Basic Energy Sciences Roundtable

Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science

October 25–26, 2017
The artwork on the cover depicts the transformation of the magnetic material magnetite (Fe₃O₄) from its low-temperature insulating state into an electrically conductive state as induced by excitation with an ultrafast laser pulse. The phase transformation, probed structurally by time-resolved x-ray scattering at the LCLS free electron laser, is found to occur in less than a trillionth of a second [S. de Jong et al., Nature Materials 12, 882 (2013)].

Image courtesy of SLAC National Accelerator Laboratory.
Report of the Basic Energy Sciences Roundtable on Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science

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### Abbreviations, Acronyms, and Initialisms

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<th>Description</th>
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<tr>
<td>ARPES</td>
<td>Angle-resolved photoemission spectroscopy</td>
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<tr>
<td>BES</td>
<td>Basic Energy Sciences</td>
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<td>DOE-BES</td>
<td>Department of Energy Office of Basic Energy Sciences</td>
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<tr>
<td>eV</td>
<td>Electron volt</td>
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<td>ICD</td>
<td>Interatomic Coulombic decay</td>
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<td>IR</td>
<td>Infrared</td>
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<tr>
<td>IXS</td>
<td>Inelastic x-ray scattering</td>
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<tr>
<td>LCLS</td>
<td>Linac Coherent Light Source</td>
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<tr>
<td>NEXAFS</td>
<td>Near edge x-ray absorption fine structure</td>
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<tr>
<td>PRO</td>
<td>Priority research opportunity</td>
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<tr>
<td>RIXS</td>
<td>Resonant inelastic x-ray scattering</td>
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<tr>
<td>tr-ARPES</td>
<td>Time-resolved angle-resolved photoemission spectroscopy</td>
</tr>
<tr>
<td>SXRS</td>
<td>Stimulated x-ray Raman scattering</td>
</tr>
<tr>
<td>tr-XRD</td>
<td>Time-resolved x-ray diffraction</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>XFEL</td>
<td>X-ray free-electron laser</td>
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<td>XPCS</td>
<td>X-ray photon correlation spectroscopy</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>XUV</td>
<td>Extreme ultraviolet</td>
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Executive Summary

Advances in science and technology over the past century have been driven by an improved understanding of matter on ultrashort length scales, reaching down to atomic dimensions. In contrast, methods aimed at understanding dynamics on the ultrafast time scales of atomic motion are comparatively new. Ultrafast characterization has already yielded crucial insights not attainable from slower measurements. The interplay between atomic-scale structure and the associated ultrafast dynamics governs the macroscopic functionality observed in matter. Understanding and controlling materials and chemical processes at these length and time scales are key to discovery and innovation to advance energy and related national priorities.

The recent availability of x-ray free-electron lasers (XFELs) provides a probe that simultaneously reaches the required resolution in both space and time. X-ray wavelengths extend down to the atomic scale, while x-ray pulse durations now lie in the femtosecond \((10^{-15} \text{ seconds})\) range. This capability allows the evolution of materials and chemical processes to be followed on their natural time and length scales, providing fundamental scientific understanding of the complexity of the world around us.

Because of the transformative potential of new ultrafast x-ray characterization tools provided by XFELs, it is imperative to lay out a roadmap for the exciting scientific opportunities that can be explored using these research tools. To identify the highest priority research opportunities, the U.S. Department of Energy Office of Basic Energy Sciences (BES) convened a roundtable of experts in chemistry, materials physics, and ultrafast and x-ray science. This group of experimentalists and theorists met on October 25–26, 2017 to explore research opportunities that will leverage current and imminent ultrafast XFEL capabilities and advance the broader BES science mission. This report summarizes major new scientific frontiers that can be addressed by emerging XFEL capabilities. The conclusions of the roundtable discussion are summarized in the following three Priority Research Opportunities (PROs).

**PRO 1: Probing and controlling electron motion within a molecule**

The heart of chemistry lies in understanding how molecules are formed and transformed through interactions among their constituent atoms and electrons. The complex rearrangement of the positions of atomic nuclei and electrons defines the process of chemical transformation. While the motion of atoms is already extremely rapid, the motion of the much lighter electrons occurs hundreds or thousands of times faster, on the femtosecond to attosecond \((10^{-18} \text{ seconds})\) timescale. Existing ultrafast techniques for capturing chemical transformation have lacked the combination of time resolution and specificity necessary to follow the motion of the electrons and determine how this movement influences atomic rearrangement. Advances in XFEL capabilities, with the creation of ever shorter and more intense pulses, permit an unparalleled view of the steps
in chemical transformation. The impact of such investigations ranges from fundamental understanding of electronic interactions to the identification of molecules with improved capacity for energy storage and conversion.

PRO 2: Discovering novel quantum phases through coherent light-matter coupling

A central issue in materials physics is understanding and controlling the diverse phases of matter – from topological insulators with conducting edge states to novel ultrathin semiconductors to superconductors. Although these varied phases of matter are the basis for current and future information and energy technologies, we currently cannot fully explain how and why they form. Recently, the unique role of ultrafast light pulses in modifying the properties of matter has been widely recognized. Such modification can create novel quantum phases in a highly controlled fashion, with specific and previously unavailable external tuning through the shape and wavelength of the pulses of light. Advancing beyond the encouraging initial steps requires tools capable of characterizing, in detail, the nature of the transient phases. XFEL-based techniques that probe materials at ultrashort and ultrafast scales, coupled with a high repetition rate for the x-ray pulses, could enable the creation and control of light-induced phases of matter and the discovery of general principles needed to design novel states of quantum matter.

PRO 3: Capturing rare events and intermediate states in the transformation of matter

A significant challenge in understanding the transformation of matter is the ability to identify and characterize the underlying ultrafast dynamics of molecules and materials that occur spontaneously. Such transformations are not driven by external stimuli, but occur naturally as a result of thermal fluctuations. Studies of these spontaneous processes would enable a detailed understanding of the intricate pathways by which phase transformations and chemical reactions occur. However, a major roadblock has been the lack of experimental probes to identify and characterize the transient states with the requisite resolution in space and time. Emerging XFEL sources capable of producing femtosecond x-ray pulses at high repetition rates hold the key to capturing the complex processes involved in molecular and material transformations. Such developments are crucially important for understanding the formation and control of chemical compounds and phases of matter that will enable revolutionary advances in diverse processes, such as catalysis and synthesis, that are essential for the energy infrastructure.

The research opportunities summarized above exemplify the enormous scientific impact of capturing the evolution of molecules and materials on their natural atomic spatial and temporal scales. Rapid progress in the capabilities of x-ray free electron lasers makes this new research frontier experimentally accessible. The scientific understanding gained from these investigations will advance energy technologies central to the national economy.
1. Introduction

Over the past century, combined experimental and theoretical advances have led to a detailed picture of the structure of matter – from the shape of molecules to the periodic arrangement of atoms in solids. The progress of twentieth century science, coupled with growing understanding of the properties of electrons in molecules and solids, serves as the foundation for even more rapid and impactful advances in this century. Paradigm-changing insights have led to the modern devices and technologies we use in everyday life – from lightweight alloys, composite materials, and polymers to information systems, communication networks, and systems for harvesting, converting, and storing energy.

Central to these scientific and technological developments is the concept of “structure-function relationships,” the basis of our ability to understand the role of structure in the functional properties of molecules and materials. Until now, this approach has been unable to reach the shortest relevant timescales necessary to analyze and control the growth, synthesis, and transformations of molecules and materials. A detailed understanding of the fundamental dynamics of materials and chemical transformations is needed. Although the overall rates for chemical reactions or phase changes in condensed matter are relatively slow, the decisive underlying microscopic events in molecules and materials occur on the angstrom (10^{-10} m) length scale and femtosecond (fs, 10^{-15} s) timescale. Important dynamical processes range from the concerted motion of electrons and nuclei in molecules undergoing chemical change to the initiation of larger multi-atom transformations in solids, including phase transitions; charge, spin, and energy transport; and formation of quasiparticle correlations in quantum materials. These functional properties lie in the realm of ultrafast chemical and materials science.

Well-established x-ray, electron, and neutron probes of matter have been crucial for accessing structural properties of materials on the atomic scale, and ultrafast optical probes have enabled time-resolved studies of dynamics down to the femtosecond scale. However, none of these techniques have been capable of simultaneously producing atomic-scale spatial information and femtosecond time resolution. In this context, the development of x-ray free-electron lasers (XFELs) represents a major breakthrough for ultrafast science. A suite of x-ray-based diffractive, spectroscopic, and imaging techniques can now be applied using ultrafast x-ray pulses.

X-ray techniques provide extremely flexible and powerful probes of matter. X-ray resonances can be exploited to provide chemical sensitivity, as well as spin, orbital, and charge contrast, through dichroic and other resonant scattering mechanisms. X-rays can have sufficient momentum to provide a complete map of the electronic and vibrational states in periodic solids. The wavelength of x-rays is also sufficiently short to reach subatomic spatial resolution through well-developed x-ray diffraction and imaging methods. Inelastic x-ray scattering spectra can yield crucial information about materials.
excitations over a wide range of energy and momentum relevant to quantum functionality. The penetrating power of x-rays allows these approaches, moreover, to be used in complex environments, such as vapor or liquid.

Over the past 50 years, the frontier of x-ray science has been advanced by research performed at storage ring facilities. These sources produced the brightest x-rays until the first XFEL, the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory, opened in 2009. One constraint of storage rings is that the nature of the recirculating electron bunches limits x-ray pulses to durations exceeding ~100 picoseconds (ps, $10^{-10}$ s) – too long to capture electronic or atomic dynamics in most systems. The first generation of XFELs represented a major advance in x-ray sources for ultrafast science, featuring pulse durations of less than 10 fs, full transverse spatial coherence, and 10 orders of magnitude greater peak brightness than has been available at state-of-the-art storage rings.

Another major step forward in x-ray science capabilities is imminent, with the impending availability of next-generation XFEL sources. These new ultrafast x-ray sources will feature significant advances in technical capability (see XFEL sidebar), most notably by a thousand-fold or more increase in the pulse repetition rate.

