LCLS-II New Instruments Workshops Report
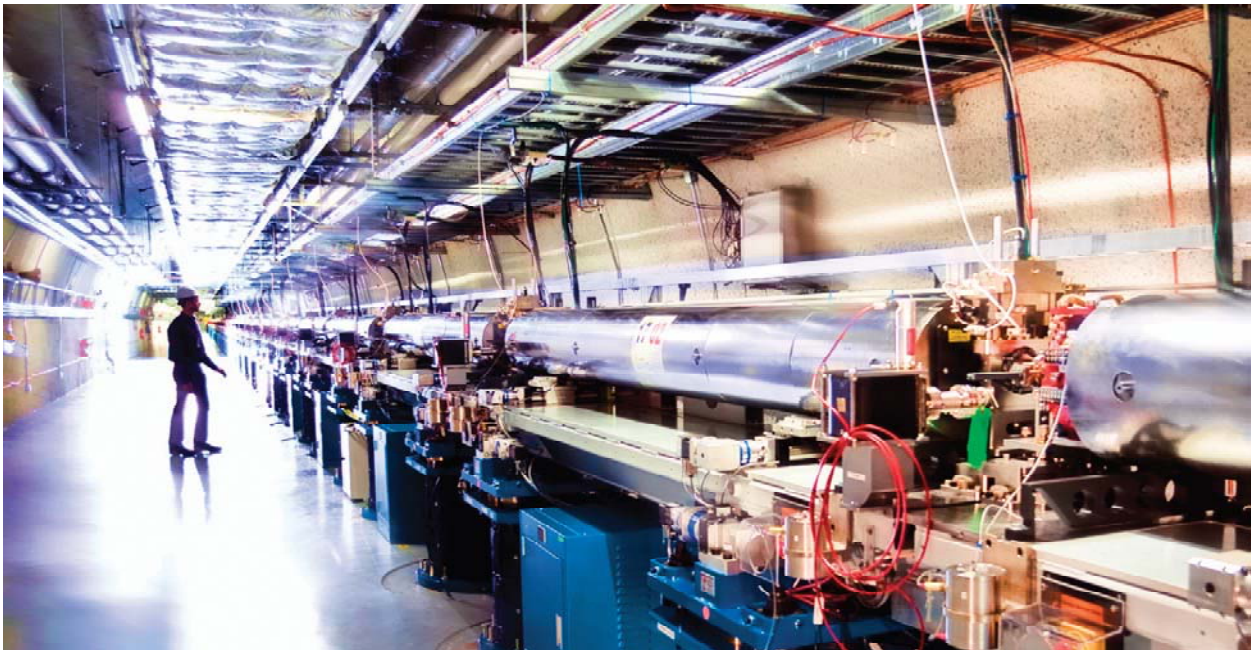
LCLS-II NEW INSTRUMENTS WORKSHOPS REPORT

SAMIRA BARADARAN
UWE BERGMANN
HERMANN DURR
KELLEY GAFFNEY
JULIA GOLDSTEIN
MARKUS GUEHR

JEROME HASTINGS
PHILIP HEIMANN
RICHARD LEE
MARVIN SEIBERT
JOACHIM STOHR

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1.0 Executive Summary

The LCLS-II New Instruments workshops chaired by Phil Heimann and Jerry Hastings were held on March 19-22, 2012 at the SLAC National Accelerator Laboratory. The goal of the workshops was to identify the most exciting science and corresponding parameters which will help define the LCLS-II instrumentation. This report gives a synopsis of the proposed investigations and an account of the workshop. Scientists from around the world have provided short descriptions of the scientific opportunities they envision at LCLS-II.

The workshops focused on four broadly defined science areas: biology, materials sciences, chemistry and atomic, molecular and optical physics (AMO). Below we summarize the identified science opportunities in the four areas.

The frontiers of structural biology lie in solving the structures of large macromolecular biological systems. Most large protein assemblies are inherently difficult to crystallize due to their numerous degrees of freedom. Serial femtosecond protein nanocrystallography, using the "diffraction-before-destruction" approach to outrun radiation damage has been very successfully pioneered at LCLS and diffraction patterns were obtained from some of the smallest protein crystals ever. The combination of femtosecond x-ray pulses of high intensity and nanosized protein crystals avoids the radiation damage encountered by conventional x-ray crystallography with focused beams and opens the door for atomic structure determinations of the previously largely inaccessible class of membrane proteins that are notoriously difficult to crystallize. The obtained structures will allow the identification of key protein functions and help in understanding the origin and control of diseases. Three dimensional coherent x-ray imaging at somewhat lower resolution may be used for larger objects such as viruses.

The chemistry research areas of primary focus are the predictive understanding of catalytic mechanisms, with particular emphasis on photo- and heterogeneous catalysis. Of particular interest is the efficient conversion of light to electrical or chemical energy, which requires understanding the non-adiabatic dynamics of electronic excited states. Ultrafast x-ray scattering presents an excellent opportunity to investigate structural dynamics of molecular systems with atomic resolution, and x-ray scattering and spectroscopy present an excellent opportunity to investigating the dynamics of the electronic charge distribution. Harnessing solar energy to generate fuels, either indirectly with photovoltaics and electrochemical catalysis or directly with photocatalysts, presents a critical technological challenge that will require the use of forefront scientific tools such as ultrafast x-rays. At the center of this technical challenge is the rational design of efficient and cost effective catalysts.

Important materials science opportunities relate to information technology applications, in particular the transport and storage of information on increasingly smaller length- and faster time-scales. Of interest are the understanding of the intrinsic size limits associated with the storage of information bits and the speed limits of information or bit processing. Key questions revolve about how electronic charges and spins of materials can be manipulated by electric and magnetic fields. This requires the exploration of speed limits subject to the fundamental conservation laws of energy and linear and angular momentum and the different coupling of polar electric and axial magnetic fields to charge and spin. Of interest are novel composite materials, including molecular systems combining multi electric and magnetic functionality. Ultrafast x-rays offer the required probing speed, can probe either the charge or spin properties through polarization control and through scattering and spectroscopy cover the entire energy-time-momentum-distance phase space.

In the field of atomic and molecular science, LCLS II promises to elucidate the fundamental interactions among electrons and between electrons and nuclei, and to explore the frontiers of light-matter interactions. The high x-ray intensities unique to LCLS II will allow for highly localized electron excitation and probing at different positions inside a molecule, thereby interrogating the fundamental electron correlations. At the ultimate intensities, a breakdown of our established model of x-ray – matter interaction is predicted, leading to possibly new regimes of plasma physics.

The identified science opportunities require the following key x-ray parameters:

- Hard and soft x-ray self-seeding has the potential to dramatically narrow the bandwidth and enhance the peak power and temporal coherence.

- Pushing the intensity limit will enhance the scattering signal in imaging of non-periodic objects and will open a new regime in non-linear atomic physics.

- For the imaging of non-periodic biological objects, the photon energy should be continuously covered from the water window at 500 eV up to 5 keV.

- The photon energy range should be extended to low photon energies for spectroscopy of carbon and nitrogen and to high photon energies for high resolution inelastic x-ray scattering and Se phasing in crystallography.

- For soft x-ray science polarization control should be provided by undulators to obtain a high degree of polarization, shot-to-shot polarization stability and energy tuning flexibility.

- Two x-ray pulses with different photon energy would allow the study of stimulated processes in analogy to two-dimensional optical, IR and NMR spectroscopies.

- Exquisite pump-probe synchronization will be required to take full advantage of the ultra-short pulses for optical pump – x-ray probe experiments.

The increase of access to sufficient beam time, i.e. capacity, has also been found to be critical in order to grow science programs to a level that will have continuing impact on their respective fields.

2.0 Synopses

2.1. AMO

The atomic, molecular and optical (AMO) science workshop included a variety of presentations geared toward better understanding of the basic physics and structure of atoms and molecules. All contributions can be sorted into one of the following three topics, presenting the forefront of AMO research at LCLS for the years to come:

1. Electron-nuclear interactions
2. Electron-electron interactions
3. High intensity interactions

All three topics make unique use of the following features of LCLS-II: short pulse duration in the femtosecond regime, element sensitivity in the soft x-ray (SXR) spectral regime, and very high peak intensities.

