been reconstructed of whole cells at 7-nm wavelength, with plans to move to 4 nm in 2009. Spatial resolution in this diffractive imaging mode is already about three times the wavelength in preliminary work, and it is improving as more experience is gained with the technique. Using the third harmonic of the FEL at 3 keV, one could therefore expect 0.7-nm resolution, sufficient to resolve alpha helices in proteins. In materials, destructive-readout experiments will also be possible with an FEL using a focused beam. Images may then be obtained in a few femtoseconds, or about a twentieth of the oscillation period of an atom in materials at room temperature. Each scattering pattern is read out before the next pulse arrives.

This destructive read-out mode with only a single exposure per target may not necessarily be restricted to two-dimensional imaging—plans exist for beam-splitting arrangements capable of providing several projections per pulse from a single target, thereby providing information needed for three-dimensional imaging [8]. Useful information can also be expected from different projections of similar (but not identical) cells of the same type.

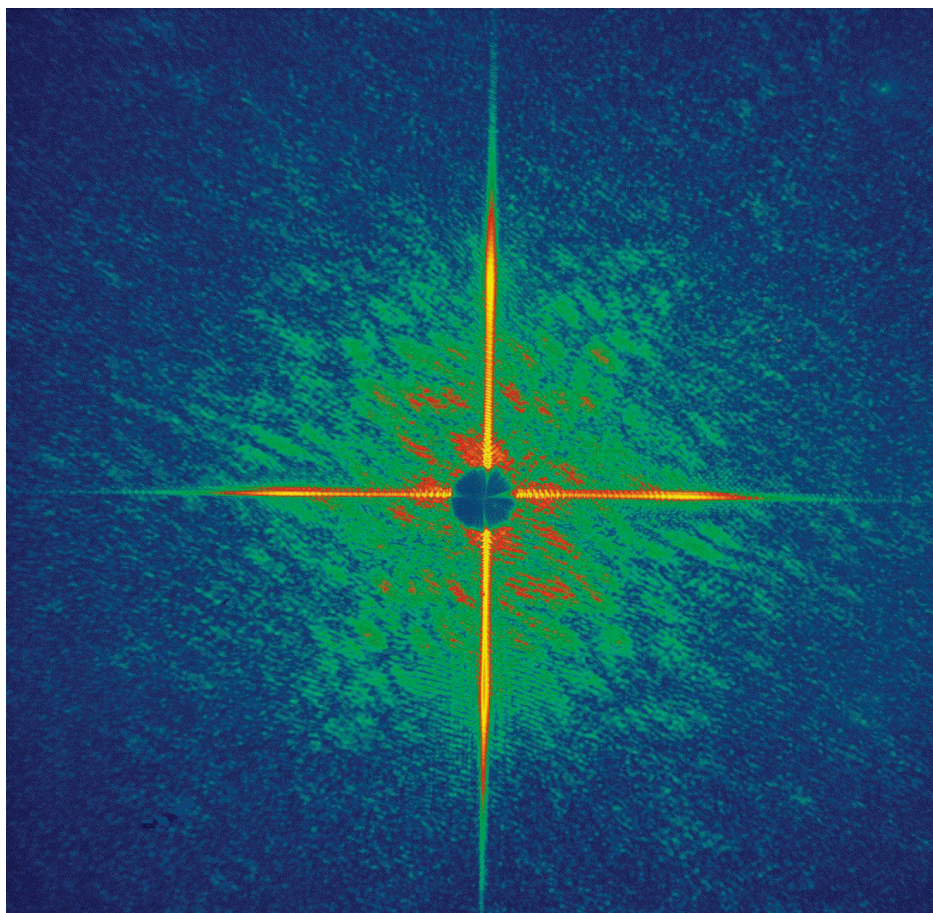


Figure 1. Ultrafast FEL diffraction pattern from a single 25-fs exposure at a wavelength of 32 nm at the FLASH FEL at DESY. The image of a test object reconstructed from the diffraction pattern achieved a diffraction-limited resolution of 62 nm, showing that diffraction events used to form the image occur before the sample is vaporized [5].

(2) *Three-dimensional imaging with “droplet-on-demand” techniques*

The multiple views needed for three-dimensional reconstruction is also possible if a supply of identical target particles (such as proteins or nanostructures) can be passed across the beam, as recently demonstrated at FLASH [7] and the ALS [9] and described in the scheme of Schmidt et al. [8]. The sorting and classification of these randomly oriented diffraction patterns for inversion to three-dimensional charge density maps is an active field of research in several national laboratories and universities. Assuming a repetition rate of about 10 kHz, total data-acquisition times for destructive readout tomography are then short; however, a detector readout time of less than a millisecond will be required, which is on the threshold of current possibility using the column-readout design. Much of this work will use a particle injector of the “droplet-on-demand” type, in which the release of a doped droplet is synchronized with the FEL. These injectors are under development in several laboratories and have produced striking diffraction patterns from membrane protein nanocrystals just 17 unit cells on a side. [9] Synchronization of additional lasers for pump-probe experiments is expected to be straightforward; however, there remain many technical challenges in, for example, the minimization of out-of-focus

background scattering, the FEL effective source lateral stability, and the variation of FEL wave front from pulse to pulse.

(3) Scientific goals and payoff

The scientific payoff from this capability will be considerable. We list below some of the high-impact experiments that can be immediately undertaken

- Whole-cell imaging. Working at a few-keV beam energy, the additional penetration of x rays over high-energy electrons gives sub-damage-threshold tomographic diffractive imaging an important advantage over cryo-electron microscopy. The goal of recording the shape of every protein in a simple cell by diffraction microscopy, and hence identifying it against a library of structures determined by x-ray crystallography, is difficult but not impossible. Recent work [6] has charted the dependence of dose D (and resulting damage) on resolution d , finding $D \sim d^{-4}$, a severe penalty for studies at higher resolution than a few nanometers.
- In-situ electrochemistry. Again taking advantage of x-ray penetration and modern lithography methods, in-situ liquid cells may be fabricated with windows transparent to x rays for use in the vacuum or helium environment of medium-energy x rays. This will make possible the direct observation of chemical reactions at the solid–liquid interface, such as electrodeposition, kinetics in all three dimensions of 3D island growth on metal surfaces, determination of critical nucleus size, and the kinetic and diffusion limits to growth processes as current and voltage conditions are varied. Thus we propose the fabrication of a nanolab in the microscope for real-time imaging below the damage threshold.
- Dynamic full-field fast imaging of defect processes in materials, such as the motion of dislocations, stacking faults, interfaces, twinning, grain-boundaries, and phase transitions. With the nanolab, this imaging will be done at far higher speed than is possible in the dynamic TEM, which is currently restricted by Coulomb interactions in the electron beam to nanosecond speeds.
- Contrast in phase-contrast imaging arises from any spatial discontinuity in refractive index. The method is therefore ideally suited to the study of ferroelectric-domain motion, pinning, and dynamics driven by synchronized signals. These may be provided to the sample through fast switches, such as the Austen switch, triggered by a laser.
- Superconducting vortex imaging. Such imaging should be possible using dichroism at the oxygen K edge, which will modulate the phase-contrast image.
- Repetitive reversible electronic processes. Imaged stroboscopically using synchronized triggers, the charge-density modulations due to, for example, a surface plasmon initiated by a synchronized laser should be visible by taking “snapshots” whose duration is much shorter than the transit time of the plasmon.

