1. Executive Summary

LCLS-II-HE at SLAC will be a transformative X-ray tool for the scientific mission of DOE Basic Energy Sciences (BES) and for the nation. It represents the vital next step in the ongoing revolution in X-ray lasers, triggered by the world’s first demonstration of a hard X-ray free-electron laser (XFEL) by LCLS in 2009. Its capability moves far beyond the present generation of XFELs and the ultimate potential of storage rings, firmly maintaining the U.S. as the international leader in the science enabled by X-ray sources. The unmatched performance of this facility will serve the needs of a broad scientific user community focused on some of the most critical challenges facing our society, while providing extraordinary potential for scientific discovery and attracting the best and brightest scientific talent.

LCLS-II-HE will provide a qualitatively new capability, unique in the world, delivering ultrafast atomic resolution at high average power. The project is a natural extension to LCLS-II, adding known technology and using existing infrastructure. It will extend operation of the high-repetition-rate beam into the critically important “hard X-ray” regime (>5 keV) that has been used in more than 75% of LCLS experiments to date, providing a major leap in performance to the broadest cross-section of the user community.

The energy reach of LCLS-II-HE (stretching from 5 keV to at least 13 keV and likely up to 20 keV) will enable the study of atomic-scale dynamics with the penetrating power and pulse structure needed for in situ and operando studies of real-world materials, functioning assemblies, and biological systems.

Figure 1.1 The performance of LCLS-II-HE will allow access to the ‘hard X-ray’ regime, providing atomic resolution capability, with an average brightness roughly 300 times the ultimate capability of a diffraction-limited storage ring (DLSR) ¹. Self-seeding will further increase the average brightness of the XFEL facilities by an additional factor of 20 to 50.
1. Executive Summary

The performance of LCLS-II-HE in comparison to other X-ray sources is shown in Figure 1.1. The facility will:

- **Deliver two to three orders of magnitude increase in average spectral brightness beyond** any proposed or envisioned diffraction-limited storage ring (DLSR), exceeding the anticipated performance of the European-XFEL.
- **Provide temporal coherence** for high-resolution spectroscopy near the Fourier transform limit with more than **300-fold increase in average spectral flux** (ph/s/meV) for high-resolution studies beyond any proposed or envisioned DLSR.
- **Generate ultrafast hard X-ray pulses in a uniform (or programmable) time structure** at a repetition rate of up to 1 MHz – a qualitative advance beyond the burst-mode nature of the European-XFEL, and a **100,000-fold improvement in temporal resolution** compared to storage ring sources.
- **Combine three independent accelerators** into a single facility, representing an unprecedented level of flexibility for the user community (a new 8 GeV superconducting linac; a separately tunable 3.6 GeV line for the LCLS-II instruments; and the existing 15 GeV Cu-linac). **No other facility in the world will have this capability.**

The LCLS-II-HE project will add 19 cryomodules of the type already being manufactured for LCLS-II, doubling the electron beam energy from the superconducting accelerator to 8 GeV and making use of the existing cryogenic cooling capacity and space within the linac tunnel.

Therefore, this solution represents a low-risk path with dramatic scientific impact. It will incorporate a linac bypass line to allow simultaneous operation of the soft X-ray and hard X-ray undulator sources with optimum electron beam energies, coupled with myriad beam-sculpting techniques developed on LCLS, including bandwidth control via seeding, multi-pulse operation, and delivery of the 3rd harmonic (opening up new areas of science in the energy range 20 to 50 keV).

This proposal **incorporates all of the elements required for the operating facility**, including accelerator systems, modifications to the instrumentation suite, and all the associated infrastructure. It thus represents a self-contained project, not reliant on subsequent funding of beamlines over an extended period.

The project cost (at $292M in FY17 dollars) includes robust contingency (>30%) and the full project infrastructure and supply chain start-up costs for a stand-alone project. Opportunities for substantial cost savings, risk reduction, and schedule optimization are highlighted in Section 1.3, taking advantage of the ongoing LCLS-II Project supply chain, partnerships, and staff. Furthermore, only a minor (5%) increase to the operations budget is required for this upgraded facility.

The design and implementation path can make use of the annual maintenance periods of the LCLS facility, allowing continuity of scientific exploitation along with flexibility in project scheduling **without any extended downtime.**
1. Executive Summary

### 1.1 Revolutionary Technical Capabilities of LCLS-II-HE

LCLS-II-HE will lead to significant scientific impact, outlined below, enabled by a suite of unmatched technical attributes:

I. **Access to the energy regime above 5 keV:** This is particularly important because it allows analysis of key chemical elements in addition to providing atomic resolution. For example, this regime encompasses Earth-abundant elements that will be needed for large-scale deployment of photocatalysts for electricity and fuel production; it allows study of strong spin-orbit coupling that underpins many aspects of quantum materials; and it reaches the biologically important selenium K-edge, used for protein crystallography. This is illustrated in Figure 1.2.

II. **High-repetition-rate, ultrafast hard X-rays** from LCLS-II-HE will reveal coupled atomic and electronic dynamics in unprecedented detail. Advanced X-ray techniques will simultaneously measure electronic structure and subtle nuclear displacements at the atomic scale, on fundamental timescales (femtosecond and longer), and in operating environments that require the penetrating capabilities of hard X-rays and the sensitivity provided by high repetition rate.

III. **Temporal resolution:** LCLS-II-HE will deliver coherent X-rays on the fastest timescales, opening up experimental opportunities that were previously unattainable due to low signal-to-noise from LCLS (at 120 Hz) and that are simply not possible on non-laser sources. The typical limit for synchrotron sources is ~100 ps (100,000 fs), whereas the performance of LCLS has progressed from initial pulse durations of 300 fs down to 5 fs, coupled to the capability for double pulses with independent control of energy, bandwidth, and timing. Ongoing development programs offer the potential for 0.5 fs pulses.

![Figure 1.2](image-url)

Figure 1.2 The spectral region above 5 keV (the design limit of LCLS-II) is a critical area for many types of measurements. Access to ångström wavelength (~12.4 keV) X-rays is a major enabling step for atomic-scale studies, while the ability to probe Earth-abundant elements and access experimental regimes central to biological structure determination and quantum materials studies will provide a fundamentally new capability for discovery science.
1. Executive Summary

Figure 1.3 A unique feature of X-ray free-electron lasers is the ability to probe the fastest timescales, providing over three orders of magnitude higher temporal resolution than a synchrotron source.

IV. Temporal coherence: Control over the XFEL bandwidth will be a major advance for high-resolution inelastic X-ray scattering and spectroscopy in the hard X-ray range (RIXS and IXS). The present scientific impact of RIXS and IXS is substantially limited by the available spectral flux (ph/s/meV) from temporally incoherent synchrotron sources. LCLS-II-HE will provide more than a 300-fold increase in average spectral flux compared to synchrotron sources, opening new areas of science and exploiting high energy resolution and dynamics near the Fourier transform limit.

<table>
<thead>
<tr>
<th>Resolution:</th>
<th>~100 meV</th>
<th>~1 meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCLS-II-HE</td>
<td>(\sim 10^{13})</td>
<td>(\sim 10^{10})</td>
</tr>
<tr>
<td>ESRF</td>
<td>(\sim 10^{13}) (UPBL6)</td>
<td>(\sim 10^{10}) (ID28)</td>
</tr>
<tr>
<td>SPring-8</td>
<td>(\sim 10^{10})</td>
<td>(\sim 10^{10})</td>
</tr>
<tr>
<td>APS</td>
<td>(\sim 10^{12}) (MERIX)</td>
<td>(\sim 10^{9}) (UHRIXS)</td>
</tr>
<tr>
<td>NSLS-II</td>
<td>(\sim 10^{10})</td>
<td>(\sim 10^{10})</td>
</tr>
</tbody>
</table>

Table 1.1. Comparison of projected LCLS-II-HE performance for RIXS and IXS, (based on data in reference 2). LCLS-II-HE performance is quoted for a seeded beam -- providing two orders of magnitude improvement in either resolution or in flux at the highest resolution.

V. Spatial coherence: The high average coherent power of LCLS-II-HE in the hard X-ray range, with programmable pulses at high repetition rate, will enable studies of spontaneous ground-state fluctuations and heterogeneity at the atomic scale from μs (or longer) down to fundamental femtosecond timescales using powerful time-domain approaches such as X-ray photon correlation spectroscopy (XPCS). LCLS-II-HE capabilities will further provide a qualitative advance for understanding non-equilibrium dynamics and fluctuations via time-domain inelastic X-ray scattering (FT-IXS) and X-ray Fourier-transform spectroscopy approaches using Bragg crystal interferometers.
VI. **Structural dynamics and complete time sequences**: LCLS achieved early success in the determination of high-resolution structures of biological systems and nanoscale matter before the onset of damage. X-ray scattering with ultrashort pulses represents a step-change in the field of protein crystallography. An important scientific challenge is to understand function as determined by structural dynamics – at the atomic scale (requiring ~1Å resolution) and under operating conditions or in physiologically relevant environments (e.g. aqueous, room temperature). The potential of dynamic pump-probe structure studies has been demonstrated in model systems, but the much higher repetition rates of LCLS-II-HE are needed in order to extract complete time sequences from biologically relevant complexes. Here, small differential scattering signals that originate from dilute concentrations of active sites and low photolysis levels are essential in order to provide interpretable results.

VII. **Heterogeneous sample ensembles and rare events**: The high repetition rate and uniform time structure of LCLS-II-HE provide a transformational capability to collect $10^8$-$10^{10}$ scattering patterns (or spectra) per day with sample replacement between pulses. By exploiting revolutionary advances in data science (e.g. Bayesian analysis, pattern recognition, manifold maps, or machine learning algorithms) it will be possible to characterize heterogeneous ensembles of particles or identify and extract new information about rare transient events from comprehensive data sets.

### 1.2 Scientific Impact

LCLS-II-HE will provide the U.S. with a true “discovery science” facility that leaps far beyond any existing X-ray source, with capabilities that are essential for the science mission of DOE. The development of user facilities within DOE Office of Science is being driven in large part by the urgent need for a deeper understanding of the phenomena underpinning the future of the energy sector, the environment, and biological sciences. New observational tools and facilities are required to address the associated scientific grand challenges, as highlighted in a wide-ranging set of reports from DOE BES.

In particular, LCLS-II-HE will enable precision measurements of structural dynamics on atomic spatial scales and and fundamental timescales. Such measurements are needed to underpin many of the transformative opportunities identified in the latest report from the Basic Energy Sciences Advisory Committee (BESAC) \(^3\), by providing detailed insight into the behavior of complex matter in real-world heterogeneous samples on fundamental scales of energy, time, and length. The solutions to many important challenges facing humanity, such as developing alternative sources of energy, mitigating environmental and climate problems, developing new “green” technologies, and delivering precision medical tools, depend on an improved understanding and control of matter.

We highlight seven broad classes of science for which LCLS-II-HE will uniquely address critical knowledge gaps that are directly related to DOE BES scientific grand challenges \(^3,6\), which are indicated in bullets:

**Coupled dynamics of energy and charge in atoms and molecules**

Flows of energy and charge in molecules are the fundamental processes that drive chemical reactions and store or release energy. They are central to energy processes ranging from combustion to natural and man-made molecular systems that convert sunlight into fuels. Understanding and controlling these processes remains a fundamental science challenge, in large part because the movement of charge is closely coupled to subtle structural changes of the molecule, and conventional chemistry models are inadequate to fully describe this. Sharper experimental tools are needed to probe these processes –
simultaneously at the atomic level and on natural (femtosecond) time scales. LCLS-II-HE will image dynamics at the atomic scale via hard X-ray scattering and coherent diffractive imaging (CDI) to reveal the coupled behavior of electrons and atoms with unprecedented clarity. The combination of hard X-rays with high peak power and high average power will enable new nonlinear spectroscopies that promise important new insights into reactive chemical flows in complex chemical environments such as combustion.

Grand-challenge science areas addressed:

- Control Matter at the Level of Electrons
- Emergent Properties from Complex Electronic and Atomic Correlations
- Master Energy and Information on the Nanoscale

Catalysis, photocatalysis, environmental & coordination chemistry

A deeper understanding of the fundamental processes in catalysis, photocatalysis, and interfacial chemistry is essential for directed design of new systems for chemical transformations, energy storage, and solar energy conversion that are efficient, chemically selective, robust, and based on Earth-abundant elements. LCLS-II-HE will reveal the critical (and often rare) transient events in these multistep processes, from light harvesting to charge separation, migration, and accumulation at catalytically active sites. Time-resolved, high-sensitivity, element-specific scattering and spectroscopy enabled by LCLS-II-HE will provide the first direct view of atomic-scale chemical dynamics at interfaces. The penetrating capability of hard X-rays will probe operating catalytic systems across multiple time and length scales. The unique LCLS-II-HE capability for simultaneous delivery of hard and soft X-ray pulses opens the possibility to follow chemical dynamics (via spectroscopy) concurrent with structural dynamics (substrate scattering) during heterogeneous catalysis. Time-resolved hard X-ray spectroscopy with high fidelity, enabled by LCLS-II-HE, will reveal the fine details of functioning biological catalysts (enzymes) and inform the design of artificial catalysts and networks with targeted functionality.

Grand-challenge science areas addressed:

- Beyond Ideal Materials and Systems
- Mastering Hierarchical Architectures in Matter Beyond Equilibrium
- Imaging Matter across Scales
- Data, Algorithms and Computing

Imaging biological function and dynamics

LCLS-II-HE is the ideal, much-desired upgrade to LCLS-II that the structural biology community requires. The combination of high spatial and time resolution with a high repetition rate will make LCLS-II-HE a revolutionary machine for many biological science fields. At high repetition rates, serial femtosecond crystallography (SFX) will advance from successful demonstration experiments to addressing some of the most pressing challenges in structural biology for which only very limited sample volumes are available (e.g. human proteins); or only very small crystal sizes can be achieved (<1 μm); or where current structural information is significantly compromised by damage from conventional X-ray methods (e.g. redox effects in metalloproteins). In all of these cases, high throughput and near-physiological conditions of room temperature crystallography will be qualitative advances. X-ray energies spanning the Se K-edge (12.6 keV) will further enable de novo phasing via molecular replacement and anomalous scattering. Time-resolved SFX and solution SAXS will advance from present few-time snapshots of model systems at high photolysis levels to full time sequences of molecular dynamics that
are most relevant for biology. Hard X-rays and high repetition rates will further enable advanced crystallography methods that exploit diffuse scattering from imperfect crystals, as well as advanced solution scattering and single particle imaging methods to map sample heterogeneity and conformational dynamics in native environments.