The ultrafast capabilities provided by the next-generation XFELs are complemented by progress in table-top instrumentation and experimental techniques, notably in the creation of ultrashort pulses with lower photon energies. Table-top approaches can currently reach pulse durations even shorter than XFELs; however, they lack the broad range of photon energy and extreme brightness of XFELs. In addition, while not yet providing access to spectroscopic information, ultrafast electron diffraction is another direct probe of structural dynamics exhibiting very high spatial resolution.

In view of these important and fast-moving developments in the field of ultrafast x-ray science, the Department of Energy Office of Basic Energy Sciences (DOE-BES) convened a roundtable on October 25–26, 2017 to identify unique research opportunities enabled by XFEL capabilities. Participants included experts in x-ray and ultrafast science, as well as generalists across a wide spectrum of chemical and materials sciences disciplines, with representation of theorists and experimentalists.

The focus of the roundtable was to identify the top priorities, key science drivers and effective strategies for the BES research portfolio that use the LCLS facility, including its prospective upgrades. The aim of the roundtable was to provide input to optimize BES investments in ultrafast x-ray science and ensure the scientific impact of this research on the broader BES mission. The roundtable placed emphasis on identifying directions not yet exploited in current XFEL or other ultrafast approaches, nor extensively considered
X-ray free-electron lasers (shown schematically for LCLS-II above on the left) generate intense x-ray pulses using electrons accelerated to highly relativistic speeds. LCLS operates, for example, at an energy of 15 billion electron volts, producing electrons traveling at 99.999999% of the speed of light. These electrons are passed through periodically modulated magnetic fields, the so-called undulators. The undulators accelerate the electrons and induce them to emit x-ray photons. At the same time, interactions between electrons, the undulator's magnetic fields, and emitted x-ray photons cause the electrons to bunch together in periodic structures. The electrons then radiate coherently in phase with one another, corresponding to laser emission. This coherent emission process can lead to extremely intense and short pulses of x-rays. It is possible to produce x-rays with peak brightness more than 10 million times greater than the brightest modern x-ray storage ring facility, as shown interacting with matter in the right panel above.

X-ray beams created by XFELs are directed to experimental stations with instrumentation optimized for research in areas of atomic and molecular physics, chemistry, materials science, and biology. Because x-ray pulses are ultrashort (on the order of 10 femtoseconds, 10,000 times shorter than pulses created by x-ray storage ring facilities), much of the research pursued at XFELs has been directed at exploring ultrafast science.

Despite their revolutionary nature, first-generation XFEL sources operate at fairly low repetition rates. LCLS, for example, operates at 120 Hz. Incorporating superconducting accelerator technology (left figure) enables the next-generation XFELs, such as LCLS-II, which will feature repetition rates up to 1 MHz. This high repetition rate will increase the total number of photons provided to the sample up to 10,000-fold, while still retaining the femtosecond pulse duration and other desirable coherence properties of the x-ray beam.

The dramatic increase in pulse repetition rate and average brightness will open up new research opportunities in ultrafast science. The new capabilities will permit collection of 10,000 times more data when conducting pump-probe experiments, as shown schematically in right panel above and described below in PRO 1 and PRO 2. The higher repetition rate will also permit snapshots that capture a wide range of rare events in matter, as presented in PRO 3. (Images courtesy of SLAC National Accelerator Laboratory.)
in previous studies. The present report thus complements the 2015 study on science opportunities enabled by LCLS-II [1].

The discussion at the roundtable was initially organized along four interdisciplinary themes chosen to highlight different potential areas of impact of ultrafast x-ray science. These research themes were imaging nuclear dynamics, imaging charge dynamics, inducing and probing collective states, and exploring the high-field attosecond \( (10^{-18}\text{s}) \) frontier. The themes were a starting point for the discussions, which led to the definition of the three, more detailed, Priority Research Opportunities (PROs) presented in this report.

The potential of XFEL techniques to address critical problems in the dynamics of chemical transformations has been well recognized. To date, approaches have aimed primarily at understanding the lifetime of different excited electronic states and the ensuing dynamics from electronic excitation, including non-adiabatic transitions. While these fundamental issues in chemistry will continue to be addressed effectively with ultrafast x-ray techniques, the roundtable participants recognized the new possibility of actually capturing the motion of electronic density excited locally and subsequently moving rapidly across a molecule. Access to such dynamics, which require time resolution into the attosecond regime, will provide an entirely new approach to fundamental questions of electron correlation and non-adiabatic processes in molecular systems.

Within the field of quantum materials, highly impactful experiments with ultrafast x-ray techniques have begun to elucidate the nature of diverse correlated electron systems, from superconductors to Mott insulators. The subtle balance among different interactions leading to a given ordered state often makes interpretation of experimental data challenging. The ability of x-ray techniques to determine separately and quantitatively structural changes from functional changes ensures the continued central role of ultrafast x-ray techniques in understanding correlated materials. Recently, there has been dramatic progress in the use of ultrafast optical pulses not only to probe, but also to create and tune new states of matter, such as photo-induced superconductors and materials with new light-induced topological properties. To date, the power of x-ray techniques is just beginning to be applied to advance this fascinating new scientific direction.

In a different vein, the roundtable participants recognized that the dominant experimental approach in ultrafast x-ray science and, more generally, in ultrafast science consists of initiating a change in the molecular or materials system by means of a pump pulse and then probing the response by a delayed, time-synchronized probe pulse. Indeed, this schema, as well as more complex variants with multiple pump and probe pulses, is so prevalent that it is often assumed to be a required part of experimental studies of ultrafast dynamics. However, this approach necessarily constrains investigations to processes
occurring significantly out of thermal equilibrium, because the experimental method itself perturbs the system with the pump pulse. With the advent of ultrafast x-ray techniques at MHz data rates, a new experimental methodology can emerge. The approach involves making a large number of experimental measurements of the state of the system under study without any external pump pulse. In this fashion, some fraction of the measurements capture the dynamics of materials and molecules undergoing spontaneous change induced by thermal and quantum fluctuations. This approach requires a large set of snapshots of the system at different times, as well as an appropriate theoretical framework for analysis. As XFELs evolve to have dramatically increased repetition rates, coupling the experiments with next-generation, large-scale computation becomes increasingly important.

Codifying these considerations, the roundtable participants identified three priority research opportunities (PROs). The scientific challenges and impact of each topic are described in the subsequent sections of the report:

- PRO 1. Probing and controlling electron motion within a molecule
- PRO 2. Discovering novel quantum phases through coherent light-matter coupling
- PRO 3. Capturing rare events and intermediate states in the transformation of matter

Additionally, the participants identified forefront research directions common to all three PROs. These included harnessing the power of multimodal time-resolved x-ray studies to probe simultaneously the physical and electronic structure of matter, and advancing the frontiers of theory describing the transient, nonequilibrium behavior of matter undergoing change on the femtosecond timescale. These opportunities are described in an additional section entitled:

- Cross-cutting research opportunities in ultrafast x-ray science

Taken as a whole, the research directions identified above – made possible by dramatic impending advances in the performance and measurement capabilities of x-ray free-electron lasers – will address fundamental, long-standing questions about the underlying mechanisms for the transformation of molecules and materials. In addition to its scientific importance, the anticipated progress will also have significant impact on diverse technologies in the energy sector and beyond.
2. Priority Research Opportunities

2.1 PRO 1: Probing and controlling electron motion within a molecule

**Summary:** Tracking the movement of electrons and the excitations associated with this motion through a molecule can provide a window into some of the most challenging and important issues in fundamental chemistry. Because electronic excitations can move across molecular bonds on the femtosecond-to-attosecond timescale, following these processes with purely optical techniques is impossible. Even a single cycle of visible light is too slow to resolve the relevant dynamics. Ultrafast x-rays, at much higher frequencies, can access the required timescales. Furthermore, ultrafast x-rays can reveal information about the motion on atomic length scales, through both spectroscopic and structural (scattering/diffraction) analyses. Thus, the forefront capabilities of ultrafast x-ray lasers can enable direct exploration of a critical regime of fundamental interactions. The high intensity and repetition rate of next generation x-ray free-electron laser sources also offer the possibility to provide sensitive probes of coherent electronic phenomena, foundational to understanding quantum chemistry. The resulting understanding will enhance our ability to test and improve theories describing molecular structure and bonding in which electron-correlation effects present major scientific challenges.

**Key questions this PRO will answer:**
- How does electronic charge move from atom to atom in a molecular system?
- How do electron-electron interactions and correlations alter this motion?
- How do the atoms rearrange following this electronic motion and, conversely, how does this atomic motion affect the coherent electronic motion?
- Can this coupled and correlated electronic motion be exploited to affect longer-timescale dynamics?

**Scientific Opportunities and Challenges**

When a molecule interacts with a *coherent attosecond* (1 as = 0.001 fs = $10^{-18}$ s) *laser pulse*, the resulting electronic excitation can be very informative because it can behave for a short time like a *spatially localized particle*. Because this excitation is not confined to a single electronic state, but rather a superposition of states separated by as much as several electron volts (eV) of energy, it exhibits attosecond timescale electronic motion that depends on electron correlation. Beyond this initial electronic evolution, which may last for up to several femtoseconds, the first steps of chemistry commence, as the positions of the atoms (nuclear coordinates) begin to respond to the charge redistribution. This overall conceptual picture, with its sequence of events, has emerged as an important chemical paradigm, supported by new experimental methods based on high-harmonic generation) [2] (Fig. 1); but to date it has not been possible to study the flow of charge...
from atom to atom in detail. Purely optical techniques cannot directly access this timescale because it requires a photon energy spread of several eV, larger than the photon energy itself for a visible photon. XFEL (x-ray free-electron laser) sources, however, can now produce attosecond pulses that can excite and probe electron dynamics within a molecule on the electronic timescale. Furthermore, only x-rays can localize electronic excitation on an atomic center, so that its motion can be tracked (see sidebar on p. 11).

Measurement of electronic motion on the natural time and length scale of the earliest steps of chemical reactivity

Electronic charge provides the screening to bond and stabilize the atoms in a molecule. The redistribution of this charge initiates all chemical changes, including isomerization, dissociation, and bond rearrangement. For example, electronic motion is correspondingly the means by which light energy is harnessed in photochemistry. What is particularly important for understanding the problem of electronic motion is a comprehensive picture of how a coherent superposition of electronic states evolves over time.