- DNA sequencing using gold nanoballs attached to each particular base in turn. Diffraction imaging of these nanoballs has already been demonstrated. This experiment will use a variant of the nanolab described above.

C. Full-Field Imaging with a Zone-Plate-Based Soft X-Ray Microscope

Pushing the scientific frontiers in nanoscience at an ultrafast facility will permit studies of femtosecond dynamics with nanometer spatial resolution. One example is the investigation of femtosecond spin dynamics with nanometer spatial resolution in multicomponent systems utilizing femtosecond pulses of polarized soft x rays with a photon energy matched to the resonant x-ray absorption edges of magnetic elements. For Fe, Co and Ni this requires the 700–900 eV spectral range, which in the near future seems hard to achieve with other than a soft x-ray FEL.

Real-space imaging such nanoscale materials and their ultrafast dynamics is possible with full-field soft x-ray microscopy based on Fresnel-zone-plate optics (see Figure 2), which at the moment achieve just over 10-nm spatial resolution [10]. But full-field soft x-ray imaging offering high spatial resolution is currently limited in temporal resolution by the inherent time structure of presently available sources for soft x rays and is restricted to fully repeatable processes by the very limited number of photons per x-ray pulse [11]. The scientific questions that can be addressed today are thus limited to fully repeatable processes that are suited for pump–probe experiments [12].

An intense femtosecond soft x-ray source will overcome both these limitations. One can also predict operation down to the femtosecond/attosecond regime, providing unique and fundamental insights into important dynamics of phenomena, such as ultrafast spin dynamics (see Section IV Magnetization and Spin Dynamics). One of the underlying questions concerns the time scale at which the exchange interaction sets in, a question that will touch upon fundamental principles of quantum mechanics and could revolutionize our understanding of solid-state physics on femtosecond time and nanometer spatial scales.

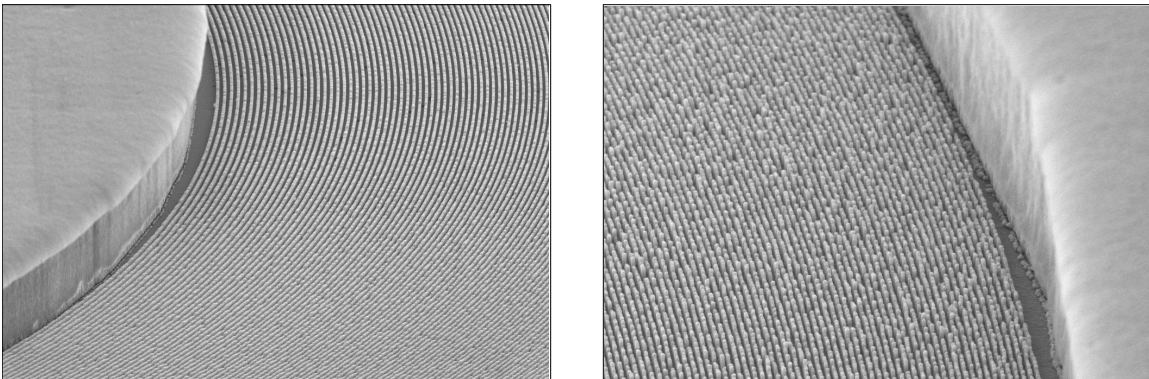


Figure 2. Left: inner zones of a high-resolution Fresnel zone plate fabricated at the LBNL Center for X-Ray Optics. Right: Outer zone region, which largely determines the spatial resolution.

Figure 3 shows that the current optical design of a high-resolution imaging soft x-ray microscope can be used even for a femtosecond soft x-ray source. Calculations of the thermal heating upon illumination with a single intense femtosecond x-ray pulse show a temperature increase of $<70\text{ C}$, suggesting that zone plates can be designed to survive the

FEL environment. The thermal robustness is largely due to the relatively large area and amount of absorbing material in the optical element [13]. This is of course not true for the sample itself, which will be destroyed after the first pulse.

D. Soft X-Ray Photon Correlation Spectroscopy (SXPCS)

In soft and hard materials alike, a large number of coupled microscopic interactions often conspire to produce properties that emerge on a length scale between a few and a few hundred nanometers. The process whereby this occurs is one hallmark of material complexity. Scattering a coherent soft x-ray beam from these emergent nanoscale inhomogeneities essentially maps this complexity, in space and time, into a far-field speckle-diffraction pattern that can be analyzed in various ways to address diverse material problems. An illustrative example is shown in Figure 4. In this case, the system is an orbital-ordered phase of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (PCMO), a half-doped colossal magnetoresistive manganite crystal. The complexity in this system stems from coupling between atomic-scale Coulomb interactions between electron charges, exchange interactions between electron spins, quadrupolar interaction between electron orbitals, and vibronic interactions between neighboring unit cells. By tuning the incident x-ray

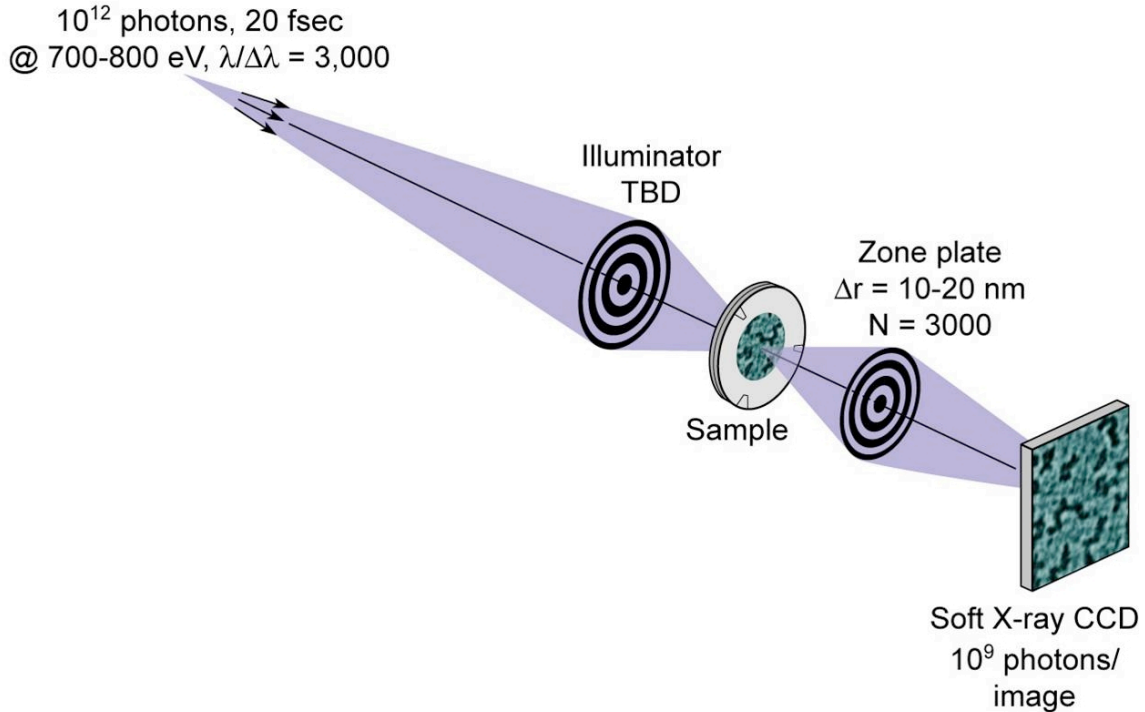


Figure 3. Optical setup of a full-field soft x-ray microscope to be implemented at a femtosecond soft x-ray light source.