Grand-challenge science areas addressed:

- Imaging Matter across Scales
- Characterize & Control Systems away from Equilibrium
- Data, Algorithms and Computing

Materials heterogeneity, fluctuations, and dynamics

Heterogeneity and fluctuations of atoms and charge-carriers – spanning the range from the atomic scale to the mesoscale – underlie the performance and energy efficiency of functional materials and hierarchical devices. Conventional models of ideal materials often break down when trying to describe the properties that arise from these complex, non-equilibrium conditions. Yet, there exists untapped potential to enhance materials performance and create new functionality if we can achieve a much deeper insight into these statistical atomic-scale dynamics. Important examples include: structural dynamics associated with ion transport in materials for energy storage devices and fuel cells; nanostructured materials for manipulating nonequilibrium thermal transport; two-dimensional materials and heterostructures with exotic properties that are strongly influenced by electron-phonon coupling, light-matter interactions, and subtle external stimuli; and perovskite photovoltaics where dynamic structural fluctuations influence power conversion efficiency. LCLS-II-HE will open an entirely new regime for time-domain coherent X-ray scattering of both statistical (e.g. XPCS) and triggered (pump-probe) dynamics with high average coherent power and penetrating capability for sensitive real-time, in situ probes of atomic-scale structure. This novel class of measurements will lead to new understanding of materials, and, ultimately, device performance, and will couple directly to both theory efforts and next-generation materials design initiatives.

Grand-challenge science areas addressed:

- Beyond Ideal Materials and Systems
- Mastering Hierarchical Architectures in Matter Beyond Equilibrium
- Imaging Matter across Scales

Quantum materials and emergent properties

There is an urgent technological need to understand and ultimately control the exotic quantum-based properties of new materials – ranging from superconductivity to ferroelectricity to magnetism. These properties emerge from the correlated interactions of the constituent matter components of charge, spin, and phonons, and are not well described by conventional band models that underpin present semiconductor technologies. A comprehensive description of the ground-state collective modes that appear at modest energies, 1-100 meV, where modern X-ray sources and spectrometers lack the required combination of photon flux and energy resolution, is critical to understanding quantum materials. High-resolution hard X-ray scattering and spectroscopy at close to the Fourier limit will provide important new insights into the collective modes in 5d transition metal oxides – where entirely new phenomena are now being discovered, owing to the combination of strong spin-orbit coupling and strong charge correlation. The ability to apply transient fields and forces (optical, THz, magnetic, pressure) with the time-structure of LCLS-II-HE will be a powerful approach for teasing apart intertwined ordering, and will be a step toward materials control that exploits coherent light-matter interaction. Deeper insight into the coupled
electronic and atomic structure in quantum materials will be achieved via simultaneous atomic-resolution scattering and bulk-sensitive photoemission enabled by LCLS-II-HE hard X-rays and high repetition rate.

Grand-challenge science areas addressed:

- Emergent Properties from Complex Electronic and Atomic Correlations
- Harnessing Coherence in Light and Matter

Materials in extreme environments

LCLS-II-HE studies of extreme materials will be important for fusion and fission materials applications and could lead to important insights into planetary physics and geoscience. The unique combination of capabilities from LCLS-II-HE will enable high-resolution spectroscopic and structural characterization of matter in extreme states that is far beyond what is achievable today. High peak brightness combined with high repetition rates and high X-ray energies are required to: (i) penetrate dynamically heated dense targets and diamond anvil cells (DAC), (ii) achieve high signal-to-noise data above the self-emission bremsstrahlung background, (iii) probe large momentum transfers on atomic scales to reveal structure and material phases, and (iv) measure inelastic X-ray scattering with sufficient energy resolution and sensitivity to determine the physical properties of materials.

Grand-challenge science areas addressed:

- Characterize & Control Systems away from Equilibrium
- Beyond Ideal Materials and Systems

Nonlinear X-ray matter interactions

A few seminal experiments on the first generation of X-ray free-electron lasers, LCLS and SACLA, have demonstrated new fundamental nonlinear hard X-ray-matter interactions, including phase-matched sum frequency generation, second harmonic generation, and two-photon Compton scattering. While nonlinear X-ray optics is still in the discovery-based science phase, advances in our understanding of these fundamental interactions will lead to powerful new tools for atomic and molecular physics, chemistry, materials science, and biology via measurement of valence charge density at atomic resolution and on the attosecond-to-femtosecond timescale of electron motion. The combination of high repetition rate and high peak intensity pulses from LCLS-II-HE will enable high-sensitivity measurements that exploit subtle nonlinear effects. This will transform the nonlinear X-ray optics field from demonstration experiments to real measurements that utilize the nonlinear interactions of “photon-in, photon-out” to simultaneously access transient spectroscopic and structural information from real materials.

Grand-challenge science areas addressed:

- Control Matter at the Level of Electrons
- Emergent Properties from Complex Electronic and Atomic Correlations

1.3 Readiness to Construct

LCLS-II-HE will take advantage of infrastructure already being installed as part of the ongoing LCLS-II construction project, minimizing the need for additional design and construction (see Figure 1.4). LCLS-II will be installed in the first 750 m of a 1 km section of the SLAC tunnel that will be cleared out in 2016, leaving room for up to 22 additional cryomodules. With regard to delivery, LCLS-II-HE capitalizes on the proven project management capability, existing project infrastructure, highly experienced staff, and integrated project team for LCLS-II. The LCLS-II-HE technical design, costs, and schedule are derived
3. Revolutionary New Scientific Capabilities

The technical capabilities of LCLS-II-HE will enable new experimental approaches in the hard X-ray range that are qualitatively different from anything available from current sources, or from any other X-ray source in the foreseeable future. Following is a brief introduction to these new scientific methods and tools, and their anticipated impact. Section 4 presents examples of the science opportunities that will exploit these new measurement methods and the capabilities of LCLS-II-HE.

3.1 Coupled atomic and electronic structure of real systems on fundamental time and length scales

High-repetition-rate, ultrafast hard X-rays from LCLS-II-HE will enable advanced X-ray techniques that simultaneously measure electronic structure and subtle nuclear displacements at the atomic scale, on fundamental timescales (femtoseconds and longer), and in operating environments that require the penetrating capabilities of hard X-rays. The power of this approach has been demonstrated in recent experiments at LCLS, in which hard X-ray scattering and X-ray emission from a model transition-metal charge-transfer complex in solution have been measured simultaneously. These experiments revealed the coupling of charge dynamics and atomic structure on the sub-Å scale and on the 100 fs timescale for the first time.1

Applying these techniques to much more complex assemblies (e.g. light-harvesting and photosynthetic complexes) will require a much higher repetition rate to extract quantitative information that can be used to inform design and synthesis. For example, studies to date at 120 Hz have been limited to relatively simple molecules in high concentrations with high photolysis yields, whereas functioning assemblies typically have low concentrations of active sites and must be investigated at low photolysis levels to properly understand how they operate.

LCLS-II-HE will enable element-specific probing of the fine details of the chemical structure, such as valence excited-state charge dynamics, by exploiting sensitive valence-to-core (Kβ2,5) X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS) in the 5-12 keV range, as illustrated in Figure 3.1. Time-resolved XFEL studies to date have been limited by the average spectral flux (ph/s/meV) to less informative X-ray emission lines (Kα, Kβ1,3), and to RIXS probing at single time snapshots of large chemical changes in simple molecules at high concentration2,3.

LCLS-II-HE will provide a similarly dramatic advance for powerful differential extended X-ray absorption fine structure (EXAFS) studies of changes in local structure at the 0.01 Å scale. The 5-12 keV range spans the core resonances of the Earth-abundant 3d transition metals (e.g. Fe and Cu K-edges at 7.1 and 9 keV) that are the basis for many biological enzymes and photocatalysts, and the 4d and 5d metals (e.g. Pt L3-edge at 11.6 keV) commonly used in man-made catalysts and photosynthetic assemblies.
3. Revolutionary New Scientific Capabilities

3.2 Temporal coherence: Dynamics, and high-resolution X-ray spectroscopy at the Fourier limit

The >300-fold increase in average spectral flux (ph/s/meV) via self-seeding will be a major advance for high-resolution inelastic X-ray scattering and spectroscopy in the hard X-ray range (both resonant, RIXS, and non-resonant, IXS), where the available spectral flux from temporally incoherent sources substantially limits the scientific impact. LCLS-II-HE will support novel instrumentation designs for ultra-high-resolution (sub-meV) IXS \(^4\,^5\) (Figure 3.2 right), will enable the use of quartz- and sapphire-based analyzers for hard X-ray RIXS at the few meV scale \(^6\), and will make possible entirely new approaches for time-resolved resonant inelastic scattering.

For example, element-specific mapping of the excited-state potential energy surfaces of reactive molecular complexes (Figure 3.2 left) will provide entirely new scientific insight for chemistry, materials science, and biology. Time-resolved RIXS is the X-ray analog of powerful femtosecond visible Raman spectroscopy \(^7\), with tunable ultrafast X-rays providing element specificity \(^8\,^9\) along with dynamics. LCLS-II-HE capabilities, combined with advanced spectrometer designs \(^6\,^10\,^11\), will enable this approach to be applied to complex reactive systems for the first time. Of particular interest is the opportunity to distinguish local bonding environments of complex molecular assemblies targeting the metal-ligand fingerprint region (200-500 cm\(^{-1}\), 24-60 meV). This requires high average spectral flux to distinguish weak signals, with <10 meV resolution at close to the Fourier transform limit at photon energies resonant with transition-metal K–edges and L-edges (up to 12 keV) \(^6\).

Inelastic X-ray scattering also has tremendous potential for characterizing ground-state and low-energy collective modes that are hallmarks of complex matter. For example, in strongly correlated materials,
3. Revolutionary New Scientific Capabilities

Collective modes of the electronic continuum determine the material properties and are described by the momentum-dependent dynamic structure factor $S_e(q,\omega) \sim \chi(q,\omega)$. However, comprehensive direct measurements of this fundamental description of quantum matter at meV energy resolution that spans the entire Brillouin zone have remained largely inaccessible. In soft matter and biological systems, low-energy collective dynamics mediate self-assembly and the development of non-equilibrium forms of matter. Our ability to understand and ultimately control such processes relies on developing much deeper insight into the low-energy potential landscape.

The full scientific potential of inelastic X-ray scattering (both resonant and non-resonant) has yet to be realized, owing to the low average spectral flux of present hard X-ray sources. The high spectral flux from LCLS-II-HE, at close to the transform limit and in a uniform pulse structure to facilitate sample replacement/recovery, will transform this field (see Section 5.1 for a comparison of LCLS-II-HE capabilities in this area with those of existing facilities). Importantly, the hard X-ray regime provides bulk sensitivity and access to sub-nm length scales (large momentum transfer), and is compatible with diamond anvil cells for pressure-dependent studies. LCLS-II-HE capabilities will support the highest-resolution spectrometer designs with unprecedented throughput.

3.3 Coherent hard X-ray scattering: Materials heterogeneity and spontaneous fluctuations

Spontaneous fluctuations and heterogeneity are pervasive in complex matter, and are often central to their functional properties. X-ray photon correlation spectroscopy (XPCS) is a powerful time-domain approach for characterizing ground-state fluctuations and heterogeneity, as illustrated in Figure 3.3. The coherent X-ray analogue of dynamic light scattering, XPCS produces a speckle pattern that is a Fourier projection of the material structure. Changes in the speckle pattern map the evolving material structure in momentum space ($q$) through the dynamic structure factor $S(q,t)$. At a fundamental level, the ability to discern structural changes at short time intervals scales inversely with the square of the X-ray source brightness ($\Delta t \sim B^{-2}$). At a practical level, accessing these timescales depends on multiple-pulse measurement schemes (with moderate peak brightness and high average brightness) and/or detector speed and sensitivity. The high average coherent power of LCLS-II-HE, with programmable pulses at high repetition rate, will enable studies of spontaneous fluctuations at the atomic scale from μs (or longer) down to fundamental femtosecond timescales, thus opening up whole new areas of science.

Figure 3.3. Multi-pulse X-ray photon correlation spectroscopy of materials heterogeneity and fluctuations.

Sequential, Two-pulse, Programmable
XPCS approaches at LCLS-II-HE include the following:

- “Sequential” XPCS measures a real-time sequence of individual speckle patterns, limited either by the repetition rate of the XFEL or by the 2D detector readout rate (see Section 5.5.3. and recent advances in time-stamping detectors\(^\text{12}\)).

- “Two-pulse” XPCS\(^\text{13,14}\) relies on superimposed pairs of speckle patterns created by time-delayed X-ray pulses. The decay in speckle visibility as a function of pulse delay is directly related to \(S(q,t)\). This approach will probe ultrafast atomic-scale statistical dynamics in materials for the first time, with a time resolution limited only by the X-ray pulse delay.

- A “programmable” XPCS mode is uniquely enabled by the CW-SCRF linac of LCLS-II-HE. In the simplest configuration, X-ray pulse pairs can be generated directly from the XFEL with time delays of \(<100\) fs up to milliseconds or longer. In addition, potentially much more powerful XPCS schemes are enabled, in which the entire time structure is encoded in the X-ray pulse sequence (e.g. in a logarithmic distribution of time intervals).

LCLS-II-HE capabilities will enable qualitative advances in emerging approaches such as time-domain inelastic X-ray scattering\(^\text{15}\) and X-ray Fourier-transform spectroscopy using Bragg crystal interferometers\(^\text{16}\), which are potentially powerful complements to IXS and XPCS. For example, FT-IXS is an important new approach for probing low-energy collective modes in condensed matter that exploits the information content of diffuse scattering and the ultrashort pulses of LCLS to map the dynamic structure factor in the non-equilibrium regime. Initial LCLS experiments using FT-IXS yielded new insight into time- and momentum-dependent phonon-phonon correlations in model bulk materials\(^\text{15}\) (Figure 3.4). The high repetition rate of LCLS-II-HE will enable this powerful approach to be applied to functional materials, nanostructures, and assemblies.

![Figure 3.4. Coherent phonon-phonon correlations and acoustic phonon dispersion function (inset) measured in bulk Ge via Fourier-transform inelastic X-ray scattering (FT-IXS)\(^\text{15}\).](image)

3.4 Coherent X-ray scattering: Complete time sequences of structural dynamics at the atomic scale

A major early success of LCLS is the determination of high-resolution structures of biological systems and nanoscale matter before the onset of damage. The combination of serial femtosecond crystallography (SFX) and “diffraction before destruction”\(^\text{17}\) has provided atomic-resolution structures of clusters, nanomaterials, and many biologically important classes of molecules\(^\text{18}\), often from micro- to nano-sized crystals that are unsuitable for study with the best conventional synchrotron X-ray sources, and with
higher resolution or with structural details more representative of the room-temperature native state. However, studies to date have been limited largely to a few snapshots of static structures.