More specifically, how do these nonstationary states couple to other degrees of freedom (e.g., nuclear motion) in a molecular system? A superposition of excited electronic states spanning several eV in binding energy can be expected to produce transient charge dynamics on the sub-femtosecond timescale. Understanding the details of this motion and the effect such transient charge motion will have on the chemistry of a molecular system

Fig. 1. Viewing motion of charge: These snapshots of the calculated response of a phenylalanine molecule reveal the motion of charge following sudden excitation in the molecule. Yellow indicates excess charge and purple shows depletion of charge. Charge localized in the area highlighted in the first frame oscillates with the dominant electron period. This charge oscillation was observed experimentally, when a 0.3 fs XUV pump pulse singly ionized phenylalanine. The right panel shows the yield of the doubly charged immonium ion produced by a strong-field IR probe pulse, which exhibits weak fragment oscillations at the predicted period. Using shorter wavelength attosecond pulses as both pump and probe will provide the basis for the direct observation of intramolecular charge dynamics and the subsequent changes in the positions of the atoms (after [2]).
remains a scientific frontier. New time-domain approaches have the potential to provide the direct insight needed to address long-standing challenges concerning the correct treatment of electron-electron correlations and non-adiabatic couplings in molecular systems. Time-domain approaches also provide the significant advantage that the experimental measurements can be used directly to validate and guide theoretical approaches based on direct time integration of the underlying quantum equations of motion.

**Correlation-driven electron motion: Earliest stages of interatomic electron motion**

Perhaps the simplest prediction that can be tested once the appropriate experimental tools are fully in place is the so-called universal attosecond response [3]. This response is characterized by the timescale for electrons to “talk to one another,” as charge redistributes in response to impulsive excitation. For core vacancies in many systems – from isolated atoms to organic polymers – the initial charge imbalance created by impulsive excitation has been predicted to decay substantially in about 80 attoseconds (Fig. 2). If confirmed by experiment, the universal attosecond response sets limits on all other measurements of charge dynamics.

On longer timescales (100s of attoseconds), depleted charge initially confined to one end of the molecule can migrate to a remote site of the molecular system and influence the bonding environment. This motion can take place faster than the nuclei can respond. Subsequently, however, if a remote bond is sufficiently weakened, it could begin to break [4]. In some cases, the electron motion is so fast that an electron can actually escape the molecule before the bond breaks, which leaves the molecule to dissociate at the

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Fig. 2. All atomic and molecular systems have been predicted to show similar local dynamics, the so-called universal attosecond response, following an initial charge imbalance. This imbalance could be created through impulsive ionization or excitation. Observation of this type of electron motion will confirm the fundamental timescale for electron-electron interactions (after [3]).
weakened bond even as the charge disturbance localizes somewhere else. This predicted scenario could explain a number of experimental observations where inadequate time resolution has prevented a detailed picture from emerging, but which clearly showed that localized excitation at one site can lead to bond breaking at a distant location [5,6]. More recent experiments, such as the work depicted in Fig. 1, further support the hypothesis that ultrafast coherent electronic motion can drive the dissociation dynamics of large molecular systems [2]. More generally, this discussion illustrates how direct measurements of the motion on the sub-femtosecond timescale can lead to mechanistic insights and ultimately to new design paradigms for chemistry.

**Interatomic Coulombic decay**

Interatomic Coulombic decay (ICD) is a non-local, ultrafast decay process in which a core-excited system transfers its excess energy to a nearby species, which then emits an electron from its outer-valence shell (Fig. 3) [7]. Because ICD is a major source of the low-energy electrons produced when aqueous molecules absorb high-energy photons, it is a contributor to solution-phase actinide chemistry, DNA damage, and many other radiation effects. ICD has been measured in systems ranging from small dimers to clusters to condensed systems and quantum wells, with timescales as short as 1 fs, depending sensitively on the local environment of the atom [8]. Current predictions of ICD lifetimes span orders of magnitude depending on the specific system. Sub-10 fs lifetimes have been confirmed indirectly by measuring photoelectron spectra in water and other systems [9-12]. Although spectroscopic signatures of ICD have been observed, direct time-domain measurements will add vital information about the temporal properties of long-range correlation effects.

![Fig. 3. Schematic of interatomic Coulombic decay (ICD). Following inner-valence ionization (a) of a system of atoms or molecules, the system can relax via electron emission. In the case of ICD, electron ejection in the isolated monomer is energetically forbidden, however, ICD provides an efficient energy transfer mechanism (b) between neighboring monomers resulting in emission of low-energy electrons (after [12]).](image-url)
Current Status, Strategic Research and Implementation

Understanding ultrafast molecular dynamics is central to a complete picture of chemical transformation. Various theoretical frameworks have been developed to describe the dynamics of a molecular system, but by and large these methods have only been applied to excitation of a single electronic state of a molecule [13]. These theories have been extended to include possible (nonadiabatic) couplings between electrons and the positions of the atoms for closely lying electronic states. In the other extreme of exciting a superposition of electronic states, researchers have considered coherent charge dynamics resulting from motion of electronic wavepackets, but only if motion of the nuclear degrees of freedom is neglected. In this limit, long-lasting charge oscillations driven by electronic coherence and correlation have been described [14].

A complete theory, which describes both coherent electronic and nuclear dynamics, has yet to be constructed. Models are being developed (for example, [15-17]), but robust and appropriate data have not been collected to validate such models. From the experimental point of view, new techniques need to be developed - techniques capable of probing coherent electronic phenomena occurring down to the attosecond timescale. In this context, new advances in attosecond x-ray pulses permit us to pump and probe specific atoms within a molecule to monitor collective charge motion on attosecond timescales. In the near future, it should become possible to single out the electron density near separate pairs of atoms in a molecule or molecular complex, create excitation at one atom, and watch the charge density ripple across to the other, all using x-ray transient spectroscopic tools reaching down to sub-femtosecond time resolution.

A great promise of next-generation XFEL facilities lies in their ability to produce attosecond-duration pulses that can excite molecular systems in new ways and observe the effect of coherent electronic phenomena. The particular properties of light required for understanding intramolecular dynamics on the timescale of electronic motion include:

- **Broad coherent bandwidth** to simultaneously and coherently excite the entire valence spectrum of a system, enabling control of the initial state of the system;
- **Attosecond pulse duration** to allow probing below the electronic timescale as defined by the energy spread between electronic states;
- **Short wavelength** to permit access to atom-specific core-to-valence transitions in molecules;
- **High repetition** rate to permit low density and subtle effects to be recorded with high fidelity;
- **High pulse energy** to make possible the use of nonlinear x-ray spectroscopic techniques.

Only next-generation XFELs, such as LCLS-II, have the potential to realize all of these properties at once. Recent developments have already demonstrated a route to generating
X-ray free-electron lasers are important tools for studying matter on its natural time and length scales due to their broad coherent bandwidth and high pulse energy. When these extremely bright beams are focused, the x-ray photon density (which is related to the field strength) can become so high that a single molecular target may interact with multiple x-ray photons. Initially these nonlinear interactions were observed through sequential ionization of the target species. The interaction of a target system with multiple laser photons has led to the development of nonlinear spectroscopy, which encodes a great deal of information compared to the linear response. In the optical regime, development of nonlinear spectroscopy has led to sophisticated probes of molecular excited states. Similar developments will be made in the x-ray domain.

As an example, consider impulsive stimulated x-ray Raman scattering (SXRS) as a nonlinear technique for preparing valence electronic wavepackets at a desired atomic site [22-24]. As shown in the diagram above, under SXRS, an inner-shell electron is excited near an unoccupied valence state or to the continuum. Before this core-excited state can decay, a second interaction with the x-ray field stimulates emission of a photon and the core-vacancy is re-filled. In the impulsive limit of SXRS both the pump and Stokes (stimulating) frequencies are contained in the same laser pulse. Therefore when the exciting laser pulse has a sufficient bandwidth, spanning the energy separation between the ground and excited electronic states, the refilling is similarly probable from multiple valence excited and/or ground states. Moreover, if the excitation borrows largely from the oscillator strength of a particular atomic site, then the wavepacket has a definite and reproducible starting location. This approach provides a way to control the time-dependent electronic distribution in a molecule and to observe how various deformations affect the persistence of charge motion.

In addition to such nonlinear excitation mechanisms, there are powerful nonlinear probing techniques that have been developed theoretically to extend multidimensional spectroscopy to atom-specific measurements in the x-ray domain [22]. Examples of the use of such methods include probing non-adiabatic dynamics near conical intersections [25] and characterizing the coupling of valence electrons near different atomic sites [26].
sub-femtosecond x-ray pulses by XFELs [18]; and, in the next five years, it is expected that new XFEL techniques will produce pulses shorter than 200 attoseconds. Pushing beyond this point is both anticipated and desirable for the proposed research, but may require more involved modeling of the XFEL. So fully meeting the needs for attosecond time resolution described herein will require further development of XFELs with ultrashort pulse duration.

Several methods have been proposed, and some developed, to observe the evolution of electrons induced by interaction with attosecond laser pulses. These approaches include strong-field streaking [19], transient absorption spectroscopy [20], and time-resolved x-ray photoelectron spectroscopy (XPS) [21]. Next generation XFELs also offer the possibility of going beyond these linear techniques to drive nonlinear interactions. Coherent Raman scattering and four-wave mixing techniques have revolutionized optical studies of ultrafast molecular dynamics. Similar approaches with sub-femtosecond x-ray pulses will do the same for electronic dynamics (see sidebar).

**Scientific Impact**

The development of high-repetition-rate XFELs with attosecond capabilities will permit experiments that pump and probe specific atoms within molecules and thus monitor collective charge motion on sub-femtosecond timescales. These new capabilities allow localized measurement of the electron density at separate pairs of atoms in a molecule or molecular complex. One can thus create excitation surrounding one atom in a molecule and watch as the charge density propagates to the other atoms, all using sub-femtosecond transient spectroscopic tools. What these unique tools can probe is the initial creation of an electronic coherence, and possibly pure electronic rearrangement as a result of this coherence. As the electrons rearrange, the forces exerted on the nuclei by the charge cloud will change. The initiation of atomic motion induces fleeting but profound changes in the relative quantum phase of the electron states, since once the atoms start to move, electronic coherences prepared on attosecond timescales irreversibly dephase, leading to electron localization and the first stages of chemistry.