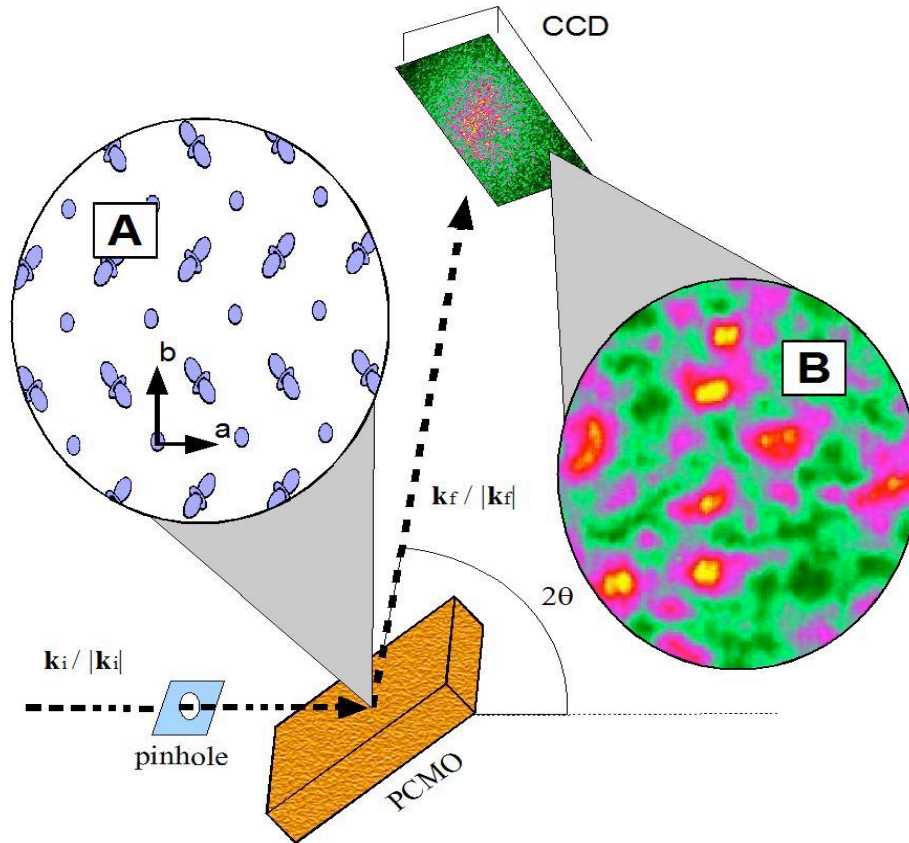


Figure 4. Coherent scattering from $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The scattering geometry is set to measure the orbital-order Bragg reflection at $Q = (0, 1/2, 0)$. Inset A schematically depicts the atoms of the Mn sub-lattice, the only sites probed with resonant scattering. The CE-type orbital ordering of the e_g electron of Mn is shown for a single domain, illustrated in the a-b plane. Coherent interference between scattered waves from the domain structure of the sample results in a “speckle” pattern. Inset B shows a close-up view of one small region of the speckle image taken with a CCD camera, demonstrating the well-developed speckle pattern.

energy to the Mn L edge and working a Bragg geometry, particular sensitivity to various ordered phases can be achieved and their complexity projected into a diffraction pattern.

(1) The need for new light sources

Such experiments remain heroic on third-generation sources, since these are very signal-limited, owing to the low coherent flux of third-generation sources, the subtlety of the underlying contrast mechanisms, and the need for high angular resolution in the detector. For example, the low transverse coherence requires that a pinhole spatial filter be inserted, as shown in Figure 3, with a consequent loss of flux and the introduction of scattering artifacts. As a result, the PCMO speckle pattern in Figure 4 requires an exposure of ~ 30 seconds, and offers a spatial resolution not much better than the average domain size. Without significantly higher coherent flux, we will not be able to probe the nuances of the orbital domains that determine the transition between local interactions and nanoscale order, the core of emergent complexity in this system.

An FEL source with full longitudinal and transverse coherence would be of enormous benefit in a multitude of such experiments. It will manifestly help probe the structure of such exotic domain structures and thereby illuminate the competition between the underlying spin, charge, orbital, and lattice interactions. In many instances, these factors will be addressed by the high coherent power available from a soft x-ray FEL source, since the improved flux will allow measurements at much higher scattering wave vector and thus with much improved spatial resolution and will probe thermally driven fluctuations at a much faster time scale.

(2) *The experimental “phase space” of SXPCS*

Figure 5 provides a very broad view of the spatiotemporal sensitivities of various techniques that can be applied to material systems. Elastic and inelastic neutron scattering continue to be invaluable in understanding many soft and hard complex materials and also in measuring the underlying excitations. However the time scale τ of the nanoscale world often lies in a broad time domain spanning from sub-microsecond to many seconds, corresponding to energies \hbar/τ of less than a nanovolt—well below the energy resolution of quasi-elastic neutron scattering. Microscopy techniques are also useful in probing nanoscale phases, but many of these are difficult to apply to measure thermally driven fluctuations at time scales much faster than ~ 1 sec. Far-field optical techniques are limited to longer length scales and near-field optical techniques often suffer from the same temporal constraints as scanned probe microscopies. In short, there is a large gap at short length scale and moderate time scale that is not naturally probed by these techniques. Indeed, many efforts exist to extend the reach of these techniques into this broad spatiotemporal domain.

(3) *Experimental opportunities in SXPCS*

Speckle-diffraction patterns like the one shown in Figure 4 have a large though not easily accessed information content. How can we extract this information to probe interesting and important material phenomena?

Diffraction imaging

As explained earlier in this chapter, one very important opportunity is diffractive imaging. If the pattern in Figure 4 can be phased, for example, we could image the underlying “orbital domains.” In PCMO, these domains exhibit short-range order, with a correlation length or domain size of ~ 20 nm. As in many marginally ordered phases, this short-range order is poorly understood yet is very important to the macroscopic material properties. This is one of a very small number of candidate imaging methodologies for orbital domains.

Dynamic soft x-ray scattering

Another largely unexplored area where coherent soft x-ray beams will have a major impact is in probing nanoscale fluctuations. Nanoscale fluctuations in complex media often adopt various non-exponential decays that are a key ingredient of emergent complexity. For example, stretched exponentials are common in polymeric systems and