An important scientific challenge for structural biology and the broader area of functional nanomaterials and self-assembly is the ability to study structural dynamics – at the atomic scale, and under operating conditions or in environments that are more physiologically relevant (e.g. aqueous, room temperature). Dynamics is an important key to understanding the function of macromolecular complexes and nanomachines whose structures change over a range of time and length scales, often in response to changes in local environment (temperature, pH) or interaction with small molecules. Determining the conformational states of molecular machines and the low-energy landscape that determines their function are important new frontiers for both biology and nanomaterial self-assembly.

Recent LCLS time-resolved SFX studies of photo-detachment dynamics in CO-myoglobin \(^{19}\) and isomerization dynamics in photoactive yellow protein \(^{20}\) illustrate the potential of dynamic pump-probe structure studies. However, these results are limited to just a few time snapshots of model systems at high concentration and at very high excitation fluences. Hard X-rays at much higher repetition rate are needed in order to extract complete time sequences from small differential scattering signals that originate from more relevant complexes, where active sites are often in dilute concentrations and where low photolysis levels are essential in order to provide interpretable results.

While crystallography is an extremely powerful tool for elucidating atomic structures, many complex biological machines defy crystallization due to weak interactions among constituent components and their intrinsic flexibility. Time-resolved solution X-ray scattering \(^{21}\), fluctuation X-ray scattering (fSAXS), and single particle imaging (SPI) \(^{17, 22, 23}\) can provide alternative paths toward understanding dynamics of non-crystalline samples at low to medium resolution. SPI continues to evolve toward higher resolution along the paths defined in the LCLS SPI roadmap \(^{24}\). Fluctuation X-ray scattering \(^{25-28}\) is a multi-particle scattering approach based on a limited ensemble of particles that is enabled by the combination of ultrafast X-ray pulses and high repetition rate. It potentially provides \(\sim 100\) times more information than conventional SAXS – sufficient for 3D reconstruction. It has emerged as a method bridging SPI and crystallography, and is potentially powerful for understanding material dynamics and protein interactions in native environments.

### 3.5 High repetition rate, heterogeneous sample ensembles, and rare events

The high repetition rate and uniform time structure of LCLS-II-HE provides a transformational capability to collect \(10^5\)-\(10^{10}\) scattering patterns (or spectra) per day with sample replacement between pulses. By exploiting revolutionary advances in data science (e.g. Bayesian analysis, pattern recognition, manifold maps, and machine learning algorithms as outlined below) it should be possible to characterize heterogeneous ensembles of particles or extract new information about rare transient events from comprehensive data sets of X-ray scattering patterns and/or spectra.

For fluctuation X-ray scattering and single particle imaging, high-intensity pulses in the 5-10 keV range hold tremendous promise for characterizing conformational heterogeneity or biological machines at different stages in their work cycle. For example, recent cryo-EM studies of the ribosome have demonstrated that it is possible to extract conformational movies from a sufficient number of snapshots of non-identical, unoriented biomolecules cryo-trapped at random points in their work cycle \(^{29}\). This approach of inferring a movie from static snapshots is directly applicable to XFEL studies, with the significance and impact determined by how finely the conformations are sampled with respect to the
underlying conformational heterogeneity \( i.e. \) a large number of snapshots are required). Among the hybrid approaches that are increasingly important for biology, the key advantages provided by XFELs include access to dynamics in near-native environments (room temperature, liquid); the ability to probe thick samples or dense media; and an unprecedented number of independent snapshots provided by high repetition rate.

### 3.6 Advanced computation, data science, and synergy with LCLS-II-HE

Dramatic advances in computational capability and advanced algorithms, coupled with massive data sets, are creating profound opportunities for data science, \( i.e. \) for scientific extraction of new knowledge and insight from data that goes far beyond what was previously possible. This is not simply doing the same analysis faster or on a larger scale, but spawning entirely new methods and establishing new paradigms for analysis. Advanced computation and data science will be integral to LCLS-II-HE, and high-repetition-rate X-ray pulses and massive data sets will further fuel advances in new algorithms and computational approaches. This powerful combination will allow scientists to envision entirely new experiments and analysis methods that will accelerate many fields. Here we highlight just three of many classes of computational techniques that LCLS-II-HE will enable and exploit.

#### 3.6.1 Mapping reaction landscapes and kinetic relationships between conformations

A sufficiently fine-grained statistical sampling of configurational space can be used to map the kinetic topology or reaction pathways of a dynamic system. By analogy, measurement of the GPS locations of an ensemble of cars every minute as they randomly traverse the interstate highway system will provide a good representation of the metropolitan layout of the United States – where cities are and how they are connected. GPS measurements at much less frequent intervals \( e.g. \) every day) would not provide the same insight. Similarly, the high repetition rate of LCLS-II-HE will enable the mapping of the configurational space of complex systems such as proteins, viruses, or chemical reactions. For instance, extensive sampling will enable researchers to determine the energy landscape of a protein \( i.e. \) the local potential energy minima and the connecting transition states) by analyzing the mutual information content between proximate samples. Because protein systems are high dimensional, consisting of many thousands of atoms (each with multiple degrees of freedom), it will be necessary to develop techniques for inferring lower dimensional representations of protein motion on which to map these dynamics. Manifold embedding, diffusion maps, kernel methods and other dimensionality reduction techniques are under intense development for application in a broad range of data science tasks, and LCLS-II-HE will make direct use of these methods and continue to drive their development. These methods will be of particular importance in the study of the structure and dynamics of molecular complexes, exploiting large datasets of scattering patterns or spectra.

#### 3.6.2 Automatic pattern recognition for distinguishing groups of data or events

Large datasets will enable users to rapidly and robustly identify what features of their data distinguish two or more sample configurations or experimental conditions – \( e.g. \) single-particle versus many-particle hits. Such approaches are already being employed at LCLS, for example to exploit the two-color SASE operating mode where the presence of either X-ray color from LCLS is a stochastic process (output may consist of either pulse-color individually or both together). Neural networks have been employed to learn to distinguish between the two single-color and two-color events (Figure 3.5). The result is a model capable of both classifying events by the X-ray FEL colors present, and understanding the patterns within the data that reveal the temporal and spectral content of the X-ray FEL beam. The data rate and volume...
from LCLS-II-HE will make manual analysis increasingly burdensome and increase the need for high-performance machine learning algorithms that perform robustly in the presence of large datasets. Similar machine learning concepts will be required for the analysis of large X-ray data sets.

Figure 3.5. Neural networks are employed to discover new structure within LCLS data. Left: Raw output image of an electron-beam diagnostic, the X-ray transverse cavity (XTCAV), which fluctuates substantially from shot to shot. Images such as these are analyzed to determine if one or both of two electron beams contribute to X-ray lasing. Right: By starting from known results, the neural network algorithm was able learn and discover this subtle pattern within the raw XTCAV image. This pattern highlights the specific regions that reveal the lasing conditions for that X-ray shot. The result is sufficiently non-trivial that discovery of this subtle pattern was only possible through machine learning.

3.6.3 Adaptive scanning of higher-dimensional parameter spaces

The experiments enabled by LCLS have grown increasingly complex over the course of the first few years of operation, and this trend will accelerate with LCLS-II and LCLS-II-HE. For instance, LCLS researchers conducted pump-probe experiments involving three different pump pulses prior to the X-ray FEL probe to study photosystem-II $^{31,32}$. LCLS-II-HE will enable experiments where scanning combinations of many controlled parameters – e.g. pump laser or FEL delays, polarizations, intensities, perhaps multiplied by many perturbations and samples – are necessary for success. Each additional experimental variable increases the required data size exponentially (for a fixed statistical power). Advanced computational techniques will not only be necessary for inference in the high-dimensional parameter spaces that result from such experiments, but will further allow closed feedback-loops to drive these experiments to combinations of input parameters the provide the greatest scientific insight.

References

4.2 Catalysis, Photocatalysis, Environmental & Coordination Chemistry

4.2.1 Coupled dynamics of energy flow: molecular structure and charge

Charge separation, migration, redistribution, and localization are central to efficient and robust energy storage and retrieval from chemical bonds through complex processes such as photosynthesis and catalysis. Indirect evidence points to the importance of the coupled evolution of electronic and nuclear wave functions in many molecular systems. However, they are not well understood at the quantum level, even in simple molecules. We have not been able to directly observe these processes to date, and they are beyond the description of conventional models.

Of particular interest are light-driven reactions that can be initiated by photon absorption in either solid state materials or molecular light harvesting systems connected to catalytic centers. In molecular light harvesters, photoexcitation generates an excited state electron and an electronic vacancy (hole). The energetic electrons can be used to drive reductive catalytic reactions, and the holes can be used to drive oxidative catalytic reactions. The electron transfer between light harvester and catalytic site can be mediated either by direct chemical bonding (e.g. in a molecular photocatalytic assembly) or through semiconductor and redox relays. The following sections will describe how experiments conducted at LCLS-II-HE will facilitate the development of systems for artificial photocatalysis and provide novel insights into natural photocatalysts.

High-repetition-rate, ultrafast hard X-rays from LCLS-II-HE will enable advanced X-ray techniques that simultaneously measure electronic structure and subtle nuclear displacements at the atomic scale, on fundamental timescales (femtoseconds and longer), and in operating environments requiring the penetrating capabilities of hard X-rays. The power of this approach (illustrated in Figure 4.2.1) has been demonstrated in recent experiments at LCLS in which hard X-ray scattering and X-ray emission spectroscopy (XES) from a model transition-metal charge transfer complex have been measured simultaneously to reveal the coupling of photo-induced charge transfer and atomic structure – on the sub-Å scale, and on the 100 fs timescale – for the first time.

Applying these techniques to much more complex light harvesting and photosynthetic assemblies, both natural and artificial, will require a much higher repetition rate to extract quantitative information that can be used to inform design and synthesis. For example, studies to date have been limited to relatively simple molecules in high concentrations with high photolysis yields, whereas functioning assemblies typically have low concentrations of active sites and must be investigated at low photolysis levels to properly understand how they operate.

Figure 4.2.1. Setup for simultaneous probing of electronic and atomic structural dynamics with hard X-rays via emission (XES) and scattering (XDS).
LCLS-II-HE will enable element-specific probing of the fine details of the valence excited-state charge dynamics by exploiting sensitive valence-to-core XES and resonant inelastic X-ray scattering (RIXS) in the 5-12 keV range. High-resolution RIXS will further enable element-specific mapping of element-specific potential-energy surfaces (PES). Time-resolved XFEL studies to date have been limited by the average spectral flux (ph/s/meV) to core-to-core X-ray emission lines, which are less informative. Although some demonstration RIXS experiments have been performed at LCLS, they have been limited to single time snapshots of large chemical changes in simple molecules at high concentration. LCLS-II-HE will provide a similarly dramatic advance for powerful differential extended X-ray absorption fine structure (EXAFS) studies of changes in local structure at the 0.01 Å scale. The 5-12 keV range spans the core resonances of the 3d transition metals (e.g. Fe and Cu K-edges at 7.1 and 9 keV) that are the basis for many biological enzymes and photocatalysts, and the 4d and 5d metals (e.g. Pt L-edge at 11.6 keV) on which existing man-made catalysts and photosynthetic assemblies have largely relied.

**Rational design of Earth-abundant light harvesters**

First row (3d) transition metals are attractive components in both light harvesting and catalytic systems, as they are typically inexpensive, Earth-abundant, and environmentally benign. Development of molecular light harvesters based on 3d transition metals has benefitted from the fact that the functionality of transition-metal-centered systems is highly tunable through ligand modification and substitution. However, functional tunability results in almost infinite possible design strategies for synthesizing new systems or improving existing ones. Therefore, experiments that capture the photoexcited electron transfer pathways and mechanisms are crucial to identify which excited potential energy surfaces should be targeted for modification. This will provide a unique opportunity to make rational design decisions for the next generation of molecular light harvesters.

The power of combined hard X-ray scattering and XES to reveal these exact charge transfer pathways and mechanisms in unprecedented detail has been demonstrated in recent experiments at LCLS. Figure 4.2.2a illustrates a model system for iron-based light harvesters, [Fe(bpy)_3]^{2+}. Hard X-ray emission and scattering studies of this complex allowed for direct quantification of the coupled electronic and structural configurations (Figure 4.2.2c, circles and gray lines).

![Figure 4.2.2](image)

**Figure 4.2.2.** Results of combined hard X-ray scattering and XES studies of a model system for light harvesting: (A) [Fe(bpy)_3]^{2+}, (B) calculated potential energy surfaces, and (C) experimentally determined electronic and atomic structural dynamics compared to a simulation from the same potential energy surfaces (K. Kjaer et al. unpublished).
In reproducing the observed dynamics (Figure 4.2.2c, black and colored lines) by simulating the trajectory of the system on the excited state potential energy surfaces (Figure 4.2.2b), it was possible to determine excited state lifetimes, structural coherence, the locations of intersections between potential energy surfaces and the transition probabilities between surfaces. Most significantly, coherent electronic transitions are observed between the $^3\text{MC}$ and $^5\text{MC}$ states (e.g. at ~300 fs) that coincide with modulation of the Fe-N bond distance.

Applied to functional systems, such details of the excited-state dynamics reveal how the molecular light harvester actually functions. It also shows which potential energy surfaces need to be modified for improved functionality. However, this high level of detail can currently be obtained only for relatively simple model complexes that exhibit large structural changes at high concentrations. LCLS-II-HE will enable the application of simultaneous X-ray scattering and XES (including valence-to-core XES) to reveal the subtle coupled changes in the atomic and electronic structure that underpin many important $3d$ transition metal complexes designed for light harvesting. Applied under operating conditions (often at dilute concentrations), this will provide revolutionary new insight towards the development of these molecular systems.