Beyond the measurement of coupled coherent dynamics of the electrons and atomic positions in molecules, and theoretical models that describe these phenomena, the future of attosecond chemistry involves precision shaping of the coherence to direct the chemistry of a system. Such charge-directed reactivity [27] is only in its infancy, and both the theory and experimental protocols need to be developed. A possibility for electronic control could involve sequences of precisely timed attosecond excitation pulses, which result in a highly specialized electronic wavepacket. This initial excitation could produce a localization of charge at a specific point in the molecule either to break a bond, or possibly to activate the molecule to direct reactions with the local environment.

In addition to charge dynamics in isolated molecular systems, XFELs that push x-ray
pulse durations below the femtosecond barrier will enable the study of electronic coherence in the condensed phase. Time-resolved photoemission from surfaces offers, for example, the opportunity to gain insights into the charge transport and screening phenomena in condensed matter. Pushing below the femtosecond barrier opens the possibility of probing electron motion and correlation down to the atomic length scale. A key example is coherent high-harmonic generation from solids. Here strong optical fields drive electrons across multiple bands throughout the Brillouin zone. Fundamental questions remain regarding the nature of the excited-state electronic structure and its connection to ground-state properties, as well as the roles of correlation, dynamical localization, and decoherence. Attosecond x-ray measurements could be employed to study the evolution of the local (within a unit cell) and transient structure within an optical cycle. Such measurements will yield critical phase information that cannot be obtained from inelastic x-ray scattering or from the high-harmonic spectra. Similar methods will aid in understanding other non-perturbative phenomena such as ultrafast metallization, light-induced superconductivity, and the control of topological properties as described in a separate section of this document.
2.2 PRO 2: Discovering novel quantum phases through coherent light-matter coupling

**Summary:** One of the most exciting recent advances in ultrafast science is the use of ultrashort light pulses to create new states of matter in quantum materials. Ultrashort light pulses can generate novel transient states in solids, initiate phase transitions to states that are unattainable in equilibrium, and create and manipulate quantum topological states. Intense infrared (IR) pulses have, for example, induced signatures of a transient superconducting state in an initially non-superconducting material [28], as well as exotic sub-picosecond light-matter mixed states (so-called Floquet-Bloch states) in topological insulators [29,30]. The use of ultrashort light pulses is a powerful approach for enabling the control of quantum states required for implementing advances at the forefront of technologies in electronics, photonics, energy, and quantum information.

While the previously cited examples illustrate the potential of using light to discover new quantum phases, further progress has been impeded by the lack of experimental tools for directly probing and controlling short-lived states. The powerful measurement capabilities afforded by the new generation of x-ray free-electron laser (XFEL) sources, all applicable on the ultrafast timescale, will provide the required probes to allow control of the excited structures. The most intriguing opportunity lies in applying tailored ultrafast laser pump pulses to control, and XFEL probes to investigate, microscopic quantum excitations (e.g., phonons, excitons, plasmons, and magnons) and their interplay, which govern the properties and phases of quantum materials. XFEL pulses probe matter with a unique combination of electronic, chemical, and structural sensitivity reaching down to picometer length and attosecond time scales. Research exploiting unique XFEL capabilities will permit exploration of the frontiers of quantum matter, including imprinting quantum coherence with light and controlling topological phenomena with light.

**Key questions this PRO will answer:**

- How can light be used to create novel quantum phases of matter, with properties that do not exist in equilibrium?
- How can ultrafast optical excitations be utilized to impose quantum coherence or create new topological states?
- How can the lifetime of novel transient quantum phases be extended and manipulated for practical use?

**Scientific Opportunities and Challenges**

Quantum materials typically have complex equilibrium phase diagrams. Transitions between phases can be associated with subtle changes in electronic properties and
structure, as well as with changes in the interplay between different microscopic excitations. While this complexity makes quantum materials challenging to model, it also endows them with nearly unlimited possibilities for new functionality. This potential remains largely unrealized in real-world applications because the strong interactions between different excitations render it difficult to bring about a desired state of matter using traditional static tuning methods, such as temperature and doping, as they simultaneously affect many degrees of freedom. Emerging methods based on ultrafast photoexcitation, applied over a range of photon energies, can overcome competing interactions by directly targeting specific excitations, resulting in novel driven states of quantum matter [31].

Fig. 4. Methods for controlling quantum phases. Elementary excitations in quantum materials and selected techniques for their control are shown schematically. They are arranged (clockwise from the top) to correspond to electromagnetic waves of increasing frequency (central image) (after [31]).
Progress in using ultrafast light to create and control quantum phases exploits the major advances over the past decade in achieving optical control of non-equilibrium, many-body phenomena in quantum materials (bottom half of Fig.4). Sub-picosecond laser pulses allow quantum materials to be strongly driven and interrogated on the fundamental timescales of electronic and atomic motion. In particular, intense terahertz (THz) fields [32] in the range of $10^6 - 10^7$ V/cm can be generated to drive quantum phases at their natural energy scales. The electric field strength can be increased by overlaying resonant THz antennas on a material surface [33]. At higher frequencies, strong fields can initiate electronic phase transitions, such as an insulator-to-metal transition [34,35]. Strong fields can also drive nonlinear effects in a material that in turn affect the coupled radiation field, leading to phenomena such as on-resonance parametric amplification and high harmonic generation [36].

More generally, intense light pulses allow modification of the electronic structure of a quantum material in order to design a desired state of matter. The use of specifically tailored pulses with circular polarization can, for example, achieve new types of topological protection. For instance, circularly polarized light enables control of coupled spin and valley excitations in the band structure of new layered materials, such as two-dimensional transition metal dichalcogenides. Furthermore, ideas from quantum optics research, such as the cooling or amplification of collective excitations of solids, are finding parallels in photon modified materials systems [37].

The above concepts have been demonstrated in a number of recent experiments that effectively use intense optical pulses at THz and infrared frequencies to deform crystal lattices in desired directions and to induce transient atomic arrangements that lead to the creation of new electronic phases [38,39]. The result is coherent control of the atomic and electronic structure by external light excitation, providing a powerful framework for using light to induce new quantum phases.

**Fig. 5.** (a) Time-resolved XRD of two specific diffraction peaks in YBCO after photoexcitation of the Bi$_2$u phonon, allowing the transient crystal structure (b) to be reconstructed (after [39]).
Creating macroscopic quantum coherence

The condensation of bosons is arguably the most dramatic manifestation of macroscopic quantum phenomena in nature. In solids, superconductivity arising from Cooper pairing with long-range phase coherence is the archetype of quantum condensation [40]. The notion of condensation extends beyond the domain of superconductivity to other bosonic excitations, including magnons, excitons, and exciton-polaritons [41-43]. All of these condensates are amenable to the full range of external manipulation sketched in Fig. 4.

A specific example of the exciting research possibilities is the recent experimental demonstration of the use of mid-IR pulses to create “light-induced superconductivity” [28] in otherwise non-superconducting, charge-ordered materials. The LCLS XFEL was used to temporally resolve the specific changes in crystal structure associated with the transient superconducting phase (Fig. 5), which could potentially enable the design of an oxide heterostructure that could stabilize this phase in equilibrium. However, a detailed understanding of how macroscopic quantum coherence – in this particular case, condensation of Cooper pairs – emerges from an insulating ground state, and the role of optical excitation in this remarkable transformation, remains one of the important puzzles of ultrafast condensed matter physics. Many other potential targets can be identified for this approach, including light-induced creation and manipulation of long-range quantum correlations in spin-density and charge-density wave condensates [44], Mott insulators, and other correlated electron systems.

The next generation of XFEL sources will make it possible, for the first time, to monitor photo-induced modifications of the Fermi surface throughout the entire Brillouin zone, as well as changes in the dispersion of low-lying electronic excitations, correlated with simultaneous studies of atomic rearrangements.

Controlling topological states

The discovery of topological insulators has revolutionized modern materials research, with far-reaching implications for electronic, photonic, communication, and computing technologies. Topology gives rise to exotic phases of matter with protected states and unconventional response functions that stem from geometric phase effects [45,46]. On-demand topological states in solids controlled by light have been theoretically predicted, and experimental tests of these forward-looking ideas are underway. Several complementary optical pump-probe protocols for manipulating Berry curvatures in Dirac systems have been proposed [47]. These protocols are expected to transform conventional materials into novel topological insulators [48-50] and chiral spin liquids [51], as well as create quantum Hall phases without external magnetic fields [52-54]. The experimental detection of photoinduced topological phases represents a frontier in ultrafast science, of which the recent experimental demonstration of Floquet states constitutes an important milestone [29,30]. Of special interest are the edge states that arise at the interface
between novel topological and conventional quantum phases (Fig. 6). Edge phenomena in optically driven systems are protected from localization and elastic backscattering by time-reversal symmetry. Thus, light-induced edge effects offer tantalizing opportunities for quantum technology.

A direct inquiry into the physics of edge states has been performed with nanoscale imaging with advanced scanning probe tools. The required nano-optical capabilities have been recently demonstrated [55-57], yet these imaging tools lack the capability to explore many important aspects of the edge states, such as the band dispersion across the entire Brillouin zone. This issue can be overcome with next-generation XFELs, which are capable of exploring the temporal evolution of the bandgap, including bandgap crossing and inversion (Fig. 6).

The notion of topological symmetry protection is not restricted to electronic or transport properties. The same universal principles apply to ultracold gases [58-60], as well as to photonic [61-67] and polaritonic phenomena [68-73]. For example, topological exciton-polaritons have been theorized for monolayer transition metal dichalcogenide films subjected to a finite magnetic field or to circularly polarized optical stimulation [69] which allows unidirectional flow of light at the sample edge (Fig. 6). Such unidirectional transport can be used for overcoming disorder in polaritonic interconnects. The propagation of topological polaritons can also be reversed by changing the helicity of the incident light. Chiral plasmons – unidirectional propagating collective oscillations of the conduction band – have also been proposed to occur at the edges of anomalous Hall metals and other multi-valley conducting media where both time reversal and inversion are broken.