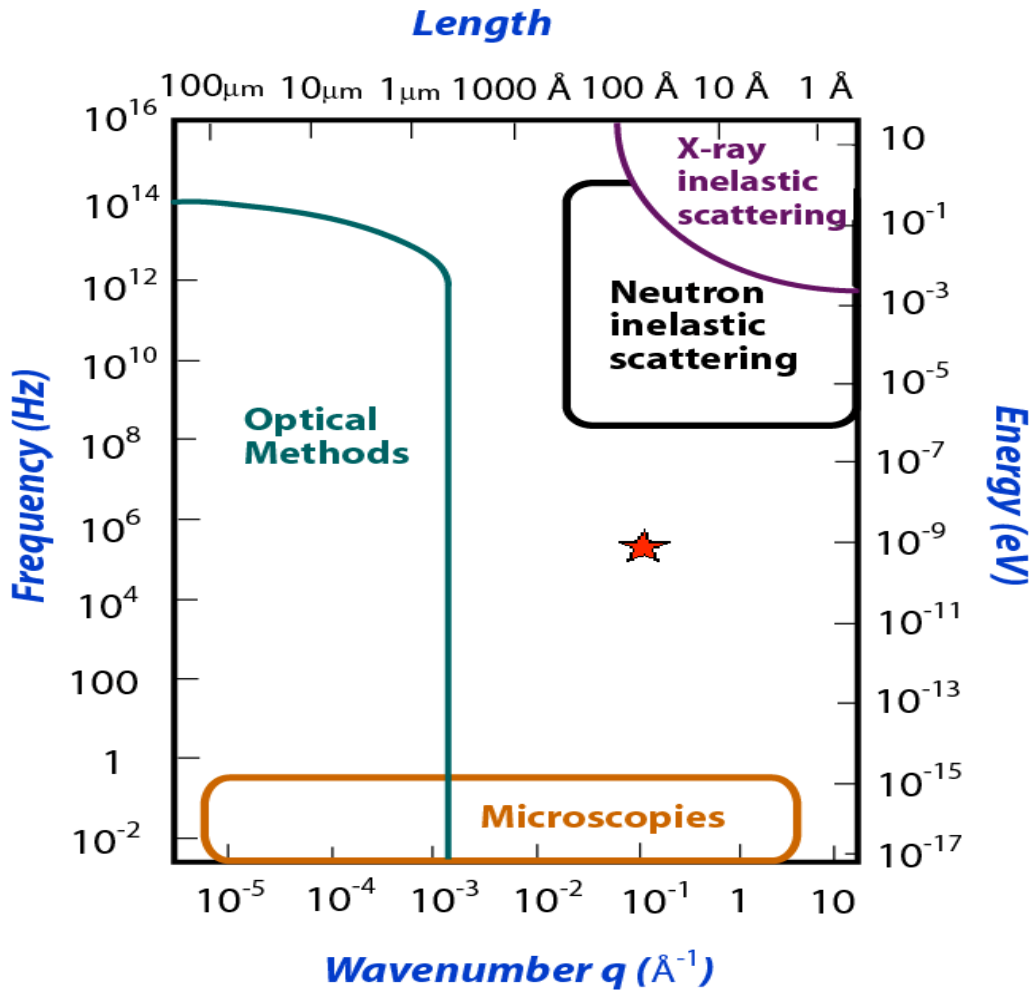


Figure 5. Spatial and temporal sensitivities of various techniques. Operating in the time domain and at short wavelength, SXPCS can address the large gap in the lower right portion of the figure (indicated by the star), providing unique access to relatively low frequency and short length scale phenomena that are relevant to complex soft and hard materials. Stated differently, photon correlation spectroscopy is also called quasi-elastic light scattering and naturally probes very low energy modes. These will often be overdamped modes related to diffusion and domain wall motion. The other techniques listed in the figure are being continually developed for application in this regime as well, with varying degrees of success.

telegraph noise is endemic to sensors and various kinds of switches, and these noise sources generally result from complex nanoscale interactions.

The application of coherent soft x-ray scattering to this problem is conceptually straightforward. For example, if the boundaries of the orbital domains probed in Figure 4 were fluctuating in time, then the speckle pattern formed in coherent scattering will also fluctuate. These fluctuations can be analyzed to deduce the intermediate scattering function, $S(\mathbf{q}, t)$, which is the Fourier transform of the dynamical structure factor, $S(\mathbf{q}, \omega)$. This function provides a key measure of spatiotemporal dynamics in neutron and laser light scattering and in principle provides a window into the gap in Figure 5. Similar

approaches are currently used in the hard x-ray regime. The higher coherent flux combined with the atomic, molecular, and magnetic contrast available near absorption edges in the soft x-ray regime suggests many fruitful dynamic scattering applications. Coherent soft x-ray beams have already been applied to fluctuating liquid-crystal films and magnetic systems [14, 15].

Generally speaking, dynamic soft x-ray scattering experiments are even more signal limited than diffractive imaging, since the goal is to measure fluctuations in time. Essentially, in dynamic scattering, one is measuring time-delayed coincidences, and incident coherent flux becomes a serious limitation. For example, with a differential scattering rate of one photon/second/speckle, one cannot easily measure frequencies very much faster than 1 Hz. Attempts to measure the fluctuations of the orbital domains in PCMO near the orbital ordering transition temperature were successful but were limited to long time scales due to the limited signal available [16].

Response of inhomogeneities to external forces

Another way to use x-ray speckle/diffraction patterns to probe nanoscale material phenomena is to mimic many applications in optical metrology to study how inhomogeneities respond to external stresses, applied fields, and currents. For example, this approach has formed the basis for recent measurements of microscopic return point memory, wherein speckle patterns from Co:Pt multilayers collected before and after traversing a magnetization loop were statistically compared [17, 18]. Such measurements can be extended to more complex structures that mix hard and soft ferromagnetic films to produce spring-magnet systems or that mix antiferromagnetic and ferromagnetic components to produce exchange-bias structures [19], as well as to more complex magnetic materials like a manganite crystal driven through the colossal-magnetoresistance transition. These systems will allow us to understand the non-ergodic processes that influence microscopic memory. An important ingredient of these studies will be the spatial length scale that is probed, and the maximum scattering wave vector measured in turn determines this scale. As in the techniques discussed above, to probe memory effects in the interesting nanoscale regime where emergent complexity occurs will require significantly more coherent flux than presently available.

Cross-correlation of speckle at different wave vectors

The final and most speculative application of coherent scattering is to investigate “nanoscale mode coupling” by cross correlating speckle intensity at different wave vectors, either in dynamical scattering or in studying microscopic memory. The basis of dynamic light scattering is van Hove’s formalism developed in the 1950’s of the space–time correlation function [20]. In that theory, each mode is associated with a particular wave vector, and in a scattering experiment the wave vector is set by the scattering geometry. The system is assumed to be linear, and the modes are independent. The theory has been broadly applied and is remarkably successful and useful. However, it is plausibly a hallmark of nanoscale complexity that the linearity assumption breaks down. Proving that, and then using the result to measure the coupling between modes, will require the high coherent power of an FEL source. The role of complexity in magnetic

and soft systems recommends formulating such an experimental program around a soft x-ray FEL.

There is sometimes a friendly discussion between practitioners of scattering techniques, who usually measure statistical averages in reciprocal space, and practitioners of microscopies, who prefer to measure images in real space. Scattering directly provides average domain sizes, for example, while microscopies can measure the shape and size of specific domains. To the extent that such competition is meaningful, one of the advantages of coherent x-ray scattering is that both real- and momentum-space information are available, depending largely on the issues being pursued. Indeed, complex mesoscale phenomena like those discussed above are best treated with equal emphasis on real-space and Fourier-space techniques.

E. Requirements of a New Soft X-Ray Source for Imaging and XPCS

Table 1. Imaging and XPCS Requirements for a New Soft X-Ray Source.