4.2.2 Photocatalysis

Model molecular photocatalytic assemblies

Linking molecular light harvesters directly to a catalytic site is an important and promising approach for solar energy conversion and related applications. However, understanding the complex excited state processes at the level of detail required for rational design remains a significant science challenge. The model photocatalyst illustrated in Figure 4.2.3 highlights the challenges that impact the performance of molecular photocatalysts. A charge-transfer excitation from the Ru(II) metal center efficiently harvests visible light. This initiates a series of ultrafast changes in electronic and atomic structure, including electron transfer, solvation between the distinct coordinating ligands, and changes in both oxidation and spin states. In principle, the transient Ru(III) and Co(II) sites can catalyze oxidation and reduction reactions. Combining XES and X-ray scattering enables identification of photoinduced electron transfer (ET) pathways, structural dynamics, and thermalization processes. However, the data quality currently achievable from low-repetition-rate XFELs does not allow a complete characterization of the underlying potential energy landscape. If we are to develop effective design rules for manipulating these charge transfer processes through intra- and inter-molecular modification, much more detailed information is essential. Moreover, understanding the catalytic reactions at the active sites of the system will require more sensitive experimental probes.

Figure 4.2.3. Non-equilibrium electron transfer across the photoexcited ($1\text{Ru}^{II}=1\text{Co}^{III}$) model photocatalyst. The fundamental timescales are indicated, as obtained from transient optical absorption spectroscopy, X-ray emission spectroscopy, and X-ray scattering.
Simultaneous measurements of the excited state electronic configuration at the active site (valence-to-core XES or RIXS) and detailed measurements of the excited state active site structural configuration (EXAFS) will provide mechanistic insights into the functionality of these systems. Moreover, high resolution vibrational RIXS will enable element-specific mapping of excited-state potential energy surfaces, as discussed in Section 3.2. Connecting such information with insight from computational chemistry is essential if we are to develop effective design rules for functional molecular catalysts.

**Natural and artificial multi-electron photocatalysts**

All reactions essential for fuel generation from sunlight (*e.g.* reduction of CO₂, oxidation of H₂O and reduction of protons to generate H₂) require two or more instances of charge transfer to complete each of the reactions. In order to design catalysts that meet this criterion, the step-by-step mechanism of the catalytic cycle (spanning femtoseconds to milliseconds) needs to be unraveled, including electron-hole separation, charge accumulation, the evolution of the atomic/molecular structure, the energetics and kinetics of each charge-state intermediate, and the reaction of photo-generated carriers with adsorbate species. The complexity of the problem calls for studies addressing multiple timescales and multiple elements. The higher energy range and higher repetition rate of LCLS-II-HE, coupled with uniform materials, will qualitatively advance the field.

Brookite (TiO₂) nanorods coupled to highly uniform Pt nanocrystal co-catalysts provide an illustrative example. In recent studies, well-defined rods have been shown to efficiently generate H₂ from the oxidation of a variety of biomass-derived organic substrates. Importantly, evidence from transient absorption spectroscopy suggests that the electron-hole recombination can be controlled by engineering the length of the nanorods (as illustrated in Figure 4.2.4), and this relates directly to catalytic reactivity.

However, optical spectroscopy does not reveal key details of the relevant electronic states of TiO₂, Pt or the interface region. High-sensitivity time-resolved hard X-ray spectroscopy enabled by LCLS-II-HE will provide a full characterization of the states associated with photocatalysis in this hybrid system under operating conditions, and thereby identify promising routes for further optimization or directed design. For example, recent time-resolved XAS studies of aqueous anatase TiO₂ nanoparticles at the Ti K-edge (4.97 keV) revealed localization of charge within 300 fs at Ti³⁺ centers. LCLS-II-HE will enable a similar approach to be applied to an operating catalytic assembly, probing both the TiO₂ states and the Pt states at the L₃-edge (11.6 keV) to provide a full picture of charge recombination events and their relation to chemical reactivity.

![Figure 4.2.4. In situ transient absorption spectroscopy of brookite nanorod TiO₂/Pt photocatalysts following photoexcitation at 4.0 eV. Bi-exponential time constant fits are shown by solid lines (a), and summarized as a function of rod length (b).](image)
Another important recent example of artificial photocatalysis is the temporally resolved observation of surface intermediates of water oxidation from a first-row metal-oxide catalyst based on $\text{Co}_3\text{O}_4$ nanoparticles \(^8\) (Figure 4.2.5). While vibrational spectroscopy has provided limited structural details of the surface intermediates during the catalytic cycle, time-resolved X-ray spectroscopy will be able to provide element-specific information on the dynamic changes of the electronic structure and coordination environment of the active metal centers during the catalytic cycle.

The multi-metal probing capability of charge dynamics (via XES and RIXS) and nuclear structure (via scattering and/or EXAFS) on timescales from femtoseconds to milliseconds will allow detection of the dynamic structural changes of active surface metal centers. Specifically, this sensitive approach enabled by LCLS-II-HE will address questions of how charges transferred to Earth-abundant metal oxides induce catalytic changes on the particle surface, and how transferred charges advance the catalytic activity through multiple sequential steps.

One important example from nature that illustrates the potential for this new class of science at LCLS-II-HE is the site for water oxidation ($\text{Mn}_4\text{CaO}_5$ cluster) that acts as a charge storage device in the reaction center of photosystem II (PS-II), accumulating oxidation equivalents after each light-induced charge separation (Figure 4.2.6). Tremendous progress has been made in the structural characterization of this catalytic center in its resting state, culminating in the recent high-resolution (1.95 Å) structure of the first cycle step based on serial crystallography at the SACLA XFEL, enabled for the first time under non-damaging conditions using ultrafast X-ray pulses \(^9\).

While low-repetition-rate XFEL studies of PS-II represent important advances \(^{10,11}\), these static pictures only scratch the surface of the information necessary to deduce the electronic configuration of the metals and the flow of charge within the catalytic center during all four steps of the reaction cycle. In particular, the electronic and atomic structures of the metastable $S_4$ state, where O-O bond formation occurs, remain largely unknown. Characterizing and understanding these subtle changes requires elaborate spectroscopic techniques such as valence-to-core XES, RIXS, high-resolution vibrational RIXS, and EXAFS, which will become available for the first time with LCLS-II-HE.
In summary, hard X-rays at high repetition rate from LCLS-II-HE will be indispensable for simultaneously following transient valence electronic configurations (via XES and RIXS) and atomic structure (via EXAFS and coherent scattering) with the required sensitivity. Importantly, the uniform pulse structure enabled by the CW-SCRF linac is ideally suited for pulse-by-pulse sample delivery/replacement, enabling $\sim 10^8-10^{10}$ independent measurements per day. By exploiting revolutionary advances in data science (as discussed in Section 3.6) it should be possible to extract information about rare transient events from comprehensive data sets.

4.2.3 Homogeneous catalysts: Correlated chemical reactivity & structural dynamics

Beyond the photocatalysts described above, catalysts that accelerate and direct chemical reactions are of vital importance in virtually all areas of energy generation, from processing fossil fuels to converting non-fossil fuel stock, producing chemicals, reducing harmful emissions from combustion, and mitigating climate change. More efficient, selective catalysts with greater yield and less waste that are simultaneously robust, chemically selective, and based on abundant materials will be essential to meeting the world’s future demand for energy, food, and chemicals, and this requires a much greater understanding of catalysis.

In nature, biological catalysts, or enzymes, enable organisms to perform thermodynamically highly demanding chemical transformations under ambient conditions and as close to the thermodynamic limit as possible, often involving only very subtle structural changes. Many exploit Earth-abundant ($3d$) transition-metal active sites. They accelerate and direct chemical reactions by introducing transient intermediate steps that quickly stabilize charge-separated states via electron transfer chains. In addition, enzymatic systems often incorporate integrated self-repair capabilities and are highly regulated to control the synthesis of desired products and minimize undesirable by-products. LCLS-II-HE will enable us to use sensitive X-ray scattering and spectroscopy techniques at transition-metal resonances to capture rare transients and follow the intertwined charge and structural dynamics associated with each step of the catalytic cycle on the atomic scale. This will qualitatively advance our understanding of natural systems and inform the design of artificial catalysts and networks with targeted functionality.
Developing and characterizing light-driven biocatalysts and bio-enzyme hybrids

While pump-probe studies at LCLS-II-HE are naturally suited to study the functioning of photocatalysts, many important biocatalysts, including hydrogenase and nitrogenase, are not directly driven by light. The hydrogenase enzyme catalyzes the reversible oxidation of molecular hydrogen (H₂), which is important for numerous biological functions and is of significant interest for applications in biofuel cells. The nitrogenase enzyme is responsible for the reduction of nitrogen (N₂) to ammonia (NH₃), which is a key step in nitrogen fixation required for all life forms.

A principal challenge in studying such redox-active enzymes and enzyme mimics lies in generating a synchronized homogeneous preparation of each transient intermediate state. Under turnover conditions, a mixture of states is typically present, with the population distribution representing the relative energies of the different species. While this provides some useful insight into the energetics of the catalytic process, a detailed structural characterization of each intermediate is critically missing. Thus, the ability to develop molecular systems for energy conversion reactions that are catalyzed by light is therefore critical not only for using sunlight as an energy source but also as an important means to synchronize intermediates for mechanistic pump probe characterization.

It has been recently shown that nickel-substituted rubredoxin (NiRd) is a highly active enzyme for proton reduction both electro-catalytically and in solution, using a low-potential electron donor or a photo-driven assay. A tentative mechanism for hydrogen evolution has been proposed by analogy to what is known about the [NiFe] hydrogenases, for which NiRd is both a structural and functional mimic. However, detailed structural and mechanistic information is needed to optimize the activity and develop increasingly active hydrogen evolution catalysts. The high repetition rate of LCLS-II-HE, combined with pump-probe spectroscopy using XES, RIXS, and EXAFS at the Ni K-edge, (8.3 keV), will provide critical new information.

Recently, a ruthenium-based photo-trigger has been successfully attached to the [NiRd]-hydrogenase protein scaffold using histidine coordination (Figure 4.2.7). Through reductive quenching of the photo-trigger by a sacrificial donor, intramolecular electron transfer between the reduced ruthenium and the nickel center initiates catalysis. Time-resolved, two-color X-ray techniques can be used to selectively interrogate the electronic structure of the nickel active site at each catalytic step while simultaneously following the redox state of the photo-trigger. By varying the site of attachment and the initial driving force for ET, we will be able to advance these studies beyond simple structural information to elucidate the kinetics and thermodynamics of catalysis. Using this approach, we can arrive at a complete
understanding of the mechanism of hydrogen evolution by NiRd. As an active-site model, these studies will lay the foundation for analogous studies on the native (NiFe) enzymes \(^{13}\).

The largest source of fixed nitrogen in the global biogeochemical cycle is the reduction of atmospheric dinitrogen (N\(_2\)) to ammonia (NH\(_3\)). Almost 80% of our nitrogen intake is produced by the industrial Haber-Bosch process via a dissociative reaction involving co-activation of dihydrogen (H\(_2\)) and N\(_2\) over an Fe-based catalyst. The reaction currently generates significant amounts of CO\(_2\) because the H\(_2\) needed for this reaction is presently produced by steam reforming of natural gas. This one process consumes up to 5% of the world’s natural gas and about 2% of the world’s energy production \(^{15}\). Recently it has been reported that cadmium sulfide (CdS) nanocrystals can be used to photosensitize the nitrogenase molybdenum-iron (MoFe) protein. Thus light harvesting by CdS nanocrystals replaces ATP hydrolysis and drives the enzymatic reduction of N\(_2\) into NH\(_3\) \(^{16}\) (see Figure 4.2.8). A turnover rate corresponding to ~60% of the ATP-coupled reaction rate for the nitrogenase complex under optimal conditions was reported. Thus these CdS:MoFe protein biohybrids provide a photochemical model for achieving light driven N\(_2\) reduction to NH\(_3\).

The ability to create complexes between nanomaterials and MoFe protein and other enzymes shows that photoexcited electrons can be used to drive difficult catalytic transformations while providing new tools for mechanistic investigations. Hard X-rays at high repetition rates will be a critical tool to study the transient structure and bonding configurations of the active sites of these intermediates. The revolutionary new capabilities of LCLS-II-HE will provide detailed atomic and electronic structure information for these hybrid systems by scattering and spectroscopy methods, in particular XES, RIXS, and EXAFS.

**4.2.4 Heterogeneous catalysis and interfacial chemistry**

In functioning heterogeneous catalysts, the materials are neither static nor homogeneous. The evolution of atomic and electronic structure, the making and breaking of chemical bonds, and the exchange of vibrational energy through intermediate states ultimately determine functionality. These interactions further lead to dynamic restructuring of catalyst materials during reaction cycles. Knowing the time evolution of the atomic and electronic structure of molecules and substrates, particularly near elusive transition states, is critical to developing a predictive understanding for design of new catalysts.

Today we are unable to develop a complete picture of this structural evolution on the femtosecond to picosecond timescale relevant to atomic motion or the nanosecond to millisecond timescale characteristic of diffusion and materials evolution. LCLS has enabled the study of simple surface reactions, and reported the first observation of a surface transition state \(^{17}\). These groundbreaking studies on ideal crystals, with reactants prepared at high concentrations in a vacuum, demonstrate the potential for XFELs to provide a full understanding of chemical reactions on surfaces. However, these studies do not address
“working” catalysts which are typically of low dimensionality (e.g. nanoclusters of metals on an oxidic support), where coupled fluctuations of the electronic and atomic structure become increasingly important.

LCLS-II-HE will enable completely new approaches for simultaneously following both the atomic and electronic structure of heterogeneous catalysts in operation. One such approach is illustrated in Figure 4.2.9, where nanocatalysts are prepared either with or without pre-adsorbed reactants and interrogated pulse by pulse using a gas-phase jet or liquid particle injector. Ultrafast X-ray spectroscopy (e.g. EXAFS, XES, or RIXS) or photoelectron spectroscopy probes the electronic structure and chemical environment, while coherent X-ray diffraction from the same hard X-ray pulse probes the atomic structure. Demonstration experiments in the soft X-ray range at FLASH and at LCLS highlight the promise of this approach for characterizing small heterogeneous ensembles of nanoparticles at the atomic scale using hard X-rays.

Metal nanoparticles on an oxide support are an important class of heterogeneous catalysts and they typically exhibit unique catalytic properties. However, the atomic-level detail of their behavior is poorly understood due in part to their complex, dynamic structure, mediated by interaction with the support. In contrast to bulk materials, nanoscale systems exhibit substantial fluctuations in electronic and atomic structure, with large surface effects that depend on temperature, pressure, local chemical interactions, and other factors of the operational environment, as illustrated in Figure 4.2.10. All measurements made to date are both time- and ensemble-averaged, and mask any fluctuations that may be present, but the experimental concept shown above (Figure 4.2.9) will allow the time-dependent electronic and structural behavior of the nanoparticles to be determined at sub-picosecond timescales. Indeed, EXAFS analysis of such systems by default assumes a static structure, with any deviation in bond length, for example, encompassed by the means square displacement, $\sigma^2$ term.