Understanding electron-nuclear interaction in molecules

Science background

Light harvesting is one of the most important research topics related to energy science. Light interacts with molecular electrons and their energy is transferred into other channels by the concerted motion of electrons and nuclei. The channel with the fastest rate usually wins in the competition for the most light energy. This principle can be demonstrated in retinals, where isomerization, triggering the vision process, happens in less than 100 femtoseconds. This is much faster than thermalization via other degrees of freedom.

In a similar way, nucleobases are protected from ultraviolet damage by channeling the light energy quickly from electronic excitation into harmless vibrational degrees of freedom (see Figure 1). The ultraviolet light excites the molecule from the ground into the $\pi\pi^*$ state (solid black line). The molecule is highly chemically reactive as long as it is in this state. The molecule undergoes a concerted motion of all nuclei until a conical intersection with the $n\pi^*$ state (dashed black line) is reached on an ultrafast timescale. At this geometry, the Born-Oppenheimer approximation is violated. The molecule can relax electronically from $\pi\pi^*$ to $n\pi^*$ thereby protecting itself from the competing reactive pathways. Figure 1 shows a 2-dimensional cut through the conical intersection, which appears as a cone in three dimensions.
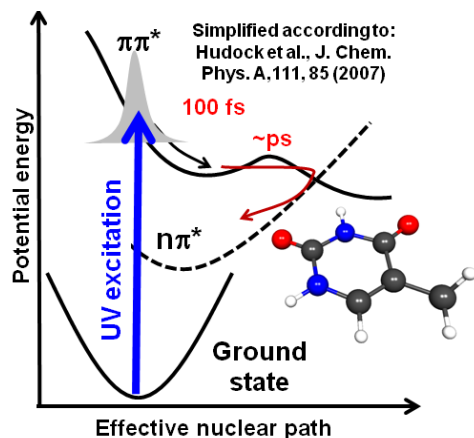
Figure 1: Simplified potential energy scheme for the nucleobase thymine, shown in the inset.

The fast coupling of different electronic states in light harvesting, vision, atmospheric chemistry and nucleobase photoprotection happens through a coupling of electronic and nuclear degrees of freedom. The Born-Oppenheimer approximation (BOA) states that electrons and nuclei are decoupled, but under certain conditions when two electronic states are close to degeneracy, this approximation is violated. A sketch of such a situation is presented in Figure 1, where two adiabatic electronic surfaces ($\pi\pi^*$ and $n\pi^*$ in the example of Figure 1) calculated by use of the BOA intersect each other in a cone. The crossing region is the conical intersection (CI) and presents a challenge for the simulation and understanding of light energy conversion in molecules.

Currently, ultrafast visible and ultraviolet spectroscopy contribute most to our understanding of non-BOA processes. This type of spectroscopy uses valence state transitions to probe the change of electronic states during the passage of CIs. The measurement is often obscured by nuclear relaxation dynamics, which can only be separated from the electronic dynamics using accurate *ab-initio* simulations, presenting another challenge for theory.

Opportunity for LCLS-II: non-BOA probing in the soft x-ray region

Ultrafast pulses in the soft x-ray region provide a precision tool for probing non-BOA dynamics, complementing existing spectroscopic methods. These pulses probe the valence electronic dynamics via core-valence transitions which are not amplitude modulated by nuclear dynamics, in contrast to pure valence transitions. In addition, the probe step is highly localized, since the core wave function is tightly bound to the nucleus. Spatial probing of valence electron distributions within the molecule in the picometer range is thus possible.

The user community is excited to extend the study of non-BOA dynamics to a larger variety of molecules. A recent experiment at LCLS-I probed non-BOA dynamics during nucleobase photoprotection using soft x-ray induced Auger decays (see Fig. 1). With the possibility of soft x-ray self seeding (SXSS) at LCLS-II, time-resolved absorption and emission spectroscopy can become a reality. These experiments can be intuitively interpreted. In absorption measurements, integrated electron emission can be recorded as a function of delay between the excitation pulse and the SXR probe pulse. As the SXR photon energy is tuned across core-valence resonances, the occupation of different valence states during non-BOA dynamics can be directly displayed in the absorption strength. Thus we will have access to electronic state dynamics during nuclear rearrangement. The nuclear arrangement itself will influence the exact position of the resonance but not its strength. The SXR fluorescence emission signal will show a complementary picture of valence state occupation even without tuning the SXR to particular resonances. Stimulated

emission schemes can compensate for the disadvantage of low emission yield in the SXR range, as explained below.

Requirements

- Small bandwidth (5000 resolution) for absorption and emission studies, ideally with SXSS

- Timing to VIS-UV laser on the order of 10 to 100 fs, either by active locking or by single shot timing tool

- X-ray fluorescence detectors, electron and ion time of flight spectrometers

Understanding electron-electron interaction in molecules

Science background

Molecular electrons form a highly entangled system interacting via Pauli and Coulomb forces. The solution to the electronic Schroedinger equation relies on highly evolved approximations that simplify electron correlation. Currently, scientists judge the quality of these complex approximations by comparing just one number, namely the energy of an electronic state, to experimental results. This greatly reduces the information content of the simulations. An ideal experiment would, in the best case, provide a detailed understanding about electron correlation, to directly compare to the theoretical approximation.

The method of two-dimensional spectroscopy is used in many fields, including 2-D nuclear magnetic resonance (NMR) to learn about interacting spins, 2-D infrared spectroscopy to examine interacting vibrational modes, and 2-D visible spectroscopy to reveal electronic couplings between different molecules. The main challenge for fourth generation light sources is the realization of 2-D SXR spectroscopy for the understanding of electronic interactions within a molecule, especially as they relate to Pauli and Coulomb forces.

Opportunity for LCLS-II: Raman transitions

At LCLS-II we will have the chance to measure 2-D SXR spectra. As mentioned above, SXR light allows for the creation of localized electron excitations in the valence and continuum domain, thus allowing for high spatial sensitivity within a molecule. Figure 2 presents a sketch of the experimental scheme. An excitation at a particular site in the molecule will trigger electron dynamics via valence charge migration and charge relaxation processes. The effect of the excitation on another site in the molecule can be probed by a second SXR pulse. The localized states will usually be disturbed or destroyed quickly by the Auger decay of the core hole, making experiments rather challenging. At LCLS-II, it would be possible to overcome this difficulty by using stimulated Raman excitations, as shown in Figure 2. In the Raman process, a core hole excited state generated by soft x-ray light will be stimulated down to a purely valence excited state by a second interaction with the SXR pulse. A possible proof of principle of the stimulated processes may have already been achieved in an atomic lasing experiment (Rohringer *et al.*) at LCLS-I, but further studies are recommended.
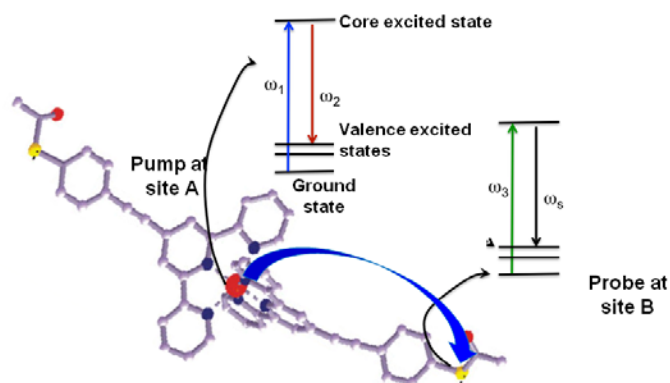
Figure 2: Sketch of an impulse Raman pump/probe process to study electronic correlation in a molecule. An electronic/vibrational wave packet is launched specifically at atomic site A, which could be a photoreaction center of a molecule. It is successively probed at atomic site B with a broad-band pulse tuned to an element specific core-resonance of atom B. The valence charge migration and charge relaxation correlate electrons at site A and B (sketched by blue arrow).

At LCLS-II, Raman excitation of molecules can be accomplished with either selective two-color excitation or broadband short pulse excitation. For the first scheme, a pulse consisting of two frequencies (ω_1 and ω_2 in Figure 2) in the SXR range needs to be prepared. The energy difference between the pulses corresponds to the valence excitation energy, so the two-color pair will predominantly excite just one valence electron state. The effect of this excitation on another site in the molecule can be probed by another Raman transition. The other option is using extremely short pulses, less than one femtosecond duration, with a broad bandwidth (up to 10 eV) covering several valence excitation energies. These pulses will create a coherent superposition of several valence states and thus a valence electron wave packet. The motion of this wave packet will occur on the attosecond time scale, providing an ultimate timescale for charge migration. In this context it will be very interesting to search for surviving valence coherence features after the Auger decay resulting from single photon resonant excitations.