Property	Comments
Time resolution	~ 5 fs for flash imaging, 20 – 50 fs for other experiments
Energy resolution	transform limited
Repetition rate	1 kHz for flash imaging, 10 – 100 kHz for other experiments
Average flux	10^{15} ph/s/0.1% BW
Peak flux	10^{12} ph/pulse/0.1% BW, 10^{10} ph/pulse/0.1% BW (third harmonic)
Tunability	500 eV – 1 keV fundamental, 1.5 keV – 3 keV (third harmonic)
Polarizability	adjustable circular/linear
Coherence	full spatial coherence, transform limited temporal coherence
Stability	< 10% pulse amplitude, $< 0.1\sigma$ transverse position
Laser synchronization	10 fs

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VII. A Soft X-Ray Light Source to Meet the Requirements of a New Generation of Soft X-Ray Science

A. Capabilities Required to Meet the Scientific Challenges

The experiments that will explore the new opportunities at a future soft x-ray light source can be very diverse, and therefore a multi-user facility would be of great interest. Correspondingly, the requirements for any new soft x-ray facility to address the majority of the science will be varied and demanding. Table 1 summarizes light-source requirements gathered from the workshop breakout sessions. This summary table expresses the range of requirements, and does not represent a self-consistent set of design goals.

Future experiments will involve a level of complexity a generation beyond that of experiments that are routinely performed at today's light sources, resulting in additional requirements for the facility. The scientific output of new facilities in the soft x-ray region can only be insured by the availability of a range of resources and infrastructure:

- Appropriate sample-preparation facilities and staging areas are required near the beamline end-stations.
- Beamlines must be designed with the ability to host researchers with custom-made end-stations; two to three beamlines per undulator are desirable to allow longer set-up times and ensure that two to three groups are always ready to make use of the beam at any time.
- Laser rooms need to be located at each beamline with sufficient room for multiple systems, instrumentation for set-up, and diagnostics.
- Pump-probe experimentation requires integrated optical and x-ray laser systems, with tight synchronization between multi-color sources varying from IR to X-ray.
- Temperature- and vibration-controlled environments will be critical in providing stability in spatial and temporal coordinates on the scale of nanometers and femtoseconds.
- Appropriate time must be allocated to successfully mount experiments in which substantial challenges will be encountered.

B. Overview of New Technologies for X-Ray Light Sources

Advances in the design of storage-ring lattices have resulted in smaller source size and divergence, and, together with insertion devices, have provided orders of magnitude greater spectral brightness from synchrotron radiation sources over the past decades. The advantages are that many photons per unit wavelength improves spectral resolution; a small source size improves the ability to image small objects; and small divergence is critical for obtaining the diffraction pattern of large crystals. Storage-ring design is now

highly mature, and significant improvements in performance will be difficult to realize with this technology.

Table 1. Facility requirements derived from breakout sessions.

Property	Facility Requirements	Comments
Energy range (eV)	10–3000	Up to 1000-eV photon energy in the fundamental. Higher energies in the third harmonic, up to 3000 eV, would also be utilized, with reduced peak power.
Repetition rate (kHz)	100 or higher 1–100	High repetition rates for coincidence experiments. Lower rep-rates also have application; 1 kHz for flash imaging, 10 – 100 kHz for other imaging experiments.
Peak power (GW)	0.1–1	For 10–1000 eV, up to 10 MW from 1000–3000 eV. High peak power required for four-wave mixing and for dilute targets. 0.3 GW peak power for attosecond pulses.
Peak flux (Photons/pulse/0.1%BW)	10^{10} – 10^{12} 10^8	10-1000 fs pulses. 0.1 fs pulses.
Average flux (Photons/s/0.1%BW)	10^{15} – 10^{17} 10^{10} – 10^{13}	10–1000 fs pulses. 0.1 fs pulses.
Power density (W/cm^2)	10^{14} – 10^{21}	High power density for study of strong nonlinear effects. Otherwise one ionization event per shot for coincidence measurements.
Pulse length (fs)	1-1000 0.1	Control of Δt and ΔE (close to transform limit). Electron dynamics requires attosecond pulses.
Energy resolution (eV)	0.01	Control of Δt and ΔE , ~2-3 times the transform limit. Use monochromator (pinhole) when necessary.
Coherence		Full spatial coherence, close to transform limited temporal coherence.
Harmonics	1% < 0.1 %	Desirable for obtaining higher photon energies, at ~1% of the fundamental power. As low as possible; for some experiments, filter elements may be needed.
Spot size (μm)	1-100 0.05	Tunable spot size at the sample. Desirable for high-intensity AMO experiments.
Intensity stability	5%	Intensity should be recorded shot by shot.
Position stability		< 0.1σ (beam size) transverse position.
Pointing stability (μ -rad)	<10	
Background signal	<0.1 %	Contrast ratio 1:1000 desirable.
Polarization	Variable, linear/circular	
Timing stability (fs)	<5 10	Laser synchronization for pump–probe experiments. Imaging applications.

For the next generation of x-ray light sources, it would be desirable to have a source with the properties of a laser beam but with photon energies tunable from the VUV into the x-ray region. These properties should be obtainable from high-harmonic generation (HHG) in gases and from a free electron laser (FEL).

Recent developments in production of high-brightness electron beams, high-power lasers, seeding, and optical manipulations of electron beams that lead to enhancement of FEL performance have engendered a broad international interest in FEL facility design. Temporally and spatially coherent photon pulses, with peak power of up to gigawatts, photon energy from eV to keV, control of pulse duration from sub-femtosecond to picosecond, and megahertz or greater repetition rate offering average power of Watts, are anticipated. The major FEL concepts are self-amplified spontaneous emission (SASE), and seeding. Seeding the FEL process with an optical laser imparts temporal coherence, narrow bandwidth in the output radiation, control of the FEL output pulse amplitude and duration, and synchronization of the x-ray pulse to the seed laser.

C. Parameters of Possible New X-Ray Light Sources

Advanced FEL technology, exploiting a high-repetition-rate, low-emittance electron source, superconducting RF accelerating modules, and optical manipulations of the electron beam with high-power lasers provides the basis for a new class of soft x-ray light sources with enhanced performance in several critical areas:

- Temporal as well as spatial coherence of the FEL output pulse
- Control of the time duration and bandwidth of the coherent FEL pulse
- High pulse-repetition rate
- Precise synchronization of the FEL pulse to the seed laser
- Control of pulse energy
- Generation of x-ray wavelengths through the use of harmonic stages
- High average flux and brightness

Based on projected technology limitations, to provide photon beams in the wavelength range 1 to 200 nm (1.2 keV to 6 eV), one can envision three general types of beamlines, and Table 2 suggests reasonable performance goals over a range of x-ray pulse durations from picosecond to attosecond regimes. Seeding of the FEL imparts temporal coherence, providing laser-like x-ray pulses with clearly defined temporal and spectral properties, and control over the output power. Longer pulses provide high energy resolution, and short pulses allow exploration of time-domain (pump-probe) experiments with exquisite temporal resolution. CW accelerator systems offer high repetition rate and high average flux and brightness, plus the attraction of stability of the photon pulse in pulse energy and timing. Optical manipulations allow control of bandwidth and energy chirp.

Table 2. Performance goals for a future seeded FEL facility.