A series of recent papers based on a combination of real-time density functional theory/molecular dynamics simulations, transient coupled-oscillator models, and statistical mechanics has predicted the significance of dynamic structural disorder (DSD) in supported Pt and PtSn nanoclusters at relevant reaction temperatures. Furthermore, the manifestation of DSD in X-ray absorption spectra has been simulated 20-23 (as shown in Figure 4.2.11). Figure 4.2.10 shows a snapshot of the DFT/MD simulation at $t = 4$ ps and a time-elapsed rendering (TER) at two different temperatures. The “blurriness” characterizes the disorder and mobility of the Pt and Sn in the Pt$_{10}$Sn$_{10}$ cluster on the $\gamma$-Al$_2$O$_3$ surface.
Large variations in the white-line intensity can be seen, reflecting substantial differences in the local density of states near the Fermi level, and these variations result from the large structural and bonding fluctuations. LCLS-II-HE will reveal these fluctuations via ultrafast spectroscopy (XES, RIXS, and EXAFS) at the Pt $L_3$-edge (11.6 keV). The dynamical non-equilibrium nature of the structural fluctuations of the nanoclusters leads to changes in valence charge transfer, which significantly influences the reactivity of the clusters. For example, picosecond fluctuations in the Pt-Sn bonding within a $\text{Pt}_{10}\text{Sn}_{10}$ cluster supported on alumina affect the electronic structure of the binding site for reactants. This then manifests itself in different local nanoreactivity. Using the dissociation of $\text{O}_2$ as a prototypical example, simulations show that certain configurations result in a lower activation energy for dissociation. With LCLS-II-HE, it will be possible to measure this local heterogeneity and its effect on the binding and dissociation of reactants. The DSD in these nanocatalysts induces additional active sites for reaction pathways, which likely accounts for the increased reaction rate in such catalysts. This in turn will further our understanding of the effects of disorder in nanocatalysts, and allow the design of improved catalysts for specific reaction steps. Moreover, this will make possible a direct investigation of the stability of the nanocatalysts towards sintering. For example, DFT/MD simulations have hinted that there is a “sweet spot” of temperature where the catalytic cluster is internally mobile (quasi-liquid), a regime that likely enhances the catalytic activity but is simultaneously well attached to the support, thus reducing the possibility of deactivation. The range of temperature is very sensitive to the size and composition of the clusters, and also to the nature of the support. Indeed, recent studies at the LCLS have observed transient melting of individual large nanocrystals of gold.

Figure 4.2.11. Comparison of DFT-MD simulations (top curves) and experimental (bottom curves) of the Pt $L_3$-edge XANES spectra for a $\text{Pt}_{10}$ cluster on an alumina support. The theoretical spectra are obtained from a configurational average over all atoms in the cluster for 32 random conformations extracted from the last 5.5 ps of the MD simulation. The error bars on the theoretical calculations indicate the standard deviation of fluctuations between the various configurations.
Another vitally important and industrially relevant class of catalysts is the zeolite-containing catalysts. Zeolites, which are crystalline microporous materials, are primarily used in the oil refining and petrochemical industries. Today, there are 191 different zeotypes identified, many of them synthesized for the first time in the last decade. However, there are still some fundamental questions regarding details of the reaction mechanism in zeolites. One of the most important zeolites is ZSM-5 (MFI framework), which has become ubiquitous in petroleum refining and chemical manufacturing. The detrimental formation of coke is one of the factors limiting the catalytic performance of zeolite materials, particularly ZSM-5, in high-demand catalytic processes, such as fluid catalytic cracking (FCC) and the methanol-to-hydrocarbons (MTH) reaction. However, the molecular-level details of how the coke forms are still not well understood.

One powerful new approach to elucidate the material properties that promote the detrimental formation of coke during the MTH reaction on ZSM-5, is to study the elementary reaction steps using excitation pulses in the UV, visible, IR or THz regions, followed by ultrafast X-ray probe pulses that are uniquely available from LCLS-II-HE. Previous attempts to understand the reaction mechanism have used in situ fast IR heating of MFI, followed by analysis using UV Raman spectroscopy. However, the constraints of the experiment meant that only long-lived intermediates could be detected. Here we envision a true in situ experiment using a scheme like that shown in Figure 4.2.9, where a jet of zeolite crystals is pre-loaded with the reactant of interest, then transiently heated with an IR pulse and probed spectroscopically with X-ray pulses. DFT calculations indicate that there can be up to 8 molecules of ethylene/unit cell. Timescales of picoseconds to milliseconds could be probed using e.g. X-ray Raman spectroscopy. Simultaneously, coherent diffraction imaging would provide information on the crystallinity of the zeolite itself and allow correlations to be drawn regarding the size and shape of the zeolite crystal. In addition, X-ray fluorescence imaging could be used to quantify the total amount of carbon in each zeolite crystal. The experiments would be conducted using different reactants (e.g. ethylene, propylene, methanol, and higher molecular weight hydrocarbons), and as a function of acid-site strength of the MFI by controlling the Si/Al ratio.

LCLS-II-HE provides a combination of enabling capabilities not available from any other source. First, ultrafast pulses and high peak power from an XFEL are essential for getting useful information from a single pulse. Second, the high repetition rate and uniform pulse structure are ideally suited for pulse-by-pulse measurement and sample replacement. The capability of making $10^8$-$10^{10}$ independent measurements per day, combined with advanced data science and computational approaches (as discussed in Section 3.6), opens a tremendous opportunity to characterize inhomogeneous ensembles of nanoparticles and reaction conditions and capture rare catalytic events.

**Nanostructured catalysts and interfaces**

The study of nanostructured catalysts is an important emerging area that can benefit dramatically from LCLS-II-HE capabilities. Today, nanocrystals can be prepared with atomic precision and are essential components in the preparation of well-defined materials with which to understand catalytic transformations. The use of more uniform nanocrystals (e.g. in the approach illustrated in Figure 4.2.9), in combination with LCLS-II-HE, will tremendously improve the data quality and facilitate the statistical analysis of the experiments by controlling structural heterogeneity. The benefits of improved nanocrystal uniformity have been demonstrated in recent X-ray scattering experiments at SSRL, and LCLS-II-HE would drastically improve the data quality. Here the dataset from a highly uniform ensemble could be treated in its entirety using algorithms that dramatically reduce the analysis time. Such approaches applied
with LCLS-II-HE will provide access to atomic-scale structural dynamics of an operating ensemble of nanostructured catalysts.

The rapid development of uniform nanostructured catalysts will open an important opportunity to understand “hybrid” systems, *i.e.* multicomponent materials, where two or more components are in contact. Investigations of single crystal surfaces have revolutionized the study of catalytic transformations in the past 40 years, and have enabled the first observation of a transition state during catalytic bond formation using LCLS. It is now well known that the interface region between multiple components forms the basis of many catalytic reaction mechanisms. One example is enhanced CO oxidation observed at the interface between monodisperse metal nanoparticles (Ni, Pt, or Pd) on alumina or ceria, as illustrated in Figure 4.2.12. A second striking example is the supported Au catalysts used in oxidation reactions and water-gas shift-reactions. Au particles less than 5 nm in size become active for reactions such as CO oxidation, but only when they are on a support material. While the importance of the Au/support interface in oxygen and water activation has been recognized, two different chemical intermediates have been proposed: (1) Au-O-S (S=support) and (2) Au-O-O-H.

Understanding the role of interfaces in catalysis is becoming increasingly important as new tools are developed for both the synthesis and the characterization of this difficult and complex reactive zone. Investigation of these interfaces at the atomic level, and with time resolution to follow structural evolution, will provide new insight into how to combine materials to create more active and selective catalytic materials. Tunable hard X-rays will enable tracking of atomic and electronic structure changes in hybrid catalysts exploiting transition-metal K- and L-edges and advanced time-resolved spectroscopy and scattering techniques (XES, EXAFS, RIXS, XPCS). Sensitivity provided by high repetition rate will be essential to probe the low concentrations of active catalytic sites (*e.g.* on the surface of nanoparticles or at the interface between a nanoparticle and the support). The combination of hard X-ray photon energy and time resolution will allow probing non-equilibrium dynamics of nanoparticles under reactive conditions, and at chemical resonances. Mapping of chemical transformations across timescales, from femtoseCONDS to milliseconds, will provide an invaluable picture of these interfaces in action. LCLS-II-HE will allow us to uncover how the charge migrates between support materials, particle surfaces, and adsorbed molecules while reactants are being converted – important information to advance our ability to predict and optimize reactivity in catalyst support assemblies.

**4.2.5 Charge and ion transfer at solid-liquid interfaces**

Heterogeneous chemistry at the liquid-solid interface plays a central role in emerging catalytic processes though electrochemistry. For example, in transforming CO$_2$ to fuels and nitrogen to ammonia, electrochemical reactions transfer protons from solvated liquid to adsorbed intermediates on the catalytic
solid material. The complexity of the solid-liquid interface includes adsorption/desorption, diffusion, solvation/desolvation, and the interaction between solvated and adsorbed species with the dynamical surface geometric and electronic structure. Relevant processes span a wide range of timescales, from slow reorganization of nuclear and solvent coordinates spanning nanoseconds (e.g. ligand exchange reaction of aqueous Li\(^+\)) to days (e.g. Cr\(^{3+}\) ion water exchange), to the establishment of transition point configurations (activation), and the subsequent ultrafast electron transfer between the electrode and the reactant molecules/ions, possibly proton-coupled, to slower energy transductions (femtoseconds to picoseconds). In spite of the importance of charge transfer processes in electrochemistry, these solid-electrolyte interfaces remain poorly understood at a fundamental level. Our current understanding is based largely on the empirical electrical double-layer model, which was developed in the mid-19\(^{th}\) to mid-20\(^{th}\) centuries\(^{28-32}\).

One important area where interfacial chemistry is central is in ion batteries for energy storage. Here metal cations move from the negative electrode to the positive electrode while discharging, and reverse during the charge cycle. The need for major advances in both energy storage capacity and density is driving numerous innovations in battery design, and further highlights the need for a deeper understanding of the interfacial chemistry at fundamental length and time scales and under operating conditions. One promising approach for achieving higher energy density is to exploit multivalent ions, such as divalent Mg, Ca, or Zn or trivalent Al ions, in place of monovalent Li ions on which present battery technology is based. One drawback, however, is that the high charge density of multivalent ions gives rise to a stiff and organized solvation shell, which acts as a barrier for charging/discharging.

Recent static hard X-ray scattering studies at the Advanced Photon Source (APS), combined with pair-distribution-function (PDF) analysis and MD modeling, have revealed the cation structure for multivalent electrolytes, as illustrated in Figure 4.2.13\(^{33}\). While this highlights the potential for hard X-ray methods to probe electrolyte structure at the atomic scale, our present knowledge is limited to a static description of the solvation shell of the bulk electrolyte. We do not know how the solvation shell evolves along the charging/discharging reaction path, and we lack the sensitivity to probe the dynamic structure in the critical interface region.

The expanded photon energy range coupled with the programmable time structure and repetition rate of LCLS-II-HE will provide important new insights into the structural dynamics of relevant electrolytes near the interface region in operating electrochemical cells. Advanced X-ray studies of interfacial chemistry \textit{operando} employ a “dip-pull” apparatus (e.g. as developed at the Advanced Light Source for ambient pressure photoemission studies) whereby a thin meniscus forms on a biased electrode pulled from the electrolyte solution to provides access to a nanometer-scale liquid film\(^{34}\). Figure 4.2.14 shows a variant of this approach with a rotating anode to provide a continuously-replenished electrolyte film of variable thickness under operating conditions. This approach can be combined with either sequential XPCS
techniques, to access longer time scales, or two-pulse XPCS, to access the fastest time scales (see Section 3.3), capturing both the structural re-arrangement and chemical transformation of solid-liquid interfaces with high spatial and spectral resolution.

The tunability of LCLS-II-HE will enable resonant XPCS for chemically selective tracking of structural changes in transition metal and post-transition metal ions, providing an invaluable picture of these electrolyte/electrode interfaces in action. While the chemical species in the electrochemical double layer (few nm thickness) transform upon electrochemical potential change, the bulk electrolyte or electrode composition does not. Signals from the electrochemical interface can be discriminated from bulk electrolyte or electrode by subtractive normalization of measurements between two electrochemical conditions. The time structure of hard X-ray pulses provided by LCLS-II-HE and its unprecedented average brightness are essential for this approach, allowing extraction of small differential scattering signals. Future extension of LCLS-II-HE capabilities to 20 keV and beyond (see Section 6) will enable time-resolved X-ray scattering studies at large $q$ to be combined with PDF analysis to map the local ion structure at the interface, and follow its evolution through changes in operating conditions.

**Figure 4.2.14.** Schematic of electrochemical cell based on the rotating electrode reactor. The working electrode (WE) and counter cylindrical electrode (CE) are partially emerged from an electrolyte solution. As the cylinder rotates, WE and CE are continuously dipped and pulled from the electrolyte. In the steady state, fresh liquid layers on WE and CE are continuously replenished. The electrochemical potential of WE is referenced to stationary electrode (RE) near the X-ray interaction point. The exposed thickness of the liquid layers on WE and CE can be controlled by the angular velocity of cylinder electrode and the arc length of the exposed part of WE and CE.

### 4.2.6 Aqueous and interfacial geochemistry: elemental cycling and contaminant mitigation

Natural Earth systems are extremely complex on all length and time scales and are dominated by compositional, structural and temporal heterogeneities, interfaces, and disorder (e.g. as illustrated in Figure 4.2.15 and highlighted in the 2015 DOE-BES report). A fundamental understanding of the behavior of geochemical systems across a broad range of time and spatial scales is critical for ensuring the future vitality of ecosystems. Understanding and controlling interfacial chemistry is at the core of this grand challenge. A 2015 BES roundtable report on subsurface technology and basic science emphasized this point, and DOE Energy Frontier Research Centers are investigating molecular-level controls of subsurface reactivity relevant to geologic carbon sequestration and solid-fluid interfaces. LCLS-II-HE capabilities will allow detailed mechanistic and kinetic studies of geochemical reactions on the timescales of bond making and breaking and electron transfer. Such studies will revolutionize our understanding of the mechanisms by which chemical contaminants such as heavy metals, radionuclides, and natural organic matter interact in complex aqueous-solid-gas systems, as described below.