Requirements:

- Beams at different angles and different colors, time delays between multiple pulses
- Self seeding for tunable colors or shortest near Fourier limited pulses
- Intensities in the range 10^{17}-10^{18} W/cm^2
- X-ray fluorescence detectors

The high intensity frontier

Science background

LCLS-I held its promise in high intensity physics, allowing users to investigate multiple core holes in atoms and molecules as well as two-photon processes in the soft x-ray range at intensities of 10^{17}-10^{18} W/cm^2. The frustrated absorption due to multiple core holes had large implications on the imaging experiments, predicting a higher destruction threshold than commonly assumed. The single molecule imaging community is pushing to even higher intensities, and LCLS-II should be able to reach those intensities with self seeding techniques. Understanding the interaction mechanisms of matter with these unprecedented x-ray intensities may lead to the discovery of completely new phenomena in light-matter-interactions.

So far, virtually nothing is known about the interaction of intense x-ray pulses with nanometer-sized matter at power densities allowing imaging of single particles with atomic resolution. Atomic or molecular clusters provide a perfect benchmark system for this purpose. Time-resolved electron and ion spectroscopy has been successfully implemented on rare gas clusters at LCLS-I, but the technique could possibly be extended to image clusters of pure metals or even molecules. The combination of spectroscopy with single shot scattering results in a detailed picture of electron and nuclear dynamics during the strong x-ray pulse interaction.

Opportunity for LCLS-II

We expect new atomic physics phenomena to be discovered at LCLS-II related to the breakdown of the perturbative approximation in the x-ray spectral range. The situation is very different at x-ray frequencies compared to optical since the distortion of the bound-state dominates and defines the breakdown of perturbation theory. The breakdown of a perturbative treatment of light relates to strong field phenomena like high harmonic generation and above-threshold ionization, commonly known in the infrared spectral region. For this domain, scaling parameters have been developed and we are extending them into the x-ray domain in the following way. The most important scaling parameter for judging this is z_1, which describes the distortion of the atomic structure by relating the energy characterizing the electromagnetic field to an energy associated with a bound state. This parameter can be expressed as $z_1 = (E/\omega)^2/I_p$ where E is the field strength, ω is the laser frequency and I_p the electron's binding energy. The intensity dependence of the continuum-state, z, is defined as the ratio of the quiver energy to the photon energy and can be expressed as $I/4\omega^3$, where I is the laser intensity. A perturbative treatment of the atom-field interaction requires that z and z_1 both be less than 1.

Figure 3: A plot of the z (continua-state: red line) and z_1 (neon K-shell state: blue line, neon L-shell: dashed-dotted blue line) intensity scaling parameter in the x-ray regime as a function of intensity. The blue dash-dotted line shows the z_1 parameter for the neon valence L-shell which distorts at much lower intensity than the core. The grey dotted line is the perturbative limit, defined as 10% of the L-shell z_1-parameter. (Image courtesy L. DiMauro, Ohio State University)

Figure 3 scales the bound, z_1, and continuum, z, intensity parameters into the x-ray regime. In the figure the $z_1 = 1$ curves are plotted for both the K-shell (blue line: core) and L-shell (blue dash-dot: valence) electrons of neon. Not surprisingly, the differential frequency scaling of z_1 and z results in the core-state distortion dominating over the continuum-state above 500 eV photon energy. Therefore, for photon energies above 500eV, the perturbative approach fails for core states at lower intensities compared to continuum states. This is in sharp contrast to the usual picture at optical frequencies of a quivering

continuum wave packet. Within this picture, entrance into the strong-field regime will require intensities of nearly 10^{20} W/cm^2, which are beyond the present performance of the LCLS. However, the total bound-state contributions (core + valence) result in a dichotomy in this definition since the strong-field limit defined by these states are clearly at odds. So the breakdown of the perturbation theory may happen at significantly lower intensities than expected since the single-electron approximation, often used in the optical regime, may not apply. The physics involved in the perturbative breakdown will be unique to the x-ray regime since it will involve many-body interactions, not seen in the optical regime.

Intense x-ray pulses from the LCLS-II focused to a few hundred nm spot will open the door to a completely new regime for the interaction with more complex matter. At currently achievable power densities, high quality scattering patterns of single clusters and nanocrystals can be recorded, giving precise structure determination with atomic resolution. Scattering patterns of clusters imaged to date give only low resolution (~10 nm) information on their shape. Determining precise structures of individual mesosopic nanoparticles with nearly atomic resolution would be a breakthrough. At the fluence related to high intensity imaging at LCLS-II, all electrons are stripped off from the individual atoms with low Z. Therefore, an understanding of the relationship between x-ray induced electron as well as nuclear dynamics and their x-ray scattering response is essential to achieve accurate imaging. The methods of choice will be time resolved experiments based on x-ray/x-ray as well as x-ray/ THz streaking pump – probe schemes.

With this approach, important new areas of science can be investigated. First, it will allow the study of ionisation and plasma dynamics of size-selected particles. Even more importantly, phase transitions in clusters, such as time-resolved studies of solid – liquid – transitions during surface melting, become feasible. LCLS-II will provide a unique chance to study the geometry and shape of nanocrystals. Presently this is a completely open field since only a few model systems, e.g. rare gas clusters, have been able to be studied so far. Heterogeneous clusters, core shell structures and fractal clusters are of particular interest. With this approach, important new areas of science can be investigated. First, it will allow the study of ionisation and plasma dynamics of size-selected particles. Even more importantly, phase transitions in clusters, such as time-resolved studies of liquid – solid – transitions during surface melting, become feasible. LCLS-II will provide a unique chance to study the geometry and shape of nanocrystals. Presently this is a completely open field since only a few model systems, e.g. rare gas clusters, have been able to be studied so far. Heterogeneous clusters, core shell structures and fractal clusters are of particular interest.

Requirements

- Focusing system with minimal loss and intensities on the order of 10^{19} W/cm^2
- Time delay for x-ray pump-probe, 1st and 3rd harmonic
- Synchronized THz source
- Electron and ion detectors
- Scattering detector

2.2. Materials Sciences

The materials science workshop focused on the impact of LCLS-II in the fields of strongly correlated quantum materials, magnetic materials and novel technique development in terms of non-linear and inelastic x-ray spectroscopy. The contributions can be organized within the following three topics:

1. Control of electrons and spins
2. Electrons, spins and lattice in quantum materials

3. Non-linear x-ray science

Research in all these fields will be enhanced by a reproducible, intense, seeded beam at LCLS-II with pulse durations on the order of femtoseconds. Elemental sensitivity in the soft x-ray (SXR) regime, polarization control, and control of both peak intensity and fluence are also important for materials science.

Optical control of electrons and spins on the nanoscale

Energy transfer and conversion is central to many processes in nature and society. One example is our ever increasing need to store and process information. Laboratory experiments suggest that the next generation of magnetic hard disk drives may be able to make use of miniaturized lasers for 'softening' magnetic bits before the magnetic field of the read/write head switches the magnetization. This would move data storage generation beyond heat-assisted magnetic recording to the realm of all-optical magnetic switching. For this to become a reality, all-optical switching has to be demonstrated at sub-100nm length scales and on materials where the written magnetic patterns remain stable. This requires investigating new materials that combine the magnetic hardness required for high-density recording with optical switchability.