	Short-pulse beamlines	High-resolution beamlines	Sub-femtosecond beamlines
Wavelength range (nm)	~ 200–1	~ 200–1	~ 40–1
Pulse length (fs)	1 – 100	100 – 1000	0.1 – 1
Photon energy (eV)	6 – 1240	6 – 1240	30 – 1240
Repetition rate (kHz)	100	100	1 – 100
Peak Power (GW)	≤ 1	≤ 1	0.1 – 0.3
Photons/pulse (@ 1 nm)	5×10^{11} (in 100 fs)	2.5×10^{12} (in 500 fs)	1.5×10^8 (in 100 as)
Timing stability (fs)	10	10	TBD
Harmonics	≤ few %	≤ few %	≤ few %
Polarization	variable, linear, circular	variable, linear, circular	variable, linear, circular

Figure 1 shows a schematic of how a multiple-beamline, multi-user facility might be configured. Such a facility would provide an array of task-designated FELs, wherein each FEL may be configured to operate in a different mode. Each FEL would have

Array of configurable FELs
 Independent control of wavelength, pulse duration, polarization
 SASE or configured with an optical manipulation technique; seeded, attosecond, ESASE

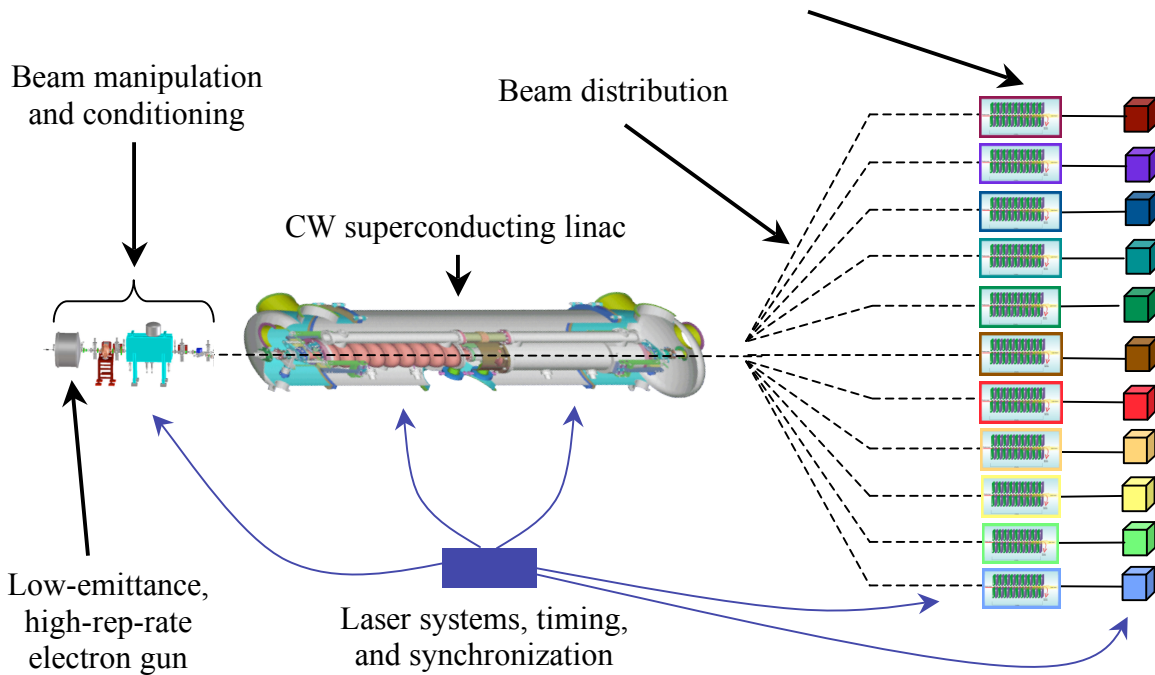


Figure 1. Schematic of a light-source facility based on an array of high-pulse-repetition-rate FELs.

independent control of wavelength and polarization, and optical manipulations of the electron beam would be used to produce x-ray pulses with controlled pulse duration, offering flexibility and versatility to many experiments simultaneously. The major components are: (1) a low-emittance, low-energy-spread RF photocathode electron gun, providing electron bunches at up to MHz repetition rate, (2) hardware for manipulating the electron-beam emittance in preparation for the FEL process, (3) a CW superconducting RF linac, (4) a beam-switching system to distribute electron bunches from the linac to each of the FELs, (5) multiple independent FELs and beamlines, and (6) lasers for the photocathode gun, FEL seeding, pump-probe experiments, and timing and synchronization. A low-energy linac is used to minimize costs. The electron beam is dumped at the end of each FEL as we do not currently believe the added cost and complexity of electron-beam recirculation and energy recovery is worthwhile for a machine of modest electron-beam power.

Figure 2 shows the range of performance of a seeded high repetition-rate FEL facility and complementary facilities in terms of brightness as a function of pulse duration.

D. Physics and Technological Limitations, and R&D for Future Light Sources

A limitation on x-ray FEL performance arises from the undulator resonance condition, which occurs at wavelengths at which the undulator period, when observed in the beam frame, is blue-shifted such that it is an integral number of wavelengths of the radiation emitted in each undulator period. APPLE-type undulators allow control of the polarization by moving segments of the magnetic material in quadrants about the beam axis. With state-of-the-art undulator technology and for the fundamental FEL output in the nanometer region, the electron-beam energy required is approximately 2.5 GeV. Developments in undulator design to periods less than 1.5 cm, gap less than 3.5 mm, and K-value around 1 offer prospects of higher-energy photons for a given electron beam energy.

Optimal FEL performance requires that the transverse phase-space of the electron beam to match that of the output radiation and that the electron-beam longitudinal phase-space (peak current and energy spread) be controlled to provide high saturated peak power and a short gain length. The current state-of-the-art for low-emittance electron sources is approximately 1 mm·mrad (normalized with respect to energy) with 1 nC charge per bunch. For an electron-beam energy of approximately 2.5 GeV, the desirable emittance is approximately half this. A smaller emittance may be obtained by using lower-charge bunches, and the required peak current (hundreds of Amperes) may be obtained by using bunch compression techniques in the accelerator prior to the FEL.

High repetition rate and high average photon flux are essential to many experimental techniques, and developments are required in the electron source to provide high-brightness beams at high repetition rate. Several technologies are being developed, including photocathode sources with DC, superconducting RF, and normal-conducting RF accelerating fields. Photocathode-materials design and high-power laser systems