Soils, sediments, and microorganisms are bathed in water or coated with water films. Water is required for microbial metabolism, solute transport, and a vast array of geochemical reactions. Consequently, studies of geochemical processes require techniques that can penetrate water. Because of their penetrating
power and ability to access molecular length scales, hard X-rays are the technique of choice for geochemical and environmental studies. Earth materials, including microbial-mineral assemblages, are chemically and physically heterogeneous at length scales down to nanometers. Nanoparticles are abundant as grain coatings and colloids and are often highly reactive. Model systems that will be employed to study dynamics in these systems must reflect this chemical and physical heterogeneity, and many must be wet. Ultrafast X-ray scattering and spectroscopy methods that can operate under dilute, heterogeneous aqueous conditions are required.

Figure 4.2.15. 3D reconstruction of pore space (yellow), organic matter (purple), and calcite and quartz (grey) in shale, Opalinus clay (from reference reproduced from reference).

Within the complex architecture of natural porous media, metals such as Cr, Mn, Fe, and Ti serve as important micronutrients for microbial and plant communities, redox controls, and mineral-forming constituents. Metals and metalloids, including Cr, Co, Cu, Zn, Se, As, Hg, and Pb, may be present as environmental contaminants. The activity of metals in geochemical settings is controlled largely by reactions occurring in aqueous solution and at mineral-water and microbe-water interfaces. In spite of the broad importance of metals and metalloids in the subsurface, ultrafast studies of such geochemical reactions are almost completely lacking.

At hard X-ray energies, XAS and XES offer the ability to penetrate water and, moreover, provide element specificity and high sensitivity (e.g., accessing μM solution concentrations). EXAFS provides quantitative information on local molecular structure, whereas XANES, XES and RIXS enable direct observation of core-to-LUMO/HOMO transitions, which are highly sensitive to chemical bonding. These methods, coupled with LCLS-II-HE capabilities, thus provide the capability to simultaneously follow the evolution of electronic and physical structure under environmentally-relevant conditions (e.g. dilute aqueous reactants, nanostructured samples) at sub-picosecond timescales.

**Interfacial geochemical dynamics: sorption, desorption, and redox**

Surface-mediated, mineral-aqueous solution interface reactions, in which ions are released from solid surfaces into solution via desorption or during chemical weathering reactions, or are removed from solution via sorption reactions, profoundly impact the compositions of natural waters, including oceans, lakes, groundwater, and subsurface brines. Mineral-water interfaces, particularly on iron and manganese oxides and iron sulfides, also strongly catalyze redox reactions that are slow or unmeasurable in aqueous solution. Chemical reactions at solid-liquid interfaces include acid-base (hydrolysis) and surface complexation or adsorption reactions, ligand exchange and electron or ion transfer reactions, dissolution of solids, as well as nucleation and growth of solids in water. The complexity of chemistry at the liquid-solid interface, as visualized in Figure 4.2.16, involves absorption/desorption, diffusion, solvation/desolvation, and the interaction between solvated and adsorbed species with the dynamical surface geometric and electronic structure.
Relevant processes span a wide range of timescales, from the slow exchange of water molecules for aqueous ions (about one day), to ligand exchange reactions of ions (~100 ps), to electron-transfer processes (femtoseconds). It is important to address: (i) How the presence, abundance, and types of surface defect sites affects ultrafast mechanisms and rates of metal ion sorption, desorption, and redox processes, (ii) How nanoparticle or nanopore diameter affect mechanisms and rates of these same reactions, and (iii) How electrons are transferred between the bulk and surface species during redox reactions. In order to answer these questions, it will be necessary to comprehensively follow the reaction (bond formation, loss) under in situ conditions at interfaces, including loss of waters of solvation, precursor states, bond activation, formation of initial adsorption complexes, and their electronic and physical evolution.

The significance of these issues is illustrated by the problem of interfacial desorption/sorption of $\text{Zn}^{2+}$ on iron oxide surfaces. Zinc is an important and widespread environmental contaminant that adsorbs strongly and reversibly to iron oxide nanoparticles (FeOOH), depending on pH and aqueous conditions. LCLS-II-HE capabilities provide a means to directly probe the ultrafast dynamics of the $\text{Zn}^{2+}$ desorption processes and characterize the associated stepwise structural and electronic changes.

FeOOH nanoparticles with adsorbed $\text{Zn}^{2+}$ (in an aqueous suspension delivered by a liquid jet) can be transiently heated via THz excitation to trigger desorption of the $\text{Zn}^{2+}$ in the electronic ground state. Transition state complexes (physical and electronic structure) and their lifetimes can be characterized via time-resolved XANES and XES to capture the breaking of $\text{Zn}^{2+}$-surface oxygen bonds and the formation of inner-sphere solvation shells around $\text{Zn}^{2+}$. Time-resolved EXAFS will detect changes in Zn-Fe and Zn-O pair correlations. The Zn$^{2+}$ first coordination shell exhibits both tetrahedral and octahedral geometries that are relatively easy to resolve in XAS spectra and are stabilized by changes in the local bonding environment, providing additional ways to probe surface dynamics.

Since such studies require low sorption densities of Zn$^{2+}$, a high average flux of tunable X-rays (in the Zn K-edge region, ~9.7 keV) will be essential to extract small differential signals. Comprehensive studies as a function of particle size, pH, ionic strength, and complexing ligands will transform our understanding of adsorption-desorption processes and the interplay between adsorbate chemistry and surface structure.

**Aqueous-phase geochemical dynamics: redox, rates, and isotope fractionation**

Complexation and redox reactions occurring in aqueous solutions control the transport of contaminants, the bioavailability of nutrients required for primary productivity, and ecosystem resilience to climate change. Moreover, aqueous systems provide valuable models to help understand more complicated
interfacial reactions. Our ability to understand the dynamics of aqueous-phase metal reactions rests on insights gained from observing stepwise component processes at shorter time and length scales. The binding of common geochemical complexing ligands, such as bicarbonate, silicate, or acetate anions or more complex dissolved organic matter, alters access of the reductants and other reactive species to metal centers and thus modifies the pathway and rates of reaction. We need to consider: (i) The molecular structures (physical and electronic) and compositions of intermediates of reactions involving aqueous metal ions, particularly in multi-electron redox transformations, (ii) The structures and compositions of the transition state complexes, and (iii) The lifetimes of intermediates and transition states.

Redox control over the environmental behavior of the common contaminant Cr, which is slightly soluble in its reduced form, Cr(III), but is highly soluble, mobile, and carcinogenic when present as Cr(VI), provides an important example. Mass-dependent fractionation of Cr isotopes arising from redox transitions are of intense interest for their ability to indicate chromium reduction in the subsurface due to remediation of contaminated sites or natural attenuation by native reductants. Crucially, these signatures depend upon the specific structural and electronic transitions involved in the overall reaction, because the rate-determining step (e.g., either electron transfer between or the change in coordination from tetrahedral Cr(VI) and Cr(V) to octahedrally coordinated Cr(IV)) determines the magnitude of the intrinsic fractionation.

![Figure 4.2.18. Chromium XANES and local structures.](image)

We envision a series of LCLS-II-HE experiments that will significantly advance our understanding of this problem. The goal is to understand the pico- and sub-picosecond physical/electronic structures and lifetimes of transition states in the Cr(III) ↔ Cr(VI) redox transition. Chromium is well suited to this study because XANES spectra (at the Cr K-edge, 5.99 keV) are rich in absorption features, providing high contrast between different oxidation states and electronic structures (Figure 4.2.18). Since aqueous chromium can be photo-oxidized or photo-reduced by visible light, visible laser pulses can be used to initiate oxidation state changes in aqueous liquid jets containing either Cr(III) or Cr(VI) over a range of relevant concentrations. Time-resolved XAS and XES measurements at LCLS-II HE will be used to characterize the transition state complexes and their lifetimes. We anticipate that, after the initial electron transfer reaction, Cr oxidation states may return to the original oxidation state, which would enable studies of the reverse reaction. Knowledge gained from such studies will significantly advance our understanding of chemical controls over isotope fraction factors and, in turn, the evolution of Earth’s environments, past and present.

References

4.4 Materials Heterogeneity, Fluctuations and Dynamics

Ultrafast, atomic-scale, dynamical motions underlie the energy efficiency and performance of functional materials and devices. There exists untapped potential to enhance materials performance and create new functionality through a much deeper insight into the atomic-scale dynamics of materials. To date, ultrafast X-ray studies of materials have focused largely on discovery-oriented science, employing time-resolution to disentangle the coupled degrees of freedom in strongly correlated materials or to capture snapshots of material transformations. LCLS-II-HE will enable sensitive real-time in situ probes of atomic-scale structure that will advance this field from demonstration experiments in model systems, to measurements that address applications-oriented materials challenges. This novel class of measurements will lead to new understanding of materials, and ultimately device performance, and will couple directly to both theory efforts and next generation materials design initiatives.

4.4.1 Charge migration at the atomic scale in complex materials for energy storage and conversion

Detailed knowledge of atomic and ionic diffusion is fundamental for the functionality, synthesis, and stability of a wide range of materials. In particular, diffusion of electroactive ions in complex electrode materials is central to the function of many technological devices for energy transformation and storage including fuel cells, batteries, and membranes used for desalination and separations. The diffusion dynamics of the ions through the crystal lattice of an electrode material (e.g. Li⁺, Na⁺, or multivalent ions in a battery) have a tremendous impact on the energy storage capacity, rate capability, and material lifetime. Slow diffusion is believed to be a factor limiting charge and discharge rates in many electrode materials, and can, for example, limit fast charging in electric vehicles.

While much is known from first-principles modeling and simulation about how ions diffuse through a lattice ¹,², little is known experimentally about the atomic-scale processes involved in ion diffusion. On fundamental length and time scales, individual ion-hopping events between adjacent interstitial sites may approach ~100 fs timescales. These events or hops are associated with significant transient changes in the crystal strain field ³, which in turn can influence the dynamics of neighboring ions at high concentrations (see Figure 4.4.1). Such statistical ultrafast local events ultimately link to longer-range dynamics spanning
many decades, since the slower coupled diffusional motions occur as a result of many local hops. Our ability to characterize such phenomena over the length and time scales required for comparison with theory is substantially limited by available experimental tools. This has restricted our ability to develop validated design guidelines to improve ion diffusion in functional materials.

The capabilities of LCLS-II-HE will enable much more detailed insight into ion and atom migration in complex materials under operating conditions. Dynamic scattering with coherent X-rays (XPCS) has already been shown to be a powerful probe of atomic diffusion, but it is limited to relatively slow timescales (typically ms and longer) by present X-ray sources. Advanced XPCS techniques with a high-repetition-rate hard X-ray laser (as outlined in Section 3.3) will enable operando studies of the local aspects of ion diffusion at a high spatial resolution due to the higher photon energy of LCLS-II-HE. Systematic studies will reveal how these processes depend on electrode nanostructure, material crystal structure, diffusion direction, and ion concentration (state of charge).

Figure 4.4.2. (a) Ab-initio simulated structure of Li$^{1+}$ intercalated into V$_2$O$_5$, and possible jump vectors along the crystallographic a- and c-directions. Note that these likely have a vastly different jump probability. (b) and (c) Calculated diffuse scattering from the obtained structures for 0, 1 and 2 Li$^{1+}$ (Mg$^{2+}$) ions intercalated into V$_2$O$_5$ along the $q_x$ direction, showing diffuse scattering due to occupational disorder. The blue arrows indicate the half-order peaks originating in partial ion occupancy. Notice the increased intensity in the case of Mg$^{2+}$ due to the larger scattering cross-section. Similar changes appear for Li$^+$ but are difficult to distinguish on the logarithmic scale.

Coherent X-ray scattering from the electrode material will directly probe transient distortions of the lattice and longer-range strain fields that arise from stochastic ion-hopping events (as illustrated in Figure 4.4.1) on relevant timescales, from <1 ps to ms, that are presently inaccessible. With LCLS-II-HE, an initial speckle pattern can be obtained from the electrode at t=0. This is followed by speckle patterns at time-delays from <100 fs up to milliseconds using the two-pulse, programmable XPCS mode on LCLS-II-HE. The ion dynamics are encoded in the time-dependent auto-correlation function of the scattering intensity, $g_2(q, t)$, which is directly related to the dynamic structure factor, $S(q,t)$. The auto-correlation function and dynamic structure factor can be analyzed by Fourier transformation or referenced to theory and modeling.

For time scales of the hops (<1 ps), this approach can determine the local distortion during the hop, which can be compared with the hop trajectory expected from theory. As an illustration, Figure 4.4.2 shows ab initio model calculations of the diffuse scattering from Li$^{1+}$ and Mg$^{2+}$ intercalated into V$_2$O$_5$. Note that
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even on a log scale, there are large changes in scattering near the half-order partial occupancy “peak” (indicated by the blue arrows), resulting from partial Mg$^{2+}$ occupancy. Changes are smaller, but still measurable for the Li$^{1+}$. Thus, we expect measurable changes even for single to few ion hops.

The LCLS-II-HE brings two advantages. Most significant is that the higher X-ray energy provides accesses to speckle data at much higher scattering momenta $q$, with consequence that the atomic motions during hops can be obtained with finer spatial resolution. The practical highest $q$ for soft X-rays from LCLS-II is small, and this dramatically limits the measurable spatial resolution. Second, higher photon energies are more able to penetrate the environments relevant to energy storage applications.

This example of ion diffusion in V$_2$O$_5$ electrodes is archetypal, and the approach can be applied to diffusion dynamics of many other types of ions or atoms in condensed matter. For example, similar studies will be relevant to diffusion of oxygen anions in solid-oxide fuel cells, membranes for chemical separations (e.g. desalination, CO$_2$ sequestration), and environmental chemistry. In addition, related XPCS studies could be used to probe the dynamics of small polarons, as shown in Figure 4.4.3. These charge localizations are associated with subtle lattice distortions, and inhibit the flow of charge in complex oxides cathode materials$^6$.

**Figure 4.4.3.** Crystal structure of V$_2$O$_5$ with typical conduction electron distribution (left), and localized electron density (polaron) associated with a subtle local distortion in the crystal structure (right)$^6$.