The development of such a dramatically simplified technology is a component of one of the grand scientific challenges for condensed matter and materials physics: How do complex phenomena emerge from simple ingredients? Material properties are governed on the nanometer (nm) length scale by the fundamental properties of the electron, its charge and spin, which evolve on the femtosecond (fs) timescale. The emergence and ultimate control of magnetic order following laser heating requires the development of suitable techniques for probing the system's intrinsic length and time scales simultaneously.
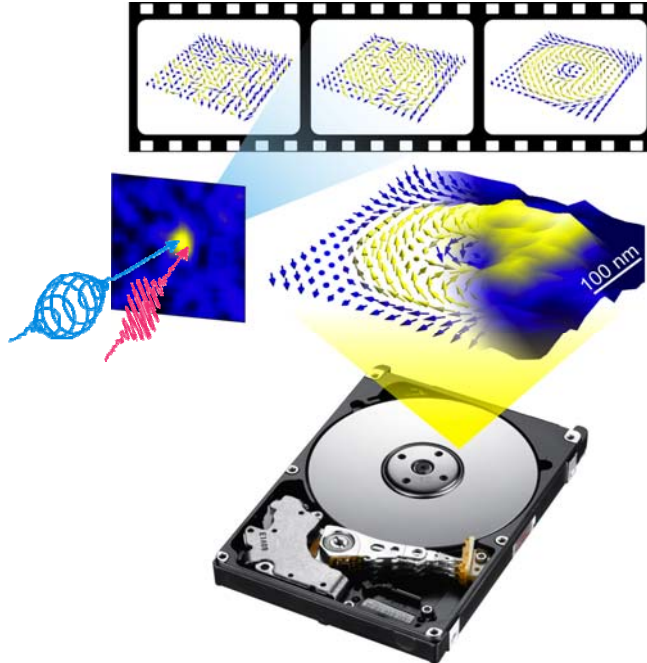

Figure 4: Illustration showing how topological magnetic structures may represent magnetic bits on future hard disk drives. A fs movie taken at LCLS-II will answer how such complex structure evolves out of simple ingredients. Figure courtesy of T. Rasing.

Opportunity for LCLS-II: probing the fs motion of electrons & spins at nm lengths

The short, intense and fully coherent x-ray pulses from LCLS-II will provide a unique opportunity for imaging extremely small objects undergoing ultrafast, often non-repetitive, dynamical processes. LCLS-I has pioneered the use of single shot x-ray imaging, where it is important to image the sample before x-ray damage of the illuminated object occurs. The conditions for the onset of damage have been established and serve as a guide to project to the resolution ultimately achievable at LCLS-II. Producing an ultrafast movie of electrons in functional materials requires full x-ray polarization control, especially for achieving sensitivity to the electron spin through the use of circularly polarized x-rays. Such measurements will be performed with the x-ray energy tuned to absorption edges of magnetic elements (up to 2 keV) and will greatly benefit from the improved energy and intensity stability provided by self-seeding. A performance increase of up to four orders of magnitude compared to LCLS-I allows reaching spatial resolution in the sub-10nm range for 10 fs x-ray pulses.

Requirements

-   Narrow bandwidth (5000 resolving power) for coherent diffraction imaging mainly using soft x-rays

-   Full polarization control for soft x-rays

-   Timing to VIS-UV laser pulses on the order of 10s of fs, done either by active locking or by single shot timing tool

-   Imaging detectors covering large solid angles to reach <10nm spatial resolution

Quantum Materials

Science background

One of the great challenges in modern condensed matter physics research is to understand the novel quantum states emergent in complex materials in which spin, charge, lattice and orbital degrees of freedom are strongly intertwined. This gives rise to interesting and unusual properties. Probably the best known is the ability of high temperature superconductors to conduct electrical currents without resistance. The response of such quantum materials to external stimuli leading to changes in their electrical conductivity or polarization has triggered intense efforts to search for applications in low power electronics. An example is depicted in Figure 5 that indicates the response of atomically engineered hybrid structures of multiferroic and ferromagnetic layers to a pulsed electric field. The ferromagnetic layers switch polarization without the need for dissipating electric currents, providing a novel way of switching the magnetization by applying only an electric field. The fascinating potential of quantum materials resembles the state of semiconductor research 50 years ago, where groundbreaking scientific discoveries were followed decades later by devices revolutionizing our everyday lives.

Figure 5: Schematic of the influence of electric field induced polarization switching in a multiferroic bottom layer on the magnetic state of the top layer. The intense electric field pulses mimic for sub-ps durations the fields typically applied in devices during switching. Image courtesy of S. Johnson and A. Lindenberg.

Opportunity for LCLS-II: A comprehensive view of electron, spin and atom motion in functional materials

The wide range of available x-ray energies at LCLS-II offers unique opportunities for studying the evolution of electronic, spin and lattice excitations on their intrinsic time and length scales. Hard x-rays typically probe atomic rearrangements, while soft x-rays allow access to transition metal L-edges where polarization control can separate electronic and spin degrees of freedom. A key feature is the synchronization to a THz source that allows peak electric fields of the order of 1GV/m. Such fields are very typical for modern devices such as field effect transistors where voltages ~1V are applied across device dimensions of ~1nm. LCLS-II will allow complementary elastic x-ray scattering following the evolution of excited states in real time and inelastic scattering that will simultaneously probe the relevant electronic, spin and lattice interactions as the states evolve. The pulsed nature of LCLS-II will enable to pair hard x-ray inelastic scattering probes of excited states with novel sample environments providing extreme conditions such as high pressure or high pulsed magnetic fields.

Requirements

- Narrow bandwidth (5000 resolution) for elastic and inelastic resonant soft x-ray diffraction and off-resonant elastic and inelastic hard x-ray scattering

- Full polarization control for soft x-rays

- Synchronized THz source

- Resonant elastic and inelastic soft x-ray scattering end stations

- Hard x-ray inelastic scattering spectrometer for extreme sample environments

The birth of non-linear x-ray science

Science background

Novel spectroscopic tools using optical lasers have been developed to probe excited states of matter. Raman scattering, for example, is widely used for probing electronic, spin and lattice excitations in the frequency domain. Ultrafast table top optical laser systems have enabled many laboratories to develop and implement stimulated Raman scattering in the time domain. LCLS-II will enable transfer of these non-linear optical techniques into the x-ray regime. LCLS-I has already resulted in several demonstrations of non-linear x-ray science investigating atoms and molecules. The seeded nature of LCLS-II beams will likely revolutionize the way we perform spectroscopy on a wide variety of materials.

Opportunity for LCLS-II: stimulated inelastic x-ray scattering

As outlined above, the complete characterization of electronic, spin and lattice interactions of emerging phases requires development of suitable probes for these interactions. Resonant inelastic soft x-ray scattering (RIXS) as well as off-resonant inelastic hard x-ray scattering have emerged as the only tools that can separate electronic, spin and lattice excitations using x-ray polarization. Compared to other existing and future XFELs, LCLS-II has the unique advantage of significantly higher x-ray peak power. This would allow scientists to more readily develop and implement novel stimulated Raman scattering techniques that could significantly enhance the potential of conventional, spontaneous inelastic scattering. In analogy to optical lasers it was proposed during the workshop to develop such techniques in the time domain with transient grating spectroscopy or the frequency domain using inelastic scattering with two x-ray colors or polarizations. This requires the development of a stimulated scattering 'toolbox' consisting of x-ray pulse splitters, polarizers and optics similar to what is now routinely available in the optical spectral region. In addition, two-color seeding schemes need to be developed in both hard and soft x-ray regions. It is important to note that there is significant overlap with AMO and chemical science requirements in this area.

Figure 6: Time- and momentum-resolved RIXS can be used to characterize fundamental interactions, such as spin exchange coupling and electron-phonon coupling in momentum-energy space as a function of time. Images courtesy of R. Schoenlein (LBNL).

Requirements

- Beams at different angles and different colors, time delays between multiple pulses

- Self seeding for tunable colors or ultrashort near Fourier limited pulses

- Fluence <1 J/cm^2

2.3. Chemistry

The key theme of the chemical sciences portion of the workshop was using the unique attributes of ultrashort duration x-ray pulses to resolve chemical transformations with atomic resolution in space and time. This objective also appeared prominently in workshops for LCLS-I, but LCLS-II has additional potential in three critical areas:

1. Photocatalysis
2. Heterogeneous catalysis
3. Liquids and glasses

The invited talks and brief presentations from workshop participants highlight the unique potential of ultrafast x-ray sources for investigating fundamental and general chemical phenomena and with the potential to solve a very broad range of problems in chemical dynamics. While this overlaps strongly with the science drivers for ultrafast optical laser sources, the interpretive limitations of optical spectroscopy make the value and motivation for ultrafast x-ray studies clear and robust. Most critically, x-ray scattering and x-ray spectroscopy have the potential to preferentially measure the changes in either nuclear or electronic structure and map those changes onto a highly intuitive molecular framework.