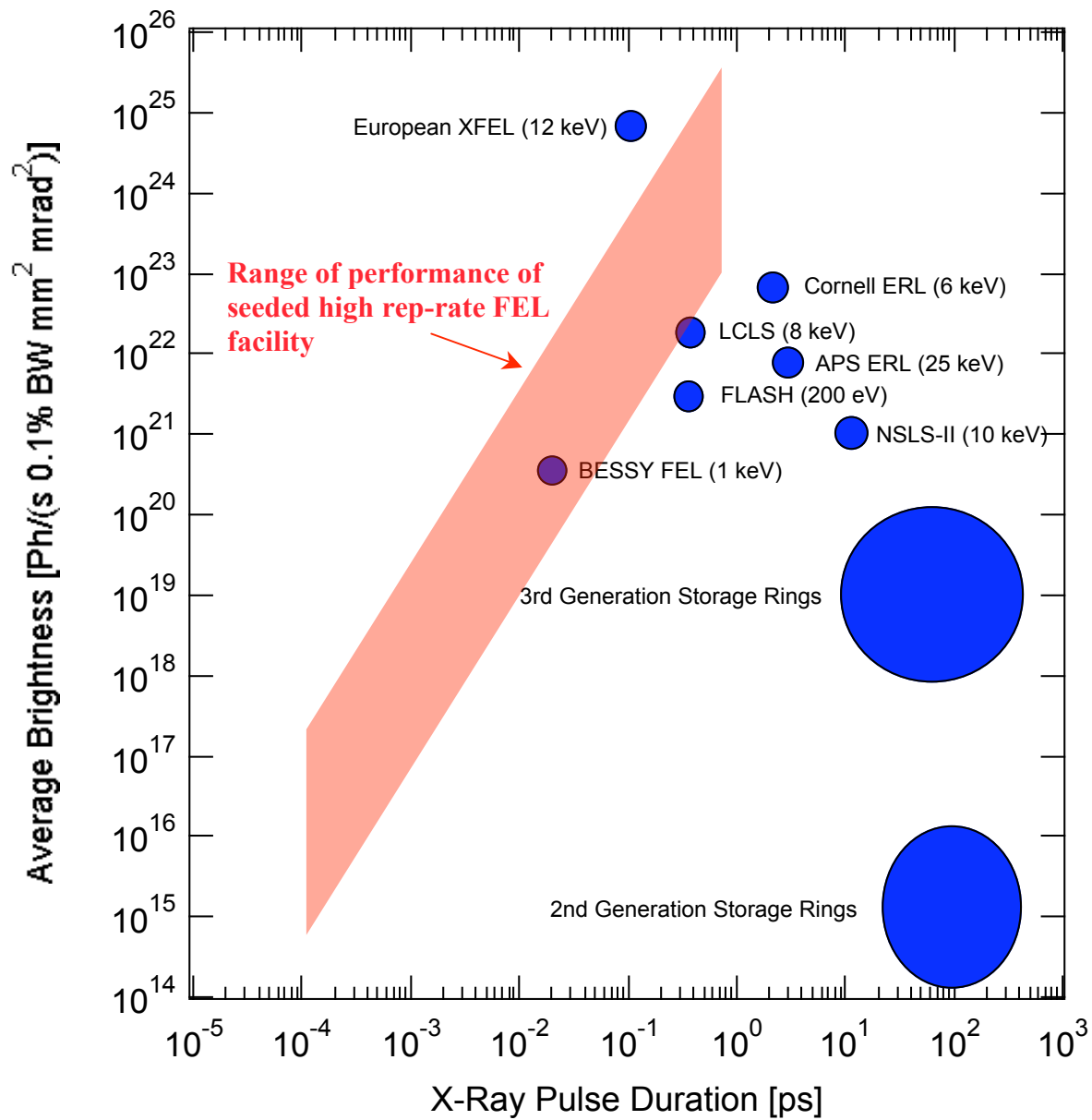


Figure 2. Average brightness versus pulse duration for representative storage ring, ERL, and FEL sources. Values for identified proposals are shown for design brightness at the photon energies indicated in parentheses, based on available data. For the XFEL and FLASH this reflects the use of bunch trains. The dashed line indicates potential for a 100-kHz seeded-FEL facility utilizing optical manipulations to control pulse duration.

are also critical to the production of high-brightness beams, and tailoring of the laser pulse to shape the electron bunch in both space and time coordinates will be an important control of electron beam quality. It is anticipated that the desired high-brightness electron source performance will be achieved in proposed R&D programs.

In addition to the source, the main accelerator must be capable of supporting high-repetition-rate beams, and superconducting radiofrequency technology is the clear choice for high-repetition-rate applications. Normal conducting accelerating structures are limited to pulsed operation at up to the kilohertz range, by thermal stress from the power deposited by RF currents in the structure walls. These losses are minimized in superconducting materials, and continuous-wave (CW) operation may be achieved, supporting electron bunch rates of up to GHz. Superconducting RF technology is being developed for a number of applications, and R&D in CW systems designs is being pursued at several institutions with goals of higher accelerating gradient, higher quality factor, and reduced higher-order-mode impedance.

Optical manipulations and seeding involve co-propagating a laser pulse with an electron bunch in the periodic magnetic field of an undulator. Electrons passing through an undulator interact coherently with the electric field of the laser when the magnetic field period is equal to the laser period in the rest frame of the electrons. At this resonance condition, an energy variation of the electrons is introduced, with a distribution duplicating that of the overlapping laser pulse. With sufficient laser power, the amplitude of induced energy variation can significantly exceed the natural energy spread in the beam. In a following dispersive section, this energy variation is converted to a charge density modulation, resulting in production of very localized concentrations of high charge density, separated by the laser wavelength. This “microbunching” of the electrons enhances coherent radiation from those electrons within a tightly bunched region, and leads to controlled lasing in a downstream FEL radiator undulator. The spectral content of the microbunched beam is rich in harmonics, and the FEL radiator may be tuned to one of these harmonics and laser output produced at a shorter wavelength than the seed. Cascading the modulator/radiator arrangement allows for successively shorter output wavelength. Using carrier-envelope-stabilized pulses of few-cycle duration allows production of x-ray output pulses with duration in the sub-femtosecond region. Several groups are active in developing techniques for enhancing FEL performance by using lasers to manipulate the electron beam with high resolution.

Future FEL facilities will require a combination of accelerator and laser technologies, and developments in high-power lasers will directly benefit future FEL facilities as photocathode, seed, diagnostics, and end-station lasers, as well as HHG sources. Developments are needed to provide highly reliable systems with high average power, easy tunability (optical parametric amplifiers), excellent mode quality, carrier-envelope phase stability, timing precision, and frequency multiplication. Also, optical timing and synchronization signals will be needed to lock the photocathode, seed, and end-station lasers, as well as the accelerator RF systems, to provide highly stable integrated systems with exquisite control over timing for high-resolution pump-probe experiments. Systems are being developed using stabilized optical fiber transmission lines that promise femtosecond-scale timing and synchronization capabilities over kilometer-scale facilities.

VIII. Efforts around the World to Establish New Soft X-Ray Light Sources

The FLASH facility at DESY currently operates a SASE FEL at wavelength as short as 6.5 nm, with typical pulses of 100 μ J, duration of tens of femtoseconds, and repetition rate of 5 Hz. FERMI@Elettra is a seeded FEL facility under construction at Sincrotrone Trieste with wavelength in the 10-nm region and pulses of hundreds of microjoules, duration of hundreds of femtoseconds, at 10-Hz repetition rate. In addition to these and other operational and under-construction facilities, several groups designing a new generation of FELs using advanced accelerator and laser technologies are actively engaged in R&D toward realizing the full potential of future FEL facilities. Figure 1 shows worldwide projects in VUV—soft x-ray FEL facilities at the time of the workshop. Most are based on linear accelerator (linac) technology with single-pass FELs, although the Elettra FEL is built on a storage ring. The BESSY, Wisconsin, 4GLS, Arc-en-Ciel, and LBNL concepts use superconducting-RF linear accelerators to support electron bunches at MHz or greater repetition rate. FERMI@Elettra, MAX-IV, SPARX, SCSS, and the SDUV-FEL are based on pulsed normal-conducting linear accelerators.

Wavelengths in the soft x-ray spectral region are also attainable through the high-order, odd harmonics produced when an intense and short optical laser pulse is focused into a gas. High-harmonic generation (HHG) can be produced with temporal and spatial coherence properties similar to the driving laser field and, under special conditions, with sub-femtosecond pulse duration. Conversion efficiency is relatively low and typically decreases with increasing harmonic order. HHG can provide a source in a single-investigator-sized laboratory with output pulses synchronized to the driving laser and produced with the same repetition rate. Such sources have been generated using commercial driving lasers at the several-watt level, with repetition rates ranging from 10 Hz to 10 kHz. The cut-off of the harmonic spectrum extends to shorter wavelength as the drive laser intensity is increased up to a saturation intensity where harmonic generation decreases. The spectral cut-off of HHG may be extended to shorter wavelength by using a gas species with a higher ionization potential and by using a longer-wavelength drive laser; however, the conversion efficiency is typically lower. Developments in high-average-power, short-pulse lasers in the micron-wavelength range, perhaps extending average powers up to the kW level, together with novel phase-matching techniques in the harmonic-generation medium, give promise of future HHG sources extending into the hundreds of eV region with conversion efficiency of the order of 10^{-6} and average soft x-ray powers in the range of milliwatts.