**Fig. 6.** Example of light-induced control of topological phases: circularly polarized ultrafast light pulse breaks time reversal and creates new electronic band structure (hybridization between the Floquet-Bloch band and the conduction band gives rise to the avoided crossing and the band inversion), resulting in topologically protected chiral edge states (after [74]).
symmetries are broken \([73,74]\). Plasmon-polariton chirality is a direct consequence of non-vanishing Berry curvature in a medium. Chirality can be induced on demand by driving valley degenerate semiconductors with circularly polarized light. Next-generation XFELs are uniquely positioned to address the nature of novel photoinduced quantum phases through the combination of time-resolved spectroscopy (accessing low-lying excitations) and simultaneous time-resolved diffraction (accessing polariton and phonon dynamics.)

The recent discovery of three-dimensional topological (Weyl and Dirac) semimetals, which exhibit unique states both at the surface (Fermi arcs) and in the bulk (Dirac cones), has led to a host of predictions for light-induced topological phenomena in these systems. The predicted phenomena include the ability to switch between topologically insulating, Dirac semimetal, and Weyl semimetal states using circularly polarized femtosecond pulses \([75]\). This has not yet been experimentally observed. Ultrafast hard x-ray photoemission experiments would be ideal for probing such light-driven phenomena \([76]\), as they are sensitive to changes in the electronic structure both at the surface and in the bulk, unlike conventional photoemission experiments with lower photon energies. Using ultrafast x-rays to study topological semimetals thus has great potential for rapidly producing high impact results.

**Current Status, Strategic Research and Implementation**

A key missing ingredient in pursuing the exciting new scientific directions described above is the ability to characterize the properties of the newly created and often transient quantum states in terms of both their structure (lattice, phonons) and a variety of electronically derived quasiparticle excitations (electrons, spins, plasmons, polaritons, excitons, etc.) on ultrafast timescales. Ultrafast x-ray diffraction combined with ultrafast x-ray spectroscopy techniques can provide a complete picture of new light-induced quantum states.

Ultrafast XFELs are uniquely suited for probing transient states of matter down to the atomic and even electronic scale in space and time. The combination of high brightness, short wavelength, access to core levels, and femtosecond-to-attosecond pulse duration provides unprecedented access to nearly instantaneous information about electronic and lattice structure in complex materials.

The ability of XFEL pulses to directly and selectively probe the charge, orbital, spin and lattice quantum coordinates of quasiparticle excitations, using a variety of techniques, represents a powerful new advance for probing quantum matter. The crucial features of new quantum states, created through light-imposed macroscopic coherence, can be characterized by measurements of the temporal evolution of the Fermi surface (using, for example, time-resolved angle-resolved photoemission spectroscopy, or tr-ARPES), throughout the entire Brillouin zone. In addition, changes in the dispersion of low-lying
electronic excitations can be measured by time-resolved resonant inelastic x-ray scattering (RIXS) recorded as a function of energy and momentum transfer (Fig. 7). Finally, time-resolved x-ray diffraction (tr-XRD) permits correlation of relevant properties with simultaneous studies of light-induced atomic rearrangements.

The first experiment in this direction has recently been implemented, combining tr-XRD and tr-ARPES to demonstrate that the critical electron-phonon coupling in the high-$T_c$ pnictide superconductor FeSe is found to be an order of magnitude greater, due to electronic correlations, than one predicted by the conventional theory [77]. Applying XFEL-based multi-modal studies (see Cross-cut chapter of this report for additional discussion of multimodal techniques) to a broad range of quantum materials will provide a complete and detailed picture of the emergence of new quantum ordered states induced by optical excitation, and provide further insight into how other exotic quantum coherent states of matter can be created using similar approaches.

In the field of topological engineering of novel quantum states, the challenge of directly accessing bandgap crossing and inversion leading to the formation of Floquet sidebands and chiral edge states can also be addressed using tr-ARPES. Because the x-ray energy and scattering geometry (incidence angle) can be tuned easily only with an XFEL source, the XFEL version of this technique can reveal detailed information about the electronic properties of both bulk and surface (edge) states. Furthermore, time-resolved RIXS/IXS can couple to a wide range of low-lying excitations, allowing researchers to obtain detailed momentum- and energy-resolved plasmon and exciton dispersions (Fig. 7) [80,81], as well as simultaneous measurements of polariton and phonon excitations by tr-XRD [38,39,82-85]. The inelastic x-ray spectroscopies (IXS and RIXS) will especially benefit from additional integrated flux provided by the high-repetition nature of the next-generation

Fig. 7. Resonant inelastic x-ray scattering (RIXS) can probe diverse quasiparticle excitations (phonons, magnons, plasmons, excitons) over a wide range of energy and momentum transfers (top after [78], bottom after [79]).
XFELs, which will in turn provide the required high energy resolution of the inelastic spectrometer. The importance and benefit of combining different time-resolved x-ray probes is discussed explicitly in the cross-cutting research theme in this document.

**Scientific Impact**

The discovery and manipulation of new quantum states of matter are the key grand challenges in condensed matter physics. Ultrafast science presents a promising new frontier for such discoveries, but until recently has lacked adequate ultrafast structural and electronic characterization tools. This shortcoming will be addressed by the next generation of XFELs and associated instrumentation. These new instruments will provide a route to the ultimate goal of understanding the spatial and time scales over which quantum correlations and novel topological states emerge and evolve. Such new understanding will lead to control of the macroscopic ordered states that govern quantum functionality. Also enabled will be the discovery of novel quantum phases through the establishment of long-range quantum coherence and deliberate manipulation of the topological properties of specific quasiparticle wavefunctions. This, in turn, will result in light-driven, highly tunable quantum states with a set of desired properties that can be turned on or off at ultrafast timescales.

In summary, future XFEL-based research can yield fundamental scientific understanding of the light-matter interactions at the ultimate limits of the ultrafast/ultrasmall frontier and the way these interactions can be manipulated to imprint macroscopic quantum coherence in correlated electron systems, or to engineer and control novel topological states. In addition, the scientific discoveries may serve to create foundations for the next generation of technologies in electronics, photonics, energy, and quantum information.
2.3 PRO 3: Capturing rare events and intermediate states in the transformation of matter

**Summary:** Many existing tools allow detailed characterization of the initial and final states of chemical reactions and material transformations – the “before” and “after” states. What has remained elusive is the direct observation of the intermediate states and pathways of these processes. Such knowledge is essential for fundamental understanding of the underlying mechanisms of material and chemical transformations. The overall rates of transformation vary over many decades and occur as a result of spontaneous, typically thermally driven fluctuations, resulting in intermittent, stochastic “rare events,” the dynamics of which have been impossible to capture on their intrinsic atomic length scale and ultrafast timescale until now.

Reconstructing transient fluctuations from billions of atomic-scale snapshots will enable a detailed understanding of the complex, rapidly evolving energy landscapes underlying chemical reactions and phase transitions. This paradigm change in studying transformations of matter will pave the way to optimizing and controlling these processes and their eventual outcomes. Next-generation XFEL facilities are uniquely positioned to capture this information thanks to their high resolution, sensitivity and repetition rates. The new facilities will enable capture of intermediate states of naturally occurring thermally driven processes down to the atomic level and, coupled with current and emerging theory and exascale computational tools, will open a completely new pathway for understanding crucial steps in the transformation of materials, quantum states and molecules.

**Key questions this PRO will answer:**

- What new fundamental knowledge and extensions to theoretical models of material transformations and chemical reactivity are needed to predict and produce novel states and phases, to stabilize previously observed intermittent transient states of matter, and to control chemical selectivity?
- How can rare events be captured without the use of external stimulation, as in conventional pump-probe measurements?
- What new theoretical advances and computational methodologies can rapidly translate large experimental datasets into detailed information about transient states and rare events?
- How can models and theories translate the newly available insights on the role of fluctuating local environments into a predictive understanding and, ultimately, control of macroscopic rates and reaction products?
Scientific Opportunities and Challenges

Understanding transformations of material and chemical systems through reactions and phase transitions represents a basic scientific problem of great depth and importance. It is also one of the most important challenges for energy because these transformations define pathways for forming new matter with desired properties and behavior. The underlying timescale in these processes is defined by electronic and nuclear motion that occurs over femtoseconds, or even attoseconds. Recent advances in ultrafast x-ray free-electron lasers have opened new doors to explore the most elementary processes in chemical and material transformation. Typical experiments, as outlined in the other PROs, are based on initial excitation with an ultrafast pump pulse, followed by recording the response of the system with an ultrafast probe. This approach, while very powerful in its own right, does not fully address the more general circumstance of thermally driven, stochastic reactions that occur as a result of random thermal or quantum fluctuations. In these processes, the overall timescale for reactions may lie in the range of seconds to hours, i.e., many orders of magnitude slower than the crucial underlying dynamical processes. This difference in timescale reflects the fact that critical steps in chemical and material transformations occur infrequently during the process and are, hence, very rare events. Indeed, material transformations and thermal chemistry are extremely heterogeneous on the atomic scale, with fluctuation-mediated processes that drive catalytic reactions, material nucleation and growth, charge and energy transport, and macroscopic phase changes occurring as the result of very infrequent atomic scale events.

Until recently, there were no approaches to probe and master this heterogeneity based on a simultaneous understanding of the fundamental, molecular-scale processes and their correlations with the average ensemble behavior and reaction rates. Instead, in current research both theory and experiments are largely conducted in two disparate regimes of atomic-scale dynamics and ensemble-averaged kinetics.