Chemical Conversions: building a better photocatalyst

Science Background

The workshop highlighted key areas in chemical dynamics where LCLS-II has an opportunity to make a critical contribution. Gaining a predictive understanding of catalytic mechanisms, with particular emphasis on photo- and heterogeneous catalysis, is one important area of interest. This research has the potential to contribute to the development of renewable energy sources. Harnessing solar energy to generate fuels, either indirectly with photovoltaics and electrochemical catalysis or directly with photocatalysts, presents a critical technological challenge that will require scientific advances to solve. At the center of this technical challenge is the rational design of efficient and cost-effective catalysts.

The efficient conversion of light to electrical or chemical energy, whether by natural photosynthesis, proton pumping in bacteriorhodopsin, or electron transfer in dye-sensitized and bulk heterojunction solar cells, invariably involves ultrafast chemical processes. Consequently, the ability to understand and eventually design molecular systems for solar applications requires a detailed understanding of chemical dynamics and the molecular properties that govern them. Ensuring that optical excitation can be converted to a long lived electrical or chemical potential represents the critical first step to efficient solar conversion.

As clearly demonstrated by photo-active proteins, the excited state dynamics are a complex interplay of intra- and inter-molecular structure and dynamics. Green fluorescent protein, in which the biomolecular environment has been manipulated to yield much higher fluorescent quantum yield than the neat chromophore in aqueous solution, is one example that demonstrates that the excited state lifetime can be modified by synthetic control. Understanding, and eventually controlling, molecular conversion of light to electricity and fuel requires understanding the non-adiabatic dynamics of electronic excited states, which in turn requires understanding the coupled motion of electrons and nuclei.

Opportunity for LCLS-II

Ultrafast x-ray scattering presents an excellent opportunity to investigate structural dynamics of molecular systems with atomic resolution. One example system is the artificial photosynthetic triad of carotene-porphyrin-fullerene (see Figure 7). X-ray scattering and spectroscopy are ideal tools for investigating the dynamics of the electronic charge distribution. Being able to resolve the dynamics of the electronic charge distribution is of particular significance, since the splitting of the photo-generated electronic exited state

into spatially separated electrons and holes represents a key step to converting a photon into an electrical or chemical potential for many systems, including photosynthetic proteins, dye-sensitized solar cells, and bulk heterojunction solar cells.

Requirements

- Time resolution ≤ 20 femtoseconds in optical pump – x-ray probe measurements

- Seeded FEL performance for RIXS and anomalous x-ray scattering in solution

- X-ray emission spectrometer for RIXS studies with 0.3 eV energy resolution.

Figure 7: Artificial photosynthetic triad, where the porphyrin (green) absorbs the light, the carotene (red) functions as the hole acceptor, and the fullerene (pink) functions as the electron acceptor. Ultrafast charge separation leads to efficient conversion of photon energy to chemical potential. Ultrafast x-ray methods provide the ability to map the time dependent charge density in this triad with atomic spatial and temporal resolution. (DOE report on Basic Research Needs in Solar Energy Conversion.

Chemical Conversions: mechanistic studies of heterogenous catalysis

Science Background

Most industrially significant catalytic processes involve chemical conversions at the interface between a catalytic surface and the chemical feedstock. Despite the widespread relevance of heterogeneous catalysis, we generally lack molecular scale, mechanistic understanding of interfacial chemical phenomena. The chemical specificity of core-hole spectroscopy, coupled to the ultrafast time resolution of the LCLS-II, presents a critical opportunity for mechanistic studies of interfacial chemical conversions.

Opportunity for LCLS-II

The critical attribute of the LCLS-II, compared to LCLS-I, is a wider photon energy range that includes the K-edges of N (400 eV) and C (280 eV). By tuning an x-ray pump pulse to an absorption peak associated with a specific molecular species, the chemical specificity of the x-ray absorption edge can be exploited to make a non-equilibrium distribution on the electronic ground state. This technique utilizes the destructive properties of x-ray absorption, where the photochemical destruction of a specific chemical species is the source of the non-equilibrium distribution.

Additionally, if tunable two color FEL performance can be achieved, the LCLS-II will provide a unique means of studying electronic ground state dynamics with x-ray photochemical hole burning. The second, independently tunable x-ray pump pulse then monitors how quickly the molecular system can re-establish an equilibrium distribution. In this manner the catalytic dynamics of the electronic ground state can be monitored with atomic specificity.

Requirements

- Time resolution $\leq$ 20 femtoseconds in optical pump – x-ray probe measurements

- Seeded FEL performance for x-ray RIXS and anomalous x-ray scattering in solution

- Two color x-ray pump – x-ray probe capability for 2-dimensional x-ray hole burning measurements

- Two color x-ray split and delay for two color x-ray pump – x-ray probe capability for 2-dimensional x-ray hole burning measurements

- X-ray emission spectrometer for RIXS studies with 0.3 eV energy resolution.

Structure and dynamics of liquids, super-cooled liquids, and glasses

Science Background

Glassy materials play an important role in engineering and the natural sciences, making the origin of glassy behavior of broad scientific and technical importance. Of particular importance is determining whether or not nanoscale spatial heterogeneity characterizes the dynamics of super-cooled liquids. The dynamic structure factor, or equivalently, the intermediate structure factor, defines the attributes of this type of material. While frequency domain inelastic x-ray and neutron scattering measurements provide access to high frequency dynamics with Ångström spatial resolution, the dynamic range of these measurements limits the ability to fully characterize the critical dynamics of these systems. Optical light scattering measurements can access the full dynamic range required for these systems, but they lack the spatial resolution necessary for explaining the origin of frustrated dynamics in glass forming materials.

Figure 8. (right) Coherent scattering image showing a typical intensity spectrum with speckle structure of a colloidal glass **(left)** Experimental results after applying the cross-correlator $C_Q(\Delta)$ to the data in *right* at different Q values. Image courtesy of A. Nilsson.

Opportunity for LCLS-II

X-ray photon correlation spectroscopy (XPCS) utilizes the transverse coherence of the LCLS to measure the intermediate structure factor of glassy materials and provides a unique approach to investigating the structure and dynamics of disordered materials. LCLS-II can provide the increased spectral brightness achievable with a seeded FEL, which will enhance the x-ray transmission of the x-ray optics used in the XPCS x-ray split and delay.

Requirements

- Time resolution of 10-100 femtoseconds in x-ray pump – x-ray probe measurements
- Seeded FEL performance for x-ray photon correlation spectroscopy (XPCS) measurements
- Single color x-ray split and delay for XPCS
- X-ray emission spectrometer for RIXS studies with 0.3 eV energy resolution.

2.4. Biology

The Biology portion of the workshop focused on fields that have achieved high profile results at LCLS-I, notably protein crystallography and single particle imaging. Most contributions made use of the 'diffraction-before-destruction' principle to obtain structural information from biological samples before they are destroyed by the LCLS pulses. The presentations covered three areas of research in which this effect can be exploited in novel experiments:

1. Nano to micron-crystallography of proteins and macromolecular complexes
2. Time resolved spectroscopy and crystallography
3. Imaging of non-periodic (noncrystalline) samples

Experiments in all three domains were reported from LCLS-I, using the CXI and AMO end stations and exploiting the femtosecond duration and high peak intensity of the LCLS pulses. Several common themes for LCLS-II emerged for the vast majority of the biological experiments.

- There is a desire for higher peak power (W)/ flux (photons/pulse).

- Improved detectors are needed, specifically low-noise and higher dynamic range.

- There is a strong demand for extensive laboratory facilities for sample preparation and handling located in close proximity to the instruments.

Nanocrystallography of proteins and macromolecular complexes

Science background

Serial femtosecond protein nano to micron-crystallography has been very successfully pioneered at LCLS, where diffraction patterns were obtained from some of the smallest protein crystals ever, in some cases containing as few as 300 molecules in the crystal lattice.

This technique is particularly attractive for proteins that systematically fail to form macroscopic crystals, which is particularly the case for the class of amyloid-forming peptides underlying neurodegenerative diseases including Alzheimer's and Parkinson's. It also offers the exciting prospect of radiation-damage free data acquisition of nano- to micron-sized crystals of challenging biological systems or of crystals that are too small for conventional synchrotron micro-beam lines.