(credit Yufeng Liang, LBNL)

### 4.4.2 Nanoscale non-equilibrium phonon dynamics & thermal transport

Understanding heat flow at nanoscale dimensions, in heterogeneous systems, and across interfaces is a fundamental problem that has the potential to provide technological solutions to our energy needs by enabling new technologies to manipulate the flow of energy. There are two well-understood limits of this problem: a macroscopic, continuum description governed by the diffusion equation, and an atomic-level description based on classical physics or quantum mechanics (e.g. classical or ab-initio molecular dynamics). However, the intermediate regime between diffusive and ballistic transport is almost completely unexplored. This intermediate regime is particularly relevant in nanostructures and heterogeneous systems, where the characteristic dimensions are comparable to the phonon mean free paths, thereby opening new approaches to nanoscale control of thermal transport.
A similar scientific challenge arises in understanding energy transport in 2D materials in the monolayer and multilayer limit, where the out-of-plane dimension is comparable to phonon wavelengths and mean free paths. An understanding of the interfacial thermal conductivity associated with a monolayer on substrate, or the ability to measure directly the cross-plane thermal conductivity in a multilayer is a requirement, for example, for the implementation of quasi-2D materials as phase-change materials within a working device. Clearly, a fundamental description of phonon transport in this crossover regime is needed for the targeted design of nanostructured materials, functional hierarchical structures, and two-dimensional heterostructures. However, this requires transformative new methods for imaging phonon propagation with microscopic (wavevector) resolution and femtosecond to nanosecond timescales. Novel XFEL sources and experiments will play a central role in the development of these technologies.

X-ray diffraction techniques at high-repetition rate open up a new window into these processes at buried interfaces by directly resolving in real time the transfer of energy within a complex heterostructure. Furthermore, new XFEL-based techniques such as Fourier-Transform Inelastic X-ray Scattering (FT-IXS) have sensitivity to the phonon wavevector across the Brillouin zone, and thus give access to the dynamics of the heat-carrying, short-wavelength phonons that have THz frequencies on ultrafast timescales. This approach is illustrated in Figure 4.4.4, which presents LCLS measurements of nonequilibrium phonon dispersion in bulk Ge.

Since the structural changes associated with phonon transport across buried interfaces are subtle, FT-IXS measurements of interface conductance are extremely challenging with existing XFEL sources. Similarly, differential X-ray scattering signals from nanostructured materials – such as those designed for manipulating thermal transport, as illustrated in Figure 4.4.5 – are extremely weak. While LCLS provides the necessary hard-X-ray photons for FT-IXS methods, these methods are limited primarily by average brightness which determines the achievable signal-to-noise ratio. Thus, the low repetition-rate and large intensity-fluctuations of LCLS restrict experiments to bulk samples and ideal model systems. Although LCLS-II will provide more stable pulses at high repetition-rate, the low photon energy (< 5 keV) limits the accessible regions of reciprocal space and prevents the study of buried structures.

The high repetition rate of the LCLS-II-HE will not only increase the data quality by orders of magnitude compared with that of LCLS but will allow in situ studies of functional materials under technologically relevant device conditions. Weakly scattering nanostructures and subtle effects from interfaces that are
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beyond the current capabilities will be open to study with LCLS-II-HE. For example, the time-domain application of techniques like coherent Bragg rod analysis (COBRA)\textsuperscript{11} can directly measure and reconstruct the time-dependent electron density distribution within a monolayer or few-layer sample. Pair-distribution-function (PDF) approaches can extract time-dependent pair correlation functions\textsuperscript{12}. The high-stability and extension of the fundamental energy of LCLS-II-HE to beyond 20 keV (in addition to the extremely high energy of the third harmonic) make these methods feasible for the first time. Furthermore, many technologically relevant materials are structurally heterogeneous at the nanoscale, requiring imaging techniques with nanoscale resolution, or complementary $q$-space techniques such as XPCS or FT-IXS (see Section 3.3). These studies require hard X-ray pulses to access large momentum transfer, moderate peak power to avoid single-pulse damage, and high repetition rate to probe weakly scattering nanostructures and 2D layers.

4.4.3 Electron-lattice interaction and material functionality

In many technologically relevant materials, electron-lattice interactions determine material functionality and performance under operational conditions. For example, electron-lattice coupling in organic photovoltaics leads to polaronic distortions which fundamentally determine charge mobility; in other cases, the material operates near or across a phase boundary, as in phase-change materials. In thermoelectric applications, the desirable properties (e.g. low thermal conductivity) depend on the interactions between valence electrons and the lattice which give rise to highly anomalous phonon modes. Pump-probe experiments can be used to decouple the electron-lattice dynamics. Here we show two examples of currently challenging experiments that are enabled by LCLS-II-HE.

**Electron-phonon coupling in 2D transition metal dichalcogenides**

Two-dimensional (2D) transition metal dichalcogenides and related materials have attracted great interest in recent years because of their novel electronic, optical, and mechanical properties. These include the emergence of a direct band gap; strong light-matter, electron-electron and electron-phonon interactions; enhanced catalytic activity; unique semiconducting and metallic structural phases; and the ability to
by stacking 2D layers as heterostructures, novel hybrid materials with unique functionalities can be synthesized, making use of the weak interlayer van der Waals bonding. This weak coupling in turn creates novel opportunities for manipulating their structural and optoelectronic properties with external fields or perturbations. Sensitive atomic-scale, time-resolved, in situ probes are required to resolve these changes.

For example, small temperature changes in these multilayer structures have been shown to drive a transition from an indirect to a direct band gap, and this is associated with changes in the interlayer coupling. Under photoexcitation, ultrafast optical studies in layered $\text{T}-\text{TaS}_2$ have revealed a hidden quantum phase. Recent preliminary work at SSRL (using hard X-ray scattering at 100 ps resolution and MHz repetition rate) has shown that light can be used to modulate and control the interlayer bonding in the prototypical transition metal dichalcogenide MoS$_2$ (Figure 4.4.6), giving rise to a surprising compressive strain at the $10^{-6}$ level, which is measurable only as a result of the MHz X-ray repetition rate. This effect can be thought of as a modulation of the van der Waals / Casimir interaction between layers, driven by electronic excitation. It opens up novel possibilities for manipulation of the functional properties of 2D materials on ultrafast timescales at high bandwidths. These measurements require high-repetition-rate probes in order to resolve these near-equilibrium responses.

![Figure 4.4.6. Interlayer light-driven dynamic compressive strain in few-layer MoS$_2$ from MHz X-ray diffraction of (0,0,16) reflection with 100 ps synchrotron pulses. Present time resolution is inadequate to resolve the underlying dynamics. Inset: Illustration of dynamical response of a monolayer transition metal dichalcogenide driven by optical excitation (A.M. Lindenberg – unpublished).](image)

Similar opportunities exist for probing exciton-phonon interactions in the quasi-2D limit. Prior studies have indicated the important role of exciton-lattice interactions in the monolayer limit, but direct probes of the atomic-scale vibrational response following optical creation of an exciton are not possible using current XFEL sources. Direct measurements of the lattice response, in parallel with existing techniques for probing the electronic response, will open a new window into the coupled electronic-structural degrees of freedom in 2D materials, which determine their functional properties. This will provide a comprehensive understanding of the flow of electronic and vibrational excitation across an interface between two van-der-Waals layers as a function of the relative crystallographic orientation of the layers. In particular, for a homo-interface between two of the same materials, misorientation from crystallographic registry provides a new approach to modifying thermal and electrical interfacial transport and a potential route to improved performance of thermoelectric materials.

The above experiments require structural probes sensitive to both the in-plane and out-of-plane unit cell dynamics. Access to high momentum transfer (provided by hard X-rays) is required to reconstruct the unit
cell dynamics and local strain fields. High repetition rates enable measurements of the small local lattice displacements associated with these materials under technologically relevant device conditions.

**Electron-phonon coupling in hybrid perovskites**

Lead-halide hybrid perovskites have emerged as disruptive materials for photovoltaics, with power conversion efficiencies now exceeding 20% – comparable to polycrystalline silicon \(^{23}\). In the prototypical methylammonium lead-halide (CH\(_3\)NH\(_3\)PbX\(_3\), X=I, Br, Cl), charge carriers in polycrystalline films show remarkably long lifetimes (>1 μs) with correspondingly long diffusion lengths, which are essential for efficient extraction of charge in a photovoltaic device. The fundamental mechanisms for these remarkable properties are not understood.

Recent studies have suggested that ultrafast structural dynamics following absorption of a photon underlie these efficiencies. For example, experiments have pointed towards the importance of coupled electronic and structural polaronic distortions in protecting charges from seeing the intrinsic defects in these materials \(^9\). These effects are connected, in turn, to proposals that the hybrid organic-inorganic structure of these materials leads to greater structural deformability, giant photostriction responses, and strong light-matter coupling \(^{24, 25}\).

Theoretical studies have pointed toward the role of dynamic structural fluctuations and coupling to electronic structure as a potential explanation for the long carrier lifetimes and slow recombination rates exhibited by these materials even in the presence of significant defects \(^{26, 27}\). Thus, there appears to exist an important connection between electronic and structural processes at early time-scales after photoexcitation – atomic-scale processes that determine the efficiency of a photovoltaic device.

Direct experimental probes of the coupled optical and structural response that likely underlie these functional properties are not available from present sources, but will be possible with the capabilities of LCLS-II-HE. The organic groups within these hybrid materials lead to fragility, making pump-probe experiments at high excitation density (as typically required for measurements with LCLS at 120 Hz) difficult to perform without perturbing the material structure. Experiments therefore need to be carried out under weak excitation conditions, corresponding to small-amplitude lattice distortions. Under conditions where the peak power of LCLS leads to damage, the high repetition rate of LCLS-II-HE would enable measurements of small-amplitude, weakly perturbative, local strain fields. These measurements require
access to high momentum transfer to enable PDF analysis and extraction of the dynamic atomic correlations that are potentially modulated through absorption of a photon.

In preliminary measurements, we have used femtosecond electron scattering to probe dynamics in methylammonium lead iodide at sufficiently high momentum transfer ($q$) to allow for extraction of a time-dependent pair correlation function, shown in Figure 4.4.7. This shows, surprisingly, that changes occur predominantly in the iodine-iodine correlation peak (whereas minimal changes occur in the lead-iodide correlation peak), corresponding to a light-induced sublattice disordering of the iodine octahedra. These measurements suggest that bonding between the organic group and the iodine octahedra play an important role in charge transport. Thus, the first steps following creation of an electron-hole pair may be influenced by both the intrinsic structural fluctuations and by light-induced enhancement of these fluctuations. These results illustrate the power of carrying out measurements at high enough momentum transfer to probe time-dependent pair correlation functions, as enabled by LCLS-II-HE (exploiting the projected fundamental energy range beyond 20 keV, or the third harmonic at higher energies). In contrast, the $q$-resolution that is achievable via ultrafast electron scattering at high electron energies is inadequate to support a careful reconstruction of the pair distribution function.

We note that in addition to the prototypical 3D hybrid perovskites, there exists a class of 2D hybrid perovskites analogous to the transition metal dichalcogenide materials discussed above. These quantum-well-like structures exhibit a host of unique opto-electronic responses, including, for example, broadband photoluminescence spanning the entire visible spectral range. It is thought that charge localization and the development of large structural distortions around a self-trapped exciton give rise to these properties, but the mechanisms are not well understood. Here, in addition to X-ray scattering, X-ray spectroscopy methods with elemental specificity will provide complementary insight into the local polaronic distortions and charge localization that may underlie these properties.

**Electron-phonon coupling and anharmonicity in thermoelectric materials**

PbTe is an example of a broad class of thermoelectric materials where the low thermal conductivity results from a balanced interplay between electron-phonon coupling and anharmonicity. PbTe, in particular, exhibits incipient ferroelectric behavior (a tendency towards ferroelectric ordering but without macroscopic order) and it is believed that the associated mode softening of the transverse optical (TO) branch accounts for the low lattice conductivity in PbTe. Research to date has concentrated on the role of lattice anharmonicity and phonon-phonon interactions. On the other hand, a few theoretical studies have focused on the importance of electron-phonon coupling as a link between the mixed ionic-covalent character of Pb–Te bonds and the soft mode behavior.

Figure 4.4.8. Left: FT-IXS spectrum of the phonon dispersion in photoexcited PbTe. Right: calculations showing that photo-excitation stiffens the TO branch at $q=0$, and pushes the system away from ferroelectricity. The experimental observation of combination modes $TO\pm TA$ (left) is a signature of this effect and can be used to identify how photo-excitation changes the interatomic forces.
A recent LCLS experiment\(^{10}\) showed that electron-phonon coupling rather than phonon-phonon interactions (anharmonicity) leads to ferroelectric tendencies in PbTe. Furthermore, with the help of first principles simulations, the relevant electronic states that couple to the ferroelectric soft mode were identified. This experiment used FT-IXS\(^{7}\) to probe the non-equilibrium phonon dispersion upon photoexcitation. The observed spectrum of phonons (obtained from a Fourier transform of the oscillatory components) contained combinations of TO±TA frequencies, and these are signatures of how the bonding forces in the photoexcited state differ from the bonding forces of the ground state (see Figure 4.4.8), resulting in eigenmodes that are linear combinations of the ground states TO and TA\(^{10}\).

Since the experiment directly measures the mixing of the eigenvectors, ideally one could extract from these data how and which of the elements of the dynamical matrix change upon photoexcitation. Unfortunately, this is out of reach for current XFEL sources; the LCLS data\(^{10}\) were limited to high signal-to-noise regions of reciprocal space, and samples were limited by the absorbed pulse energy rather than the average power. The high repetition rate and high stability of LCLS-II-HE will provide a transformative opportunity to reveal the fine details of how the valence electrons affect the interatomic forces by probing the phonon spectrum out of equilibrium.

References

4.6 Matter in Extreme Environments

In the field of high-energy-density physics and high-power high-intensity laser-matter interactions, LCLS-II-HE will enable new experiments with high impact. The most important scientific questions are related to the physical and structural properties of extreme states of matter that can be produced only in dynamic experiments lasting a billionth of a second, and in very small quantities. The combination of high repetition rates and hard X-rays from LCLS-II-HE will generate high-resolution spectroscopic and structural information of matter in extreme states that has previously been inaccessible. Although most of these studies are discovery-class science, measurements in the areas of extreme materials will be important for applications related to fusion and fission materials and will lead to important insights into planetary physics and geoscience. Here, high peak brightness combined with high repetition rates and high X-ray energies are required to:

- Penetrate through dynamically heated dense targets and diamond anvil cells (DACs).
- Generate high signal-to-noise data above the self-emission bremsstrahlung background.
- Probe atomic scale lengths at large wavenumbers that reveal structure and material phases.