High-repetition-rate XFELs combined with petascale and exascale computing resources now provide the basis for a paradigm shift in fundamental chemical and materials research. A central advance of next-generation XFEL facilities is the ability to perform synchronous x-ray diffraction and spectroscopy measurements, enabling simultaneous probing of the electronic and geometric structure with sensitivity approaching the single molecule level; and to repeat these measurements billions of times during a single experiment. Scientists can thereby sample an ensemble with enough statistics to filter out rare events and transition states under equilibrium reaction conditions. These experiments provide vast datasets of snapshots containing partial structural information and spectroscopic information about the corresponding electronic structure. Sorting these snapshots with advanced computational techniques, driven by improved theoretical methodologies, can reconstruct the reaction pathways from billions of measurements captured by the ultrafast x-ray probe while the system evolves and fluctuates spontaneously without the need for an external stimulus. This approach will provide
direct access to the dynamic energy landscape of reaction pathways, as well as to the decisive moments (“rare events”) of fluctuation-driven processes.

**Chemical transformations beyond statistical averages**

*Probing energy landscapes and the transition states:* For energy applications, chemical and material transformations and fluctuations become useful when the average behavior of an ensemble leads to the desired product, such as a transportable fuel, clean water, or a novel material. Ensemble averages, however, do not provide direct insight into the fundamental *microscopic* dynamics that lead to the emergence of this product. In fact, based solely on average quantities, such transformations may seem virtually impossible. Catalytic reactions proceeding at certain temperatures would, for example, not be possible if all molecules had the same (average) velocity, orientation, and internal structure and energy. It is rather the case that the energy levels and electronic structure of reactants in solution fluctuate stochastically as molecules bump and jostle at thermal equilibrium, and the few reactive events arise out of the high-energy tail of the distribution as these random perturbations eventually drive the reactants to the transition state and on to products. While theories for chemical reaction rates (*e.g.*, transition-state theory) are based on this microscopic picture, experiments typically only see the average behavior and reduce the varied distribution of trajectories to a single number – a rate constant. While the globally averaged rate at which a reaction or phase transformation occurs may be well established, the microscopic, atomic-scale mechanism for these processes has remained a grand challenge for understanding the fundamental underpinnings of chemistry and materials science. A key solution to this problem is development of ultrafast atomistic probes capable of measuring the vast energy landscape of reactions driven by thermal fluctuations. This approach effectively amounts to detecting and cataloguing the type and number of each reactant’s electronic and geometric configurations and determining how these configurations can be connected as trajectories that take reactants to products. To achieve this goal, we must employ experiments without the use of an initial stimulus that could mask the naturally occurring thermal reaction processes.

*Charge transfer and solvent-solute interactions underlying transition-state theories:* A detailed understanding of chemical reaction dynamics in the liquid phase is an enduring challenge of tremendous importance for novel molecular synthesis, environmental chemistry, and catalysis [86]. The surrounding solvent affects chemical reaction dynamics in numerous ways, including solute-solvent complexation, solvent caging, and structural changes to the solvation shell in response to the altered chemical identity of the solutes (Fig. 8a).

While transition-state formulations such as Marcus theory [87] have been extraordinarily successful in predicting the orders-of-magnitude span in rate constants for the simplest chemical reaction of electron transfer, the aggregation of solvent effects into a single
parameter, the well-known reorganization energy ($\lambda$), does not yield a microscopic understanding of the dynamics (Fig. 8b). To develop this type of atomistic understanding, a robust experimental technique is needed, such as has become possible with XFEL probes, that can follow the evolving solvent-solute interactions with atomic resolution and electronic structure information.

**Fig. 8.** a) Representation of solvent-mediated electron transfer. Electron transfer is driven by solvent fluctuations, occurring when the energetics of donor and acceptor match, as shown in the bottom snapshots. b) Marcus theory representation, showing energy as a function of reaction coordinate (after [88]).

**Beyond order-parameter-based descriptions of solid state phase transitions**

The physical and chemical properties of solids are governed by their geometric and electronic structure and the coupling between electron, spin, orbital, and lattice degrees of freedom. These interactions give rise to a rich variety of functional properties and complex phase diagrams that exhibit transitions between various phases of a different order in these degrees of freedom. Phase transitions are typically mediated by thermal fluctuations, which are strongly enhanced near the critical temperature. Currently, the physics of phase transitions is often described by one or more order parameters that average over these spatiotemporal fluctuations. It is well known that phase transformation phenomena such as nucleation, domain-wall formation and motion play an important role in determining the dynamical properties of such systems. These heterogeneities challenge the Ginzburg-Landau theory that is based on ensemble-averaged, macroscopic order parameters. A deeper understanding of phase transitions in correlated systems, for example, may require a microscopic description of spatiotemporally dependent order parameters.

Fundamental material transformations – from the freezing of liquids to the formation of intermetallic alloys and metal-to-insulator transitions – are common examples of nucleation and growth processes that fall into the class of thermally driven “rare events.” The dynamics of these events remain poorly understood due to the lack of experimental tools capable of capturing such rare events at atomic resolution. The unpredictable,
stochastic nature of these events requires high-repetition probes, like the systems now in place to record and analyze earthquakes, but operating at one trillionth the time and length scale in order to reach the required atomic-scale sensitivity. Next-generation, high-repetition XFELs will, for the first time, provide the capabilities to perform such tasks.

Detailed understanding of nucleation and growth processes at the limits of the ultrafast and ultrasmall will be made possible by next-generation XFELs. This understanding may further speed the evolution from “trial and error” materials discovery to a materials synthesis strategy based on a detailed atomistic knowledge of the dynamical processes leading to novel materials.

Optimizing the density of atomic defects or dopants has been a major research objective for materials engineering in contexts ranging from electronic and optoelectronic materials to light-weight alloys used in the aerospace and construction industries. Fundamental understanding of the conditions that lead to atomic-scale defect formation during crystallization, as well as understanding the subsequent thermally driven defect dynamics, is crucially important to our ability to control or optimize defect density – both in the functional materials we use today and in those of the future.

![Fig. 9](image)

**Fig. 9.** (a) Nano-optical imaging of the insulator–metal transition in a V$_2$O$_3$ film. (b) Coexisting phases during warming of the film through the phase transition (scale bar 1 μm). These results highlight the underlying spatial inhomogeneity. Fluctuations also occur in the time domain and can only be fully characterized by a method with adequate simultaneous spatial and temporal resolution [after [89]].

An example of the spatial evolution of a thermally induced first-order phase transition is shown in Fig. 9 for the insulator-to-metal transition of V$_2$O$_3$ [89]. This transition is highly inhomogeneous, exhibiting multiple length and time scales. Existing near-field imaging techniques provide nanoscale spatial information, but lack temporal resolution. Experimental techniques are needed that can record ultrafast snapshots on timescales faster than the fluctuations of the electronic system and without the need for an initial stimulus. Probing the spatiotemporal fluctuations of relevant local order parameters, such as the electronic and lattice structure, during phase transitions on their natural length and time scales will provide crucial microscopic insights into spatiotemporal correlations down to the quantum limit. This unprecedented microscopic view of materials and their
evolution will significantly impact our ability to understand the underlying mechanism in various ordering phenomena from magnetism, ferroelectricity, density waves, and superconductivity to more exotic phases of quantum materials, such as quantum spin liquids and exciton condensates.

**Current Status, Strategic Research and Implementation**

The promise to peer behind the statistical averages associated with rate constants, in particular, for pathways associated with rare events, has already inspired several studies. For example, theory can explore the energy landscape of the water octamer and elucidate paths through the landscape linking two structures [90]. Another example is the derivation of a comprehensive global reaction coordinate for the light-activated cis-trans isomerization of the azobenzene molecule, which is enabled by a combination of 100s of nonadiabatic molecular dynamics simulations with machine-learning algorithms that can simultaneously evaluate the impact of all intramolecular degrees of freedom (Fig. 10, [91]). By constructing a sufficient number of reaction pathways, researchers have obtained accurate predictions of the micro-canonical rate constants. Importantly, such a model provides information about the individual pathways – not solely information about the average of all pathways. Such a detailed picture of how reactions occur provides an incisive test for the microscopic basis of statistical theories – it is essentially an image of the reaction mechanism. By analyzing this distribution, we can identify efficient or fast pathways and therefore learn how to control the reaction by changing the structure, environment, etc.

Experimental techniques to complement the theoretical modeling are emerging, but are currently hampered by the lack of adequate light sources. For example, x-ray photon correlation spectroscopy (XPCS) can, in principle, access fluctuation-induced dynamics across many temporal and spatial scales (Fig. 11a). Using an XFEL, atomic structure sequences may be paired with corresponding spectroscopic sequences, enabling researchers to associate electronic properties, such as changes in the frontier orbitals, with specific atomic arrangements. However, acquiring a sufficiently large dataset of simultaneously recorded single-shot coherent scattering images [92] and simultaneously recorded emission spectra [93] that freeze molecular motion and enable multimodal XPCS requires a high-repetition-rate XFEL (Fig. 11b). It is the only light source that can simultaneously access elemental site-specific chemical information across timescales ranging from femtoseconds to milliseconds and across length scales ranging from
angstroms to micrometers. Only a high-repetition-rate XFEL provides enough photons per pulse to generate meaningful single-shot data at a sufficient data collection rate to acquire the large number of snapshots necessary to sample and study singular reaction pathways among a sea of non-reactive trajectories.

The full potential of high-repetition-rate XFELs can be exploited only by complementing the enormous amount of available data with state-of-the-art data analysis techniques that are capable of piecing together reaction pathways from a gigantic series of x-ray snapshots. For example, a method of large dataset analysis, termed manifold mapping, has recently been introduced to extract dynamics from noisy data on timescales extending even below the pulse duration [95] and to survey ribosome structures from the thermal distribution of conformations using cryo-electron microscopy. By analyzing these random snapshots using manifold mapping, researchers determined the time sequence of conformational changes in its work cycle (Fig. 12 from [96]). The key to extracting information resulting from thermal fluctuations and capturing rare events is to acquire many snapshots, as the total number of snapshots determines the largest accessible energy

![Fig. 11. Schematic representations of a) monitoring fluctuation-induced dynamics by XPCS (from [94]), and b) the impact of the exposure time $\Delta t$ relative to the characteristic timescale of molecular motion, $\tau$, on the information content of XPCS snapshots (after [92]).](image-url)

![Fig. 12. Conformational changes of a ribosome inferred from a series of randomly acquired cryo-TEM images using manifold mapping (after [96]).](image-url)
$E_{\text{max}} = k_B T \ln (N_{\text{shots}})$ and, hence, the possibility of observing the rare events. For context, a billion snapshots, for which $E_{\text{max}} > 20 k_B T$, can, in principle, be acquired in less than an hour at an XFEL operating at a 1 MHz repetition rate.