Opportunities for LCLS-II

Experiments at LCLS-I have shown that the achievable resolution is frequently not limited by the X-ray wavelength but by quality of cystalline samples, making longer wavelengths desirable for their higher scattering power. A photon energy range between 2 and 6 keV could provide the right compromise between signal strength and resolution for such crystals. With the current suite of instruments at LCLS, the photon energy range between 2 and 5 keV is inaccessible for biological scattering experiments, but LCLS-II could fill this gap. However, higher photon energies are needed to reach the anomalous edges of commonly used elements (such as Se) for anomalous experimental phasing.

Requirements

- Pulses with the highest possible peak intensity, ideally TW-level peak power focused to a spot with less than 0.3-3 micron diameter.

- Dedicated nanocrystallography end station operating in the 2 – 14 keV photon energy range.

- Low noise photon detectors with 3000 x 3000 pixels arranged to capture high scattering angles and separate low-noise detectors for spectroscopy.

Time resolved spectroscopy and nanocrystallography

Science background

Light energy conversion is one of the central research topics in basic energy science. In nature, photosynthesis is accomplished by a handful of membrane proteins. One of these, photosystem II, catalyzes the water oxidation reaction responsible for all oxygen in the earth's atmosphere. Despite extensive biophysical research, the exact mechanism of the water oxidation reaction and the structure of the Mn_4Ca cluster at the active site remain unknown. Combined femtosecond X-ray diffraction and spectroscopy studies hold the promise to outrun radiation damage processes that destroy this information in synchrotron-based experiments. Solving structures of the short-lived intermediate states may lead to a molecular movie of the complete water-splitting cycle.

Opportunities for LCLS-II

- Resonant inelastic X-ray scattering (RIXS)

- Weak transitions, e.g. valence to core resolvable with higher flux.

Requirements

- Higher flux to resolve weak transitions (such as valence to core), for polarized spectroscopy or to use a monochromatized beam for RIXS

- Optimized spectroscopy instrument integrated into the beamline.

- An alternative approach not employing the 'diffraction-before-destruction' approach would utilize a broad, lower-intensity X-ray beam with a unique and novel pulse structure to probe the same crystal more than once.

Imaging of non-periodic samples

Science background

Coherent X-ray diffractive imaging (CXDI) of single non-periodic objects allows scientists to study non-reproducible biological structures ranging in size up to individual cells or entire viruses. CXDI experiments are especially dependent on peak photon flux because, unlike diffraction from nanocrystals, diffraction intensity does not get amplified by multiple copies of the same molecules in repeating unit cells.

Opportunities for LCLS-II

X-ray pulses from the current LCLS are starting to approach the photon density required for moderate-resolution CXDI, but only when tightly focused.

The tight focus of a 100 nm spot is excellent for studying samples smaller than 10 nm in diameter. Many of the proteins in this size range are relatively simple, containing 2000 or fewer folds, and have already been solved. There are over a million complex biological structures in the mesoscale size range, very few of which are understood. This domain includes viruses and other intriguing structures that could be probed with a high intensity beam focused to a spot size in the μm range.

Requirements

- Flux of 10^{13-14} photons / pulse

- Focused to a 1-3 micron spot

- Photon energy range of 3-5 keV for smaller objects or 0.5 -2 keV for the largest objects

- Low-noise, high dynamic range detectors

- Sample injectors on-site to accomodate various sample types

3.0 Workshop Account

Scientists from SLAC and the worldwide user community are enthusiastic about the potential of the new Linac Coherent Light Source (LCLS-II). Nearly all the talks at the New Instruments Workshops, held March 19-22, 2012 at SLAC and chaired by Phil Heimann and Jerry Hastings, generated many questions and lively discussion. The goal of the workshops was to get input from the user community as part of the process of determining what to include in LUSI-II, the new instrument suite that can accommodate up to six instruments to run scientific experiments at LCLS-II.

The workshops were organized into three scientific areas representing the range of scientific disciplines that can take advantage of LCLS-II capabilities: biology, materials/chemistry, and atomic/molecular/optical science. Scientists presented research they have done on the existing LCLS-I and proposed future experiments that would justify new capabilities in LUSI-II. Following each set of talks, Hastings led a discussion to shed light on the desired instrumentation and beam characteristics to enable scientific discovery in the specific discipline.

Janos Hadju (Uppsala University and European XFEL) started the biology workshop with his talk, "Requirements for Single Molecule Imaging." A 250-molecule cluster creates a good image using the coherent x-ray imaging (CXI) instrument on the LCLS-I, but with a stronger x-ray pulse (100 to 200 times that of LCLS), Hadju says they could image single molecules. In response to a question about whether electron diffraction is an option, Hadju explained that it would likely not be possible to create a strong enough beam of electrons, and even if the beam were strong enough the focus would not be sufficient.

David Eisenberg (UCLA) discussed "Exploring the Amyloid State of Proteins by Micro- and Nano-cystallography." Amyloid fibers are important in the study of many diseases, including Alzheimer's and diabetes, but the crystals are extremely small and hard to image. Powder x-ray diffraction yielded beautiful images but no structural data. Eisenberg believes the LCLS-II could enable x-ray diffraction of small crystals without the sample damage that occurs using a conventional synchrotron beam.

In his talk on "Time-Resolved X-ray Studies of Biological Systems" Philip Anfinrud (NIH) explained that synchrotrons produce static images of proteins, but it is important to see dynamic changes, or "movies on a chemical time scale." With multiple, short laser beam pulses (on the order of fs) it would be possible to construct an electron density map showing structural changes over time. Anfinrud requested a seeded laser beam at 9-12 keV capable of 100 ns pulses in triple-pulse sequence.

The final biology talk was "Water Oxidation in Natural and Artificial Photosynthesis and Time-Resolved X-ray Spectroscopy" by Vittal Yachandra (LBNL). Artificial catalysts that mimic natural photosynthesis undergo chemical reactions on time scales ranging from femtoseconds to miliseconds, and Yachandra has tried to understand the cycle using x-ray spectroscopy. Sample damage is a major challenge, as is interpreting the results.

The discussion session focused on summarizing the biology community's needs for LUSI-II. One science driver in this field is imaging single molecules. It is important to have high peak pulse intensity and a highly focused beam. There is, however, a trade-off between focus and hit rate, since if the focus is too small it is harder to target sub-micron crystals. Optimum focus size is probably around 1 μm. Pulse length for imaging of single molecules should be around 10 fs but depends on object size. Other types of experiments, such as those examining cells, need pulse lengths on the order of 100 fs.

Some in the biology community want detectors for soft x-ray imaging in the range of 0.5 to 3.0 keV. The technical issue is dynamic range: the common dynamic range of 10^4 to 10^5 is not sufficient for soft x-ray

imaging. Detectors need to have very low noise, and commercially available detectors are not optimized for these applications. SLAC does have a detector group in place to investigate options.

Different experiments need different x-ray energies, and the most problematic range is between 2 and 5 keV for soft condensed matter, a range that isn't covered by existing beam lines. Some imaging experiments need soft x-rays below 2 keV. Hadju believes that including 3 to 5 keV capability could lead to scientific breakthroughs and be a selling point for LCLS-II, but the rest of the community doesn't appear convinced that it's worth the effort to overcome the technical challenges posed by that range.

Biologists definitely want to see an on-site sample preparation lab that includes centrifuges and incubators. Sample environments should include cooling capability for cryogenic samples and the ability to set the humidity. High vacuum is not needed. One option could be using an SEM sample chamber with increased humidity for experiments that need a wet environment. This adds the advantage of direct sample inspection but is not compatible with XRF spectroscopy. A flexible setup with changeable sample chambers may be able to best meet everyone's needs.

One concern involves the study of biohazards such as viruses, where safety and handing are critical. Having one dedicated, confined end station would be necessary, but what about decontaminating the line so viruses aren't pumped out of the building into the air? A biosafety level 2 (P2) is sufficient for some viruses, but others need P3, and including P3 capability would be expensive and perhaps not realistic in terms of balancing the needs of the entire scientific community.

Looking at x-ray pulse generation, the scientists discussed implementing a microsecond shift to improve sample hit rate for small samples in dilute solution. Consensus wasn't clear on whether triggering the LINAC would work. Results may depend on the focus size.

Two days were devoted to materials and chemistry, separated into soft x-ray and hard x-ray experiments. The goal of "Ultrafast X-Ray Studies of Correlated Materials," presented by Robert Schoenlein (LBNL), was to examine how valence structure and spin correlate to atomic structure in a variety of compounds. He is looking at phenomena occurring over a range of time scales, making dynamic measurement critical. Scheonlein's instrumentation requests include a resonant soft x-ray scattering (RSXS) chamber with sample orientation control, x-ray pulses shorter than 100 fs with 100 meV resolution, and capability for stimulated x-ray scattering. For experiments on magnetic materials, the system needs to be able to apply a high magnetic field.

Andreas Sherz' research (SLAC), "Imaging Low-Energy Excitations in Complex Magnetic Materials," also requires magnetic fields and stimulated x-ray scattering. He proposes using two seeded, phase-locked beams with orthogonal polarizations to avoid the decay of magnetic scattering that occurs at high fluence rates using the synchtrotron. The stimulated scattering approach also minimizes sample damage. Beam requirements include pulse length less than 10 fs, 0.1 mJ/pulse, various incident angles, and 100 meV bandwidth.

In his talk on "Challenges in Catalysis and Dynamics of Surface Chemistry," Martin Wolf (FHI Berlin) described work on conversion of CO_2 into methane. His group has been able to study adsorption in catalysis using the soft x-ray capabilities of LCLS-I, but LCLS-II could yield better understanding of the full catalysis reaction cycle. Wolf would like to do two-color x-ray experiments with stimulated Raman spectroscopy to get time and spatial resolution. He requests a beam at > 250 eV, jitter of 10 fs or better, pump/probe capability, and polarization control and says the short pulse times will enable him to observe transient intermediate states in situ.

The afternoon started with several short presentations. One scientist requested a 400 to 2000 eV seeded beam with low jitter and THz to mid-IR pumping for time-resolved RIXS on correlated materials such as cuprates. Another application for stimulated RIXS is observation of oxidation states as a function of time. Researchers want to be able to study molecules in liquids under cryogenic conditions, which may require a separate dedicated chamber or a flexible setup. Scientists working on surface chemistry also requested a

dedicated end station that may need vacuum as well as two spectrometers to see orientation effects on the surface with a polarized source.

It is not clear how to configure RIXS to accommodate liquids, catalysis, and surface experiments in a common instrument. One suggestion to accommodate experiments with various sample types was to use instruments for a certain class of experiments for several months and then swap instruments periodically. Flexible configuration ideas included giving alignment time on some instruments while others were using the laser beam.

Regarding beam parameters, LCLS scientists have proposed a resolving power of 5000, combined with a monochromater on one beam line for increased resolution, and most users believe this will be sufficient. The highest resolving power being considered at this time is 10,000, so the few experiments that would need higher resolution may need to wait until a later phase of operation beyond LUSI-II.

The remainder of the discussion concentrated on how to implement two pulses for stimulated scattering experiments. The pulses could be at either the same or different energies, and it is important to consider delay time and polarization. For two colors, it may be good to introduce a delay time of a few 10s of fs, and the pulses may need to be seeded. There was discussion over producing two colors within the SASE bandwidth with soft x-rays. Some people suggested a workshop with theorists to combine theoretical and practical knowledge.

Anders Nilsson (SLAC) opened the hard x-ray session with his talk, "Probing Water and other Liquids with LCLS-II." He described experiments with super-cooled water, explaining that probing at low temperatures and high pressures with the LCLS-II may yield information about the glassy transition. Nilsson's wish list includes small focus CXI, a detector with uniform response, THz to mid-IR pumping, and capability for correlation spectroscopy on a 100 fs to ms time scale.

James McCusker (Michigan State University) explained that studying "Ultrafast Excited-state Dynamics of Transition Metal Chromophores" with either hard or soft x-rays is important for development of new synthetic compounds. Time resolved x-ray spectroscopy may give insight into excited state transitions that deactivate after 100 to 200 fs.

Lin Chen's research (Northwestern University) on "Probing Ultrafast Electronic and Nuclear Coherence in Chemical Sciences" also focuses on transient states that cannot be observed without a very fast FEL. Experiments at LCLS with a 30 fs pulse gave some insight into distortion and charge transfer dynamics, but Chen wants a 10 fs pulse and timing stability between pump and probe. She also requested a THz pump and a chemistry lab in the same building as the instruments.

Theo Rasing (Raboud University) reported on "Magnetism on the Timescale of Exchange Interaction," and his vision of making a movie of the magnetization/demagnetization process. He is interested in time scales in the 10 to 100 fs range and length scales on the order of nanometers. Rasing's work requires polarized light, either circularly or linear polarization. He requested a THz pump.

The final talk, "High Resolution Inelastic Scattering with Self-Seeding" by Chi-Chang Kao (SLAC), gave a different perspective. He talked about experiments looking at electron-phonon coupling in disordered systems such as glasses and liquids. This work needs a seeded high intensity beam (10^{12} photons per pulse) in the range of 5 to 10 keV with 50 meV resolution. Kao believes sample damage should not be an issue for this class of experiments.

One-page talks started with "Displacement Cascade Dynamics" by Ben Larson (ORNL), looking at radiation damage on a ps to ms time scale. His work would benefit from a 8-20 keV seeded beam with a duration of 100 fs or less and 10^{12} photons per pulse. "Four-Wave Mixing" experiments, presented by Felix Hofmann (MIT), are investigating nanoscale thermal transport. Hofmann requested a 7 to 8 keV SASE pump/probe with time delay and x-ray gratings to split the beam.

The afternoon discussion examined the implications of each of the morning presentations, beginning with manipulation of magnetization with photons. The question was, could a small femtosecond laser be part of an ultrafast disk drive in the future? While scientists and engineers cannot do this today, some don't see why it couldn't be done. The LCLS-II may provide the needed information on time and length scale evolution and understanding of amorphous, non-homogeneous materials. Relevant length scales are 10 to 50 nm or smaller.

The study of dynamics in transition metal complexes may have broad applications beyond solar cells, prompting the facetious comment, "Time-resolved RIXS is going to solve all the problems of mankind." Realistically, the advantage is measuring charge transfer on a short time scale. One possible grand challenge is for LCLS-II is CO_2 reduction using photochemistry.

The issue for inelastic hard x-ray scattering is the number of photons per pulse, an area where LCLS-II may have an advantage. It may be advantageous to be able to look at extreme conditions of elevated pressure and temperature by tailoring the pulse.

The areas of highest priority for the LCLS-II are seeding and polarization control. The new system should be tunable within the SASE bandwidth. Regarding polarization, stability is an issue and it may be hard to build an inline polarimeter.

For hard x-rays, the suggested upper limit of 13 keV comes from biology, but some say experiments on disordered materials need higher energy, up to 18-20 keV. There is demand for a 100 nm focus, compared to ~1 μm for the SXR instrument on LCLS-I. Challenges for hard x-ray detectors include uniformity of detector response, good signal to noise ratio for sufficient contrast, and dynamic range up to four orders of magnitude.

One idea suggested to maximize scientific output may not be feasible. The concept is to give scientists a short amount of beam time rather than an entire shift to try out new experiments and test instruments. Work done on storage rings may not translate directly to a pulsed laser source, so they would like to try out the LCLS-II system before committing huge research funds. The concern from SLAC staff is that opening this to all users would require proposals and management, and it would become another entire beam line.

The final day of the workshops focused on atomic, molecular and optical science. Lou DiMauro (Ohio State University) asked, "Where is the Strong-Field Regime for X-Rays?" The LCLS-I does not have the capabilities for this research, but DiMauro believes that an LCLS-II with 10^{21} W/cm^2 field strength, 1μm focus, 1fs duration, 1keV may work. He has requested a dedicated soft x-ray beam line with a chamber to accommodate gas, plasma, and condensed matter samples for this extreme intensity research exploring a "new frontier in laser-matter interaction."

Albert Stolow (NRC) reported on "Time-Resolved Photoelectron Spectroscopy" to understand the basic physics of molecules, looking at the coupling between atomic and electron motion. Stolow's focus is stimulated Raman scattering on dilute gas phase samples. His work involves spectroscopy while the molecule is in a fixed position in space, which requires measurements on a very fast time scale.