Such advances in laser technology will benefit both HHG source development and FELs where high-power lasers are required for the photocathode source, FEL seeding, end-station lasers, and optical timing and synchronization systems, all operating at high repetition rate. Therefore, sophisticated short-pulse laser systems, with high average powers need to be developed. HHG sources will be needed to provide the seeding power for FELs, which then act as amplifiers to generate soft x-ray powers in the range of watts.

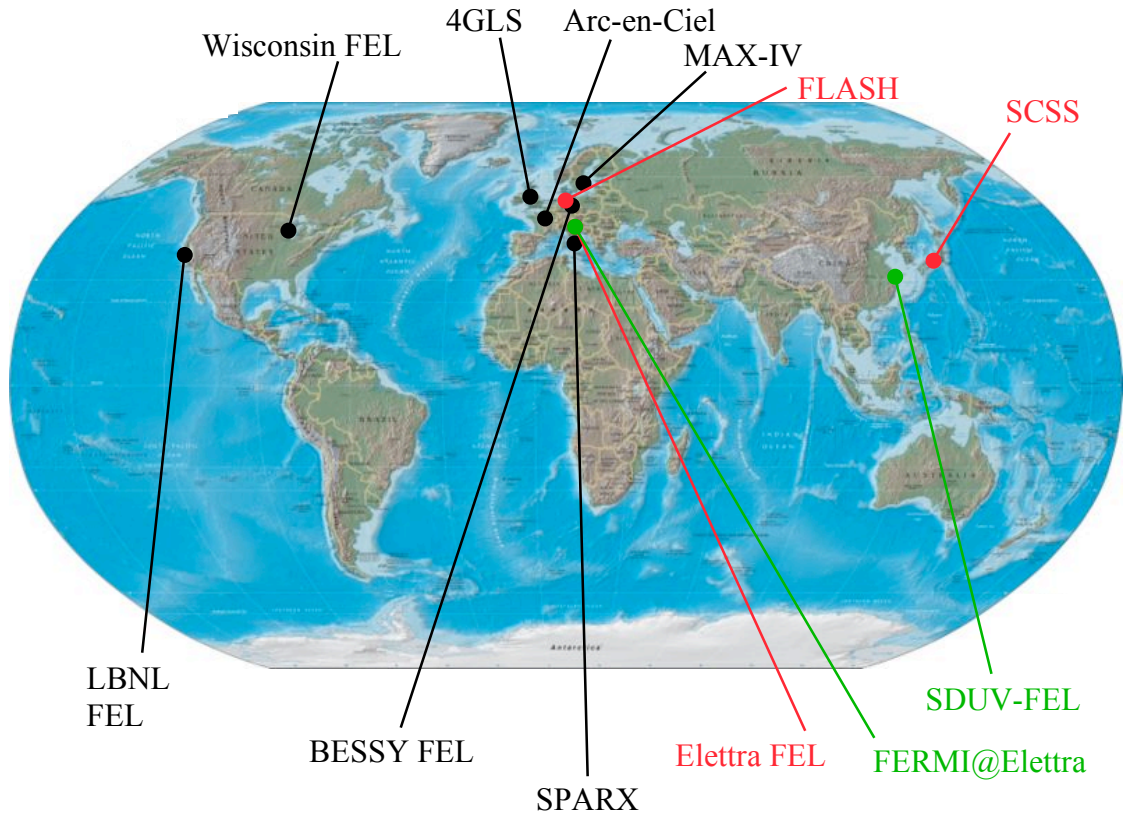


Figure 1. VUV–soft x-ray (from 200 nm to 1 nm) FEL projects worldwide. Key: red: operational, green: funded for construction, black: proposal or concept under development.

Appendix. Workshop Agenda

Science for a New Class of Soft X-Ray Light Sources

Doubletree Hotel & Executive Meeting Center, Berkeley Marina

Berkeley, California October 8 – 10, 2007

ORGANIZING COMMITTEE

Ali Belkacem (*LBNL*)

John Corlett (*LBNL*)

Roger Falcone (*LBNL/UC Berkeley*)

Graham Fleming (*LBNL/UC Berkeley*)

Bill McCurdy (*LBNL/UC Davis*)

Dan Neumark (*LBNL/UC Berkeley*)

Bob Schoenlein (*LBNL*)

AGENDA

Monday, October 8

08:30 - 09:00 | Directing Matter & Energy: Five Challenges for Science and the Imagination | Graham Fleming

09:00 - 09:45 | Parameters of New Soft X-Ray Light Sources | John Corlett

09:45 - 10:30 | Atomic and Molecular Physics | Joachim Ullrich

10:30 - 10:45 ~ Continued discussions, refreshments served ~

10:45 - 11:30 | Magnetization and Spin Dynamics | Joachim Stöhr

11:30 - 12:15 | Chemical Physics | Steve Leone

12:15 - 01:15 ~ Working lunch and discussions of morning talks ~

01:15 - 02:00 | Nanoscience and Coherence | Paul Alivisatos

02:00 - 02:45 | Complex Material Dynamics | Andrea Cavalleri

02:45 - 03:00 ~ Continued discussions, refreshments served ~

03:00 - 05:30 | Breakout Sessions in parallel |

(each with 10-15 minute invited panel presentations)

1. Atomic, Molecular and Optical Physics
2. Chemical Physics

3. Correlated Materials
4. Magnetization and Spin Dynamics
5. Nanoscience and Coherence

Tuesday, October 9

08:30 - 09:15 | Time-resolved Molecular Dynamics | Majed Chergui

09:15 - 10:00 | Magnetization Dynamics | Wolfgang Eberhardt

10:00 - 10:15 ~ Continued discussions, refreshments served ~

10:15 - 11:00 | Correlated Materials | Z. X. Shen

11:00 - 11:45 | Atomic and Molecular Physics | Paul Corkum

12:00 - 01:00 ~ Working lunch and discussions of morning talks ~

01:00 - 01:30 | Coherent Imaging | Henry Chapman

01:30 - 03:00 | Breakout Sessions in parallel |

03:00 - 03:15 ~ Continued discussions, refreshments served ~

03:15 - 05:30 | Breakout Sessions in parallel |

06:00 | Dinner buses depart from Doubletree Hotel for Berkeley City Club |

06:30 ~ Working Dinner: "Discussion of Optimal Performance Parameters for Soft X-Ray Light Sources" ~

Ballroom, Berkeley City Club, 2315 Durant Avenue

Wednesday, October 10

08:30 - 10:10 | Preliminary reports from Breakout Groups in each of five areas |

10:10 - 10:30 ~ Continued discussions, refreshments served ~

10:30 - 12:00 | Final preparation of reports in each of five areas |

12:00 - 01:00 ~ Working lunch and final discussions~



Attendees at the October 2007 workshop “Science for a New Class of Soft X-Ray Light Sources” pose for the traditional group photograph at the Berkeley Marina outside the Doubletree Hotel & Executive Meeting Center.

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Report available online at <http://hpcrd.lbl.gov/sxls/home.html>.

Report prepared at Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

Editor: Arthur L. Robinson (Advanced Light Source Division)

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