**Scientific Impact**

The envisioned capabilities of high-repetition-rate XFELs for fundamental chemical and materials research represent a paradigm shift from measuring average rates to reconstructing reaction pathways. Within the context of time-domain studies, they represent a step beyond the study of driven processes to probing and understanding spontaneous dynamics. These new capabilities will enable a shift from rate constant modeling to accessing previously inaccessible details that underpin the microscopic basis of rate theories, thereby allowing scientists to elucidate and ultimately predict and control the mechanisms of chemical and materials transformations more incisively. These new insights will enable optimization of energy-relevant chemistry and catalysis, and will aid our understanding of energy transduction. Similarly, probing the fluctuations of the electronic and lattice structure during the phase transition of a solid on its natural length and time scales can provide novel microscopic understanding of spatiotemporal correlations and underlying factors defining the properties of quantum materials. These insights would impact understanding of ordering phenomena like magnetism, electron-phonon driven periodic lattice distortions, superconductivity, and other exotic phases in quantum materials. Understanding critical rare events in phase transformations could, moreover, open new avenues for the discovery of new materials with a wide range of functionalities.

In addition to the impact on bulk chemical and material transformations, interfacial processes such as heterogeneous catalysis offer enormous opportunities for directed chemistry and, at the same time, tremendous challenges for experimentalists to probe their underlying mechanisms. Recently, IR-pump/x-ray probe femtosecond time-resolved x-ray spectroscopy has been used to examine the transition-state region of the CO oxidation reaction of a vibrationally excited adsorbate layer on a metal surface [97]. While this experiment demonstrates the sensitivity of XFEL-based spectroscopy techniques to transient reaction intermediates under well-controlled conditions, the envisioned capabilities of high-repetition-rate sources permit access to structural and local geometric information of reactive sites under quasi-equilibrium conditions. This transformative capability will address long-standing challenges of heterogeneous catalysis, identifying active sites and the influence of the local environment for high-performance catalysts. The approach could impact understanding of nucleation at interfaces, yielding new insights for materials and chemical discovery.
3. **Cross-cutting research opportunities for ultrafast x-ray science**

The wide range of scientific areas covered in the roundtable discussions of PRO 1 through PRO 3 identified several common cross-cutting themes. In particular, multimodal ultrafast measurements were viewed as a promising approach for next-generation x-ray free-electron laser (XFEL) research. Multimodal techniques have the potential to impact many disciplines, from chemistry to materials sciences to quantum physics. Similarly, advances in theoretical and computational approaches applied to highly non-equilibrium systems were deemed crucial to research efforts across all three PROs.

**Multimodal ultrafast measurements using XFELs**

An important frontier for ultrafast science is the synchronized measurement of atomic structure and electronic properties to reveal basic structure-function relationships, now extended to include ultrafast materials and chemical dynamics. Ultrafast x-ray techniques of diffraction (for atomic structure) and spectroscopy (for electronic properties) using current and next-generation XFEL sources are key to obtaining this combined information. Having the capability to precisely perform such measurements could have a major impact on understanding the fundamental issues in both materials physics (e.g., inducing and probing new states in quantum materials with coupled parameters) and chemical sciences (e.g., following coupled dynamics in molecules). Although these two complementary types of measurements are commonly used in ultrafast XFEL research, the ability to apply them simultaneously has the potential to dramatically advance the field.

The ability of XFELs to directly and selectively characterize charge, orbital, spin, and lattice degrees of freedom using a variety of techniques provides significant advantages for probing quantum matter. Furthermore, x-rays (using a dichroic contrast mechanism) are able to directly probe ultrafast dynamics of certain ordered states, such as magnetic skyrmions and ferroelectric vortices. Therefore, the use of ultrashort pulsed XFELs is essential for studying the dynamic properties of these states.

The power of combining ultrafast probes of the atomic structure with ultrafast probes of electronic properties is exemplified by recent time-resolved angle-resolved photoemission spectroscopy (ARPES) and time-resolved x-ray diffraction (XRD) measurements (Fig. 13). In this study, phonons corresponding to specific time-varying lattice displacements in a FeSe crystal were created by an ultrashort optical excitation pulse [77]. The resulting atomic displacements in the material were precisely determined by ultrafast time-resolved XRD. In a complementary investigation, the periodic oscillation induced in the electronic structure of the crystal was measured by time-resolved ARPES measurements. Combining these two studies provided the mode-specific
electron-phonon coupling, the central parameter in evaluating the superconducting behavior within any phonon-mediated Cooper pairing mechanism.

While each of the time-resolved measurements (XRD and ARPES) illustrated in Fig. 13 provides valuable information, the breakthrough in understanding comes from a quantitative combination of the two studies. The set of problems that would benefit from combined characterization of structural and electron dynamics is far broader than the specific experiment highlighted here, as are the types of structural and electronic probes that may be applied.

The probe of the electronic response could, for example, be resonant inelastic x-ray scattering (RIXS, see sidebar in PRO 2) for the investigation of low-energy excitations over a complete range of crystal momentum vectors. Indeed, electronic properties extend to charge- and spin-ordering, magnetism, and other materials properties that are strongly coupled to the physical structure of the system. The central commonality is the unique ability of ultrafast x-rays from XFEL sources to probe the dynamic structure-function relationship.

Multimodal time-resolved x-ray measurements capable of simultaneously addressing structural and electronic dynamics are also critical to unraveling key questions in non-adiabatic molecular dynamics. In the non-adiabatic regime, dynamics are determined by the interaction of electronic and nuclear motion, rather than by nuclear motion evolving.

![Fig. 13.](image)

**Fig. 13.** Experimental scheme (A) for a simultaneous measurement of the structural dynamics and the corresponding change in electronic properties. FeSe/SrTiO3 films were separately probed by time-resolved XRD (B) and by time-resolved ARPES (C). The combination of the measurements gives the electronic response to a specific type of change in position of the atoms, i.e., the mode-specific deformation potential (after [77]).
on a single well-defined electronic potential energy surface. These interactions play a central role in many phenomena, for example in non-radiative relaxation of molecules and in limiting the effectiveness of many potential photocatalysts. Independently tracing the evolution of the electronic state and the structure of a photoexcited molecule through complementary time-resolved x-ray measurements could provide the experimental underpinnings to establish general principles for dynamic structure-function relationships.

Like in the case of quantum materials, the value of combining complementary ultrafast x-ray measurements is reflected in other areas of forefront experimental research. As an illustration, consider the fundamental process of ring opening for cyclohexadiene shown in Fig. 14a. The evolution of the electronic states during the ring-opening process was traced using near edge x-ray absorption fine structure (NEXAFS) spectra corresponding to core-to-valence excitations [98]. The ring opening was also studied using time-resolved x-ray scattering [99], as shown in Fig. 14b, which provided independent information about the details of the motion of the atoms. Although the combination of these separate measurements provides another demonstration of the value of multimodal characterization, simultaneous measurements would enable studies of more complex molecular and materials systems in which it is often difficult to ensure that the sample and excitation conditions are consistent for separate experiments.

Another important aspect of multimodal ultrafast XFEL measurements is the ability of x-ray techniques to probe the response of materials to tailored ultrafast excitation pulses across a broad spectral range. Ultrashort light pulses can selectively excite

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Fig. 14. Time-resolved x-ray studies of the dynamics of the fundamental chemical transformation of a ring-opening process in cyclohexadiene, as shown schematically in the inset on the left side of (a). (a) The time evolution of the electronic structure was probed by near-edge x-ray absorption spectroscopy (NEXAFS) (after [98]). (b) A complementary time-resolved x-ray scattering measurement provided details of the motion of the atoms during the ring-opening process (after [99]).
vibrations/phonons with THz to infrared wavelengths, valence electronic states with visible to ultraviolet, and core levels of atoms with x-rays. The spectroscopic and structural probing of ultrafast x-rays described above, when coupled with these diverse types of excitations, can provide a comprehensive picture of light-induced processes in quantum materials. Similarly, following the response of molecules after controlled excitation of various selected electronic and vibrational states is often crucial to obtaining a complete understanding of the ultrafast dynamics in more complex systems. To enable these studies, XFEL facilities, in addition to providing a broad range of ultrafast x-ray probing methodologies, must offer ultrashort excitation pulses across the spectrum.

Finally, a different aspect of multimodal measurements in chemical dynamics research involves combining and correlating ultrafast x-ray measurements with detailed final state analysis, such as velocity and angular distributions of reaction products. Although such approaches have been used with some success, a dramatic increase in the repetition rates of XFEL sources (from around 100 Hz for LCLS to around 100 kHz for LCLS-II) would permit measurements of a wider range of chemical systems with increasingly complex competing reaction pathways.

**Theory of dynamical processes far from equilibrium**

Advances in the theory of processes far from equilibrium are of central importance to all of the PROs presented above. In PRO 1, the ultrafast dynamics of electronic and nuclear motion in molecules are investigated in a regime far from equilibrium after excitation by an ultrashort pulse. Similarly, in PRO 2, new phases of matter are created and studied under highly non-equilibrium conditions induced by intense light fields. In PRO 3, while spontaneous changes in molecules and materials are examined, the aim of this research opportunity is to capture those rare events that deviate strongly from the average behavior and determine the pathways of change.

For the ultrafast science of chemistry and of materials, advanced theoretical and computational tools are needed to interpret photon spectroscopies, especially photon-in/photon-out scattering and time-domain pump-probe experiments. Such developments in theory could extend many tools for equilibrium spectroscopy into the non-equilibrium domain. Progress in this field requires designing tests of competing theoretical scenarios, developing new numerical techniques, implementing new algorithms, and developing a new language to describe out-of-equilibrium systems where conventional equilibrium concepts fail.