Stimulated Raman scattering is also important for Nina Rohringer's work (CFEL) on "Self-Amplification of X-Rays in Atomic and Molecular Gases." Her experiments on neon using the AMO chamber at LCLS-I required pulse energy of 0.8 mJ or higher for good results, and the bandwidth of the SASE pulse complicated analysis. Her preferred configuration for LCLS-II would be a seeded source producing two colors within a 10 eV bandwidth. With $5x10^{12}$ photons per pulse, a 5 fs pulse and 1um focus they could achieve 10^{18} to 10^{19} W/cm^2 on target. Rohringer mentioned a color mixing cell as an alternative if a two color beam is not feasible.

Thomas Moeller (TU Berlin) is looking at nanocrystal clusters, as he explained in his talk, "Clusters Structure and Dynamics Studied with X-ray FEL." He has been able to observe single clusters with

LCLS-I, examining scattering patterns and the formation of twin clusters but would like to do time-resolved two-color pump/probe experiments to learn more about phase transitions and temperature-dependent structural changes. Moeller's wish list for LCLS-II includes a 250 eV to 6 keV, 5 to 200 fs pulse with 100 nm variable focus. He also requests a time delay between the two pulses and an energy dispersive pixel detector to see two images, separated by color.

Nine presenters gave one-slide talks on various topics relating to atomic structure. While desired x-ray energy varied, most scientists wanted seeded beams. Pulse duration ranged from 40 down to 10 or fewer fs. Some experiments need high field strength, perhaps as high as 10^{22} W/cm^2. Controlling pump/probe delay is important. Other requests included VMI and fluorescence detectors, capability to scan through zero delay and a higher rep rate for improved efficiency.

The AMO science discussion included both technical and practical considerations. Regarding seeded pulses, someone asked whether an external laser seed would be an option. Consensus was that laser seeding is over five years away, so it is best to concentrate on developing two-color soft x-ray self-seeding. Focusing optics is another concern. A 50 nm focus may be possible for hard x-rays. R&D for state of the art mirrors needs to begin right away.

It is not clear how to best distribute wavelength capabilities between LCLS-I and LCLS-II, and an instrument to cover 0.5 to 3 keV at LCLS-I may be an option. The biology community has some interest in soft x-rays above 2 keV, and for gas phase scattering the AMO community may want to join them.

Scientific areas where LCLS-II may be uniquely qualified include the non-perturbative limit at short wavelengths, which cannot be investigated in the lab, and various molecular applications. High power and short pulses are conducive to the study of nonlinear phenomenon. Capability to incorporate an element-specific view may be an important differentiator. Combining time and spatial resolution is another advantage. Lab-based sources are not intense enough to analyze 50-100 nm particles. For particle clusters, spectroscopy alone is not sufficient, and the ability to combine spectroscopy with imaging may be a selling point to use molecular clusters as a "poster child" experiment.

There is clearly a high demand from the scientific community for a new light source that can provide more beam time and additional capabilities beyond what is available at LCLS-I. It is difficult, however, to really look long-term. It is obvious that having seeded, two-color beams is a high priority, but it is not clear how to accomplish that. Many scientists talked about how they could potentially expand their existing research if they had a dedicated station at LCLS-II optimized based on their current experimental needs. Even if that were feasible, scientific results obtained over the next six years may change the balance of requirements by the time LCLS-II comes online. A successful proposal to the DOE will probably incorporate most of the high demand features, with the flexibility to adjust to accommodate future scientific needs.

4.0 Workshop Contributions from Participants

4.1. AMO

4.1.1. An Electron Beam Ion Trap as a User Instrument at the LCLS-II

Greg Brown(gregbrown@llnl.gov)
Peter Beiersdorfer(beiersdorfer1@llnl.gov)
Lawrence Livermore National Laboratory, Livermore, CA

José R. Crespo López-Urrutia(crespojr@mpi-hd.mpg.de)
Max Planck Institute for Nuclear Physics, Heidelberg, Germany

We propose to build an electron beam ion trap (EBIT) as a user instrument for the LCLS-II. An EBIT provides a high-density ensemble of highly charged ion targets for the LCLS-II free electron laser X-ray pulses. The EBIT user instrument would include a suite of X-ray spectrometers for detecting fluorescence photons with high timing resolution, large collection area, and high-energy resolution, including a microcalorimeter array designed and built at the NASA/Goddard Space Flight Center. Also included would be an ion extraction system used to detect photoions. The EBIT proposed here would be designed to create and trap all astrophysically relevant ions as well as ions relevant for magnetic and inertial confinement fusion, such as highly charged tungsten up to and beyond W^{64+}. The EBIT would be highly portable, so that it (or any of its associated diagnostics) could be easily moved to any of the LCLS hutches and used in conjunction with other instruments. The coupling of an EBIT with the LCLS-II would extend our fundamental understanding of the physics of few to multi-electron highly charged ions, and is a natural extension of previous successful EBIT work conducted both at the LCLS-I FEL and the FLASH FEL.

Some experiments made possible by this coupling include quantitative measurements of photoexcitation and photoionization cross-sections including fluorescent and Auger branching ratios, high accuracy measurements of QED contributions to ionic level structure, and measurements of sub-picosecond lifetimes of excited states. The ultra-bright, ultra-fast LCLS-type pulses are required for these measurements to increase signal-to-noise ratios, which can be prohibitively low in third generation light sources. This is especially important when studying open L-shell ions. In addition, only the ultra-bright, ultra-short pulses of an X-ray FEL can be used in pump-probe experiments to measure sub-picosecond lifetimes. By taking advantage of the high intensities and high X-ray energies of the focused LCLS X-ray pulses, it will also be possible for the first time to induce and measure non-linear effects in highly charged ions in a well-controlled environment.

Measurements of atomic parameters using an EBIT at the LCLS-II have applications across many fields transcending fundamental understanding of multi-electron highly charged ions. Highly charged ions are pervasive in our Universe. Their X-ray signatures can be found in stellar coronae including our Sun, planetary atmospheres, comets, active galactic nuclei, black holes, X-ray binaries, clusters of galaxies, and the cosmic X-ray background, to name a few. The X-rays emitted from these sources have been harnessed for their diagnostic power by premier X-ray observatories currently in orbit, such as Chandra, XMM-Newton, and Suzaku. Decoding the high resolution X-ray spectra provided by these observatories has in many cases been limited by, and

in some cases precluded by, our understanding of the underlying atomic physics. In 2014, with the launch of the Astro-H X-ray observatory, the first ever high-resolution absorption spectra of some of the largest, hottest objects in our universe will be measured using a quantum microcalorimeter. The calorimeter will for the first time measure K-shell X-ray absorption features from ions of iron group elements that enable characterization of the plasma closest to the event horizon of black holes, and in some cases these measurements will be used to measure the actual mass of the black hole. Unfortunately, almost no systematic measurements of the absorption properties of these ions have been completed and the uncertainty in the calculations, where they exist, is often larger than the uncertainties expected in the measurements.

Highly charged ions also play a significant role in a variety of terrestrial sources. For example, the interaction of highly charged ions with strong fields and high temperature plasmas governs the energy transfer in both magnetic and inertial confinement fusion plasmas. Highly charged tungsten will be present throughout the ITER Tokamak and accurate knowledge of its absorption properties will be crucial to our understanding of the ITER reactor. Similarly, the opacity of highly charged ions created during the compression process in inertial confinement fusion plasmas must be better understood before ICF can be employed as a viable energy source.

The first measurements using an EBIT at the LCLS have uncovered a significant problem with the calculations of relative oscillator strengths of two of the stronger transitions in neon-like Fe^{16+}. The results show that the calculations are at least 30% larger than the measurement (see Fig. 1). This reveals a significant problem in the ability of even the most advanced calculations to model the atomic structure in highly correlated multi-electron systems. Many advanced calculations for other, often more complex, systems have been completed or are now in progress using some of the fastest computers in the world, many supported by the Department of Energy. A vast majority of these calculations remain unchecked experimentally owing to the fact that little or no experimental data exist, and more importantly that there is no apparatus available that can provide systematic experimental benchmarks for many of the regimes being studied. Adding an EBIT to the suite of user instruments at the LCLS-II would help alleviate this problem and provide theoretical physicists much desired benchmarks that can be used to guide months of computer time.

Studies of the atomic processes taking place in few- and multi-electron systems are at the brink of an era of profound growth owing to the discovery space created by the LCLS X-ray FEL. An EBIT user instrument provides a novel experimental platform for the LCLS-II that will be used by the atomic physics, the X-ray astrophysics