These studies will further require the coupling of LCLS-II-HE with optical pump lasers. High-repetition-rate lasers with mJ pulse energies that match the repetition rate of the X-ray beam exist for dynamic pump-probe measurements. In addition, LCLS-II-HE will enable experiments that employ X-ray pump and X-ray probe techniques using two-color operation or multiple X-ray pulses with advanced detectors. Use of LCLS-II-HE and the experimental requirements are consistent with:

- Data that exist from LCLS or synchrotron sources that demonstrate that LCLS-II-HE provides sufficient photon flux to achieve the scientific goals.
- Novel target technologies that have been developed and are suitable for producing matter in extreme conditions compatible with high repetition rates.

New developments in target technology include cryogenic jets, gas jets, and dynamic DACs to access dense cryogenic hydrogen, light and heavy liquids including water, and high-Z matter including tungsten or composite steels used in extreme radiation environments. It is especially important to accurately measure the equation of state (EOS), which requires precision data on compression and material phase transitions for which X-ray diffraction enabled by XFELs is the method of choice. These techniques are also suitable for characterizing stacking faults or discovering entirely new materials and material phases. Important examples include metallic phases of hydrogen, high-pressure electride states, nano-diamonds and harder diamonds (lonsdaleites).

Besides the discovery and characterization of the material structural properties, LCLS-II-HE will further enable measurements of the physical properties including strength, optical, and transport properties. Inelastic X-ray scattering techniques and angularly resolved X-ray scattering are the techniques of choice and have been demonstrated to provide information about conductivity, electron temperature, density, and the ionization state. Accurate data of super-ionic phases and the conductivity of warm dense matter are especially important for hydrodynamic modeling of fusion plasmas, laboratory astrophysics experiments, and intense laboratory radiation sources.
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4.6.1 Structure and equation of state of matter at megabar pressures

Dense hydrogen

Hydrogen is the simplest and most abundant of all the elements, and yet its behavior at high density is extremely complicated and still not well understood. It has long been theorized that under sufficient compression the hydrogen molecule will dissociate, resulting in an atomic form. This atomic form has been predicted to have a liquid ground state with exotic properties such as superconductivity and superfluidity.

Hydrogen also exhibits several other unusual behaviors at high density, such as an extremely pronounced temperature minimum in the melting point of the molecular solid above 250 GPa. This minimum is also a feature of the alkali metals such as lithium, and, as is the case in the alkali metals, is accompanied by the emergence of several complex solid phases near the minimum.

There is also a proposed liquid-liquid insulator-metal transition (LL-IMT) in hot liquid hydrogen, attributed to the transformation from a molecular to an atomic liquid. The exact condition under which this transition occurs is disputed both in theory and experiment.

There is very little structural information available on hydrogen, and none outside the three hexagonal close-packed-like phases I, II and III. This is due to the very low X-ray scattering intensity of hydrogen, such that even with the best modern synchrotrons it is very difficult to obtain an acceptable signal. The high brightness of LCLS-II-HE will open the way to many novel experiments for revealing the nature of dense hydrogen, in addition to other low-Z materials such as deuterium, lithium, lithium hydride, and helium. Here, a laser-pulsed DAC will be invaluable for probing this element at elevated temperature.

The fundamental understanding of hydrogen is also important for applications. Examples include planetary physics and inertial confinement fusion. Peculiar liquid-liquid and metallic transformations might occur inside giant gas planets like Jupiter, whose interior is comprised largely of liquid hydrogen. At high pressure and temperature, this material switches from its normal electrically insulating state into a conducting (metallic) phase. Experiments will need to rapidly heat a compressed sample of liquid deuterium and use LCLS-II-HE X-rays to probe the subsequent structural changes.

Figure 4.6.1. An artist’s conception shows the Juno spacecraft arrival at Jupiter. LCLS-II-HE experiments on the structure of dense hydrogen will accurately determine the equation of state, the material phases, and phase transition regions. The data are expected to characterize the much-contested metallic state and help determine if Jupiter has a solid core. The latter question is important for our understanding of the evolution of the planetary system.

The dense hydrogen properties of Jupiter play an important role in determining the evolution of our planetary system. The goal of the Juno mission (the Juno spacecraft arrived at Jupiter in July 2016) is to perform precision measurements of the magnetic field and the interior mass distribution of Jupiter. An
accurate EOS will then be needed to make estimates of Jupiter’s core. A solid core would indicate that a rocky planet swept up the initial hydrogen in our planetary system. On the other hand, a non-rocky core would indicate that the giant gas planets were formed due to gravitational instabilities.

The phase diagram of dense hydrogen shows that there is wide disagreement about the conditions under which dense liquid hydrogen will dissociate in the LL-IMT. Both experiment and theory indicate different conditions. Furthermore, there is complete lack of structural data on phase IV and any higher phases, and only very limited data on phase III. The existence of phase I is suggested by changes in the behavior of the vibron in phase I above 200 GPa, but structural data is needed to understand this phase.

LCLS-II-HE will enable the structural investigation of the dense hydrogen phase diagram. The high peak brightness combined with high photon flux will allow data collection from small hydrogen samples. Tight focusing is particularly important, as the DAC gasket in the cell is made from rhenium which scatters over 5600 times more intensely than hydrogen. It is therefore vital that the X-rays be well-focused on the sample and not impinge on the gasket. Smaller samples allow access to higher pressure and high temperature, where gasket stability and containment are more difficult.

It should be noted that due to absorption in the diamond anvils and the limited observable range of scattering angles, 20, (due to the aperture of the cell) hard X-rays above 10 keV are required for DAC studies.

The new LCLS-II-HE capabilities will allow probing of hydrogen at and above room temperature at pressures up to 200 GPa. This covers a region where a change in the sign and magnitude of $\partial \nu / \partial P$, the rate of change of vibron frequency with pressure, is observed in the solid phase I \(^4\), and where at high temperature the LL-IMT may be observed \(^7\). It is also important to pursue the first-ever diffraction data on hydrogen phase IV above 220 GPa at room temperature. Phase IV is predicted to have an unusual layered structure which appears to be a prelude to metallization \(^{15-17}\). Such data is much needed to confirm or disprove theoretical models of this phase.
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The pulsed nature of LCLS-II-HE is also useful for high-temperature experiments in which the containment of hydrogen and integrity of the diamond anvils are both problematic. By using pulsed laser heating, the sample can be briefly brought to high temperature to coincide with the X-ray pulses from LCLS-II-HE, thus allowing measurement of hydrogen at high $P-T$ conditions without losing the sample from diffusion or containment failure. Such pulsed laser heating of DACs has been described elsewhere, including for use with hydrogen $^{11, 18, 19}$.

Figure 4.6.3. DAC setup with diamond anvils (white), rhenium gasket (dark grey), hydrogen-proof diamond protection (yellow), and loaded with a hydrogen sample (blue). Before loading, an annular thin metal foil (light grey) is placed in the sample chamber suspended on ruby spheres (dark red) which allow measurement of pressure. A pulsed laser (pale red) is focused onto the coupler to isochorically heat the sample. Hydrogen in the central section of the ring is heated from all sides while the hole allows the X-ray pulse (black arrow) to pass through hot dense hydrogen without diffraction from the coupler.

To date, no direct measurement has been made on hydrogen over the LL-IMT. Rather, studies have used VISAR $^8$ or the temperature of a laser coupler $^7, 11$. A direct measure would be an important advancement in hydrogen physics and could reveal more of the nature of this transition, which would settle the many disagreements in experiment and theory. A cross section schematic of a diamond anvil cell suited to this experiment is shown in Figure 4.6.3.

**Liquid jets**

Cryogenic liquid jet targets are a new source that is now becoming available for high-repetition rate experiments that require high photon flux and integrate over many pulses. In particular, hydrogen micro-jets have recently been shown to provide excellent targets to study extreme material states. In addition to hydrogen jets, deuterium, methane, neon and argon jets have recently become available. These jets offer great opportunities for X-ray pump and X-ray or optical probe studies of isochorically-heated matter (see Figure 4.6.4).

Moreover, these jets provide a new way to access non-equilibrium states. Micrometer hydrogen jets operate by shooting a stream of liquid hydrogen several micrometers in diameter into a vacuum, at which point evaporative cooling from the surface rapidly crystallizes the jet. Raman scattering studies indicate that the rapidly crystallized hydrogen includes a significant fraction of face-centered cubic (fcc) crystallites in addition to hexagonally close-packed (hcp) ones. Intriguingly, it appears that the fcc fraction that is visible in the Raman spectrum may be due to a high concentration of stacking defects in the hcp lattice. The high thermal expansion coefficient of hydrogen may also build up strain in the hcp lattice, causing similar effects.
Figure 4.6.4. A continuously flowing cryogenic hydrogen jet is shown. The jet expands into the vacuum at 100 m/s, suitable for high-repetition rate pump-probe experiments. The image shows blue emission from hydrogen that was heated by a 40 fs short-pulse laser a few millimeters under the nozzle.

X-ray extension to high-Z dense matter physics

The high flux available at LCLS-II-HE is also well suited to investigate other light elements, e.g., Li and He, and light compounds such as LiH. Lithium exhibits cold melting under pressure, much like hydrogen. It is observed to melt on isothermal compression from a close-packed fcc structure, showing a massive failing of the hard sphere model. With the increased flux of LCLS-II-HE it may be possible to obtain liquid diffraction data from lithium to see if there is a change in the liquid structure over the melting maxima – the flux of current synchrotron sources does not allow this measurement to be made. It will also be possible to explore the high-pressure and high-temperature region of the phase diagram, which is as yet unknown. The phase diagram of lithium is shown in Figure 4.6.5.

The short pulse duration of LCLS-II-HE may enable following phase transitions in real time. By using a dynamic DAC, in which a piezoelectric element is included to provide additional load on the cell, pressure can be rapidly cycled or increased at very high rates (~500GPa/s). Such devices are described elsewhere. By tuning the pressure such that a phase transition of interest is repeatedly crossed it may be possible to observe the mechanisms of pressure driven phase transitions in real time.

4.6.2 Physical properties of matter in extreme conditions

LCLS-II-HE will provide the capability to accurately probe the dynamic structure factor of warm dense matter with unprecedented precision. These studies are important to understand the intrinsic properties of radiation hydrodynamics. Accurate data on radiation transport, opacity, electrical conductivity, and thermal conductivity are all of high interest and urgently needed for modeling of matter in extreme
conditions. In recent years, density functional theory has been successfully applied to warm dense matter studies, but experiments are needed to determine the functional and to develop physics models that can be applied in this difficult regime.

**Structure factor**

The structure factor is a central quantity for calculations of particle and radiation transport coefficients. Moreover, electron-ion collisions and the ion excess pressure are directly related to the structure factor. Thus, calculations of the equation of state, spectral line-broadening and particle stopping powers depend on our knowledge of this quantity. LCLS-II-HE will further develop angularly-resolved X-ray scattering techniques that have previously been used to directly measure the structure factor in warm dense matter.

In particular, the high repetition rates will allow measurements on states of warm dense matter, such as warm dense hydrogen, that provide only small scattering signals. Figure 4.6.6 shows predictions from density functional theory for X-ray scattering measurements, comparing the signal from correlated molecules, partially dissociated hydrogen, and a metallic hydrogen state. The figure illustrates that these measurements will provide a unique signature of the material state and will allow inference of the physical properties.

![Figure 4.6.6.](image)

It is important to note that in recent years several theories have been developed to estimate structure factors for use in simulations codes. Experiments have shown that simple estimates based on Thomas-Fermi functionals are not accurate and only Kohn-Sham functionals with detailed configuration accounting provides correct estimates. However, such calculations need large computing resources and can only be performed for specific experimental data points. Consequently, accurate experimental data that test efficient theoretical approximations in this regime are needed to develop the modeling tools for warm dense matter.
Plasmon scattering

Spectrally-resolved X-ray scattering techniques have recently been demonstrated at LCLS to directly measure plasmons. This capability exists for isochorically-heated matter either using single X-ray pulses, two-color operations, or X-ray bursts. The capabilities of LCLS-II-HE will enable plasmon measurements to determine the correct functionals for density functional theory coupled to molecular dynamics (DFT-MD) simulations of warm dense matter. These studies require X-ray scattering data with sufficiently low noise to distinguish subtle differences in plasmon damping predicted for conditions that can be accessed by LCLS-II-HE. Figure 4.6.7 shows results for the conductivity of warm dense aluminum. The calculations indicate the sensitivity of plasmon damping on non-Drude dissipative processes that cannot be treated with perturbation theory. Such findings will be important for the study of strongly coupled plasmas.

![Graph showing the dynamical electrical conductivity for warm dense aluminum. The calculations use DFT-MD simulations, applying the PBE functional after Perdew, Burke, and Ernzerhof and HSE functional after Heyd, Scuseria and Ernzerhof at a temperature of $T = 0.5$ eV. The non-Drude-like behavior of aluminum for $\Delta E > 20$ eV is evident by the deviations from the Drude fits to the simulations. Testing these theories will require highly accurate measurements with high photon flux that precisely determine the plasmon spectrum and damping.]

Ion acoustic waves

Understanding the state and the evolution of planetary cores, brown dwarfs, and neutron star crusts requires accurate measurements of microscopic properties, such as viscosity and thermal conductivity, of the dense matter of which such systems are made. Due to the inherent difficulties in modeling strongly coupled plasmas, where classical long-range Coulomb forces dominate interactions between ions, current predictions of transport coefficients differ by many orders of magnitude. Here, LCLS-II-HE will deliver the photon flux to measure the ion collective modes, either electrostatic or acoustic waves, that serve as an important tool to determine transport coefficient and to validate theoretical predictions. Until recently, only electron modes (plasmons) could be measured experimentally. LCLS-II-HE will provide X-rays with small enough bandwidth to allow the investigation of the low-frequency ion modes in dense matter as well. Recent experiments at LCLS have demonstrated proof-of-principle measurements of ion-acoustic waves, but less than five spectra could be measured with current repetition rates during one beam time. A thorough investigation of the warm dense matter phase space with high repetition rates will have profound consequences for the understanding of transport coefficients in dense plasmas. In particular, a strong diffusive mode around zero frequency has been predicted allowing novel measurements of friction.
Figure 4.6.8. The sensitivity of the dynamic ion-ion structure factor to various friction parameters is shown. A value of $4 \times 10^{13} \text{s}^{-1}$ results in two pronounced ion acoustic peaks (red curve) while $10^{14} \text{s}^{-1}$ provides a central peak (dashed black dotted curve). The sensitivity of the central peak indicates that LCS-II-HE will allow us, for the first time, to determine friction in the strongly coupled plasma state.

References