Ultimately, these developments help to shape the landscape for predictive models of novel quantum phenomena and materials. Theory, modeling, and interpretation of spectroscopies, especially in the time domain, are needed to extract, and therefore exploit, the physical and chemical information encoded in a vast volume of experimental data across multiple scales in the energy, momentum, spin, and space/time domains.
Issues at the forefront of theory and simulation reflect core challenges in understanding the behavior of electronically excited molecular systems, including the role of electron-electron correlations, dynamic coupling of electronic and nuclear motion or of electronic and collective (e.g., polaritonic) modes, and non-spin-conserving processes. The combination of first-principles electronic structure methods and molecular dynamics approaches can, in principle, determine both the electronic and nuclear wave functions and are thus well suited to describing quantum phenomena such as bond rearrangement, electron transfer, and transport of energy and coherence.

At present, however, many electronic structure methods do not treat excited states or electron correlation phenomena accurately. Conical intersections and other degeneracy points are areas where further research is particularly needed. These regions are now understood to play a dominant role in controlling non-adiabatic processes and the eventual outcome of chemical transformations, but are precisely the regions where the assumptions underlying present theories may break down [100]. Similarly, the simulation of molecular dynamics with both internal conversion (spin-conserving electronic state transitions) and intersystem crossing (spin-flipping electronic state transitions) remains challenging [101]. These processes are central to energy conversion and photocatalysis, which often involve organometallic complexes with multiple low-lying spin states.

Additional theoretical challenges arise from the wealth of possibilities discussed in PRO 2 for controlling matter with intense, ultrafast radiation fields. Key issues range from the existence of non-equilibrium phases of matter and the nature of transitions between non-equilibrium and more conventional equilibrium phases, to the understanding and modeling of the flow of energy and quantum mechanical coherence. Important progress has occurred; an example of the power of theory to predict new phases of matter under intense electromagnetic radiation is presented in Fig. 15. However, the physics discussed in the PROs suggest a number of important open challenges. For example, in nonlinear phononics [101], highly exciting a given lattice degree of freedom can create an apparent superconducting-like low resistance state [102] or switch a ferroelectric order parameter [101]. But neither the nature of the low resistance state nor the paths by which an optically active mode excitation changes the electronic properties has been conclusively identified.

Direct calculation of experimental observables by theory and simulation is necessary for the desired tight coupling between experiment and modeling. In this context, quantification of the degree to which theory can predict experimental results will enable a sharper focus on the new information that is being uncovered by experiments [103]. The theoretical framework must include treatment of nonlinear interactions of x-ray pulses with matter. Inclusion of nonlinear interactions is important both for extending powerful multidimensional spectroscopic techniques for probing molecules into the x-ray regime.
and for understanding the creation of novel types of excitations, such as the localized excitation of valence states by stimulated x-ray Raman scattering discussed in PRO 1.

A promising base exists on which to build the needed theory. Time dependent density functional theory \[104\] captures, with materials realism, the dynamics of light-matter coupling but (in common with equilibrium density functional theory) does not incorporate the many-body physics needed to understand novel electronic phases or energy and coherence relaxation pathways. Modern many-body methods, such as dynamical mean field theory \[105\] and the density matrix renormalization group/tensor network methodologies \[106\], have been extended to the non-equilibrium domain, but to date these extensions function primarily on the model-system level. Combining material specificity with modern non-equilibrium many-body theory represents a new technique that will contribute greatly to advancing our progress in creating and controlling novel states of matter on ultrafast timescales.

Beyond the tremendous impact that theoretical advances in understanding processes occurring far from equilibrium can have on both materials and chemical sciences in the ultrafast regime, progress in this direction is particularly significant for experimental...

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**Fig. 15.** Theoretical studies predict that a strong optical field can be used to transform a Dirac semimetal into a Weyl semimetal. This behavior is illustrated for the band structure of NaBi\(_3\) shown in (a) without the influence of a strong light field. Under the influence of a strong light field (b), each Dirac cone (blue) is split (red) to yield a material with the band structure of a Weyl semimetal. These calculations were performed using a newly developed method of Floquet time-dependent density functional theory that permits study of new topological states of matter created with light fields (after [75]).
research conducted with XFEL facilities. The constrained availability of beam time makes it essential to take advantage of the theoretical component of research. Such analysis is, as described above, critical for obtaining the greatest scientific impact from studies conducted at this new measurement frontier. Predictive theory can guide the choice of materials or chemical system to be studied, making the valuable beam time more productive. Going still further, an ambitious goal of comprehensive theory and simulation is to provide real-time feedback to experimentalists during the course of XFEL measurements. This full integration of experiment and theory, as noted in a recent DOE Basic Research Needs report on Transformative Experimental Tools [107], has the potential to revolutionize the way science is performed at major facilities like XFELs.
4. References


A. Kumar, A. Nemilentsau, K. H. Fung, G. Hanson, N. X. Fang, and T. Low, "Chiral plasmon in gapped Dirac systems," Physical Review B 93, 041413 (2016).


APPENDIX A: WORKSHOP PARTICIPANTS

BES Roundtable on Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science

Panel: Imaging Nuclear Dynamics
Nora Berrah, University of Connecticut
Kelly Gaffney, SLAC National Accelerator Laboratory
Todd Martinez, SLAC National Accelerator Laboratory
Andy Millis, Columbia University
Albert Stolow, University of Ottawa
Haidan Wen, Argonne National Laboratory

Panel: Imaging Charge Dynamics
Tom Devereaux, SLAC National Accelerator Laboratory
Oliver Gessner, Lawrence Berkeley National Laboratory
Venkat Gopalan, Pennsylvania State University
Alessandra Lanzara, Lawrence Berkeley National Laboratory
Ken Schafer, Louisiana State University
Greg Scholes, Princeton University

Panel: Inducing and Probing Collective States
Dimitri Basov, Columbia University
Phil Bucksbaum, SLAC National Accelerator Laboratory
Zahid Hasan, Princeton University
Martin Wolf, Fritz Haber Institute of the Max Planck Society
Di Xiao, Carnegie Mellon University
Linda Young, Argonne National Laboratory

Panel: High Field, Attosecond frontier
Shaul Mukamel, University of California, Irvine
Margaret Murnane, University of Colorado
Keith Nelson, Massachusetts Institute of Technology
Rohit Prasankumar, Los Alamos National Laboratory
David Reis, SLAC National Accelerator Laboratory
Z.-X. Shen, SLAC National Accelerator Laboratory

Participants

Co-Chairs:
Tony Heinz, SLAC National Accelerator Laboratory
Oleg Shpyrko, University of California San Diego

Speakers:
David Fritz, SLAC National Accelerator Laboratory
Linda Young, Argonne National Laboratory

Dimitri Basov, Columbia University
Nora Berrah, University of Connecticut
Phil Bucksbaum, SLAC National Accelerator Laboratory
Tom Devereaux, SLAC National Accelerator Laboratory
Kelly Gaffney, SLAC National Accelerator Laboratory
Oliver Gessner, Lawrence Berkeley National Laboratory
Venkat Gopalan, Pennsylvania State University
Zahid Hasan, Princeton University
Alessandra Lanzara, Lawrence Berkeley National Laboratory
Todd Martínez, SLAC National Accelerator Laboratory
Andy Millis, Columbia University
Shaul Mukamel, University of California, Irvine
Margaret Murnane, University of Colorado
Keith Nelson, Massachusetts Institute of Technology
Rohit Prasankumar, Los Alamos National Laboratory
David Reis, SLAC National Accelerator Laboratory
Ken Schafer, Louisiana State University
Greg Scholes, Princeton University
Z.-X. Shen, SLAC National Accelerator Laboratory
Albert Stolow, University of Ottawa
Haidan Wen, Argonne National Laboratory
Martin Wolf, Fritz Haber Institute of the Max Planck Society
Di Xiao, Carnegie Mellon University
Linda Young, Argonne National Laboratory
**APPENDIX B: WORKSHOP AGENDA**

**BES Roundtable on**

**Research Opportunities at the Frontiers of XFEL Ultrafast Science**

Gaithersburg Marriott Washingtonian Center

October 25 – October 26, 2017

**Wednesday, October 25, 2017**

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<tr>
<td>8:00 – 8:15 AM</td>
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<td></td>
<td>Harriet Kung, Associate Director of Science for Basic Energy Sciences</td>
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<td>8:15 – 8:45 AM</td>
<td><strong>Welcome, Roundtable Goals, and Logistics</strong></td>
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<td></td>
<td>Tony Heinz, SLAC National Accelerator Laboratory</td>
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<td></td>
<td>Oleg Shpyrko, University of California, San Diego</td>
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<td>8:45 – 9:30 AM</td>
<td><strong>Retrospective Science Highlights in Ultrafast with an International Perspective</strong></td>
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<td>Linda Young, Argonne National Laboratory</td>
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<td>9:30 – 10:15 AM</td>
<td><strong>Summary of Homework Assignments (Tony Heinz &amp; Oleg Shpyrko)</strong></td>
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<td>10:15 – 10:30 AM</td>
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<td>10:30 – Noon</td>
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<td>Panel 3: Inducing and Probing Collective States — Salon D/E</td>
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<td>Panel 4: High Field, Attosecond Frontier — Salon B</td>
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<td>1:30 – 3:30 PM</td>
<td><strong>Breakout Session II – Science Focus con’t</strong></td>
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<td>3:30 – 4:00 PM</td>
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<td><strong>Plenary Session I – Panel Reports: Research Opportunities — Salon D/E</strong></td>
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<td>5:30 – 7:30 PM</td>
<td><strong>Dinner on your own</strong></td>
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<td>7:30 – 9:00 PM</td>
<td><strong>Plenary Session II – Discussion and Identification of Potential PROs — Salon D/E</strong></td>
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**Thursday, October 26, 2017**

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<tr>
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<td>8:00 – 11:00 AM</td>
<td><strong>Breakout Session III – Science and Gap/Synergy Crosscut Discussion</strong></td>
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<tr>
<td>11:00 – Noon</td>
<td><strong>Plenary III -- Presentation of PRO’s/Closing Remarks/Adjourn — Salon D/E</strong></td>
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<td></td>
<td>Tony Heinz, SLAC National Accelerator Laboratory</td>
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<tr>
<td></td>
<td>Oleg Shpyrko, University of California, San Diego</td>
</tr>
<tr>
<td>Noon – 5:00 PM</td>
<td><strong>Working Lunch/writing</strong></td>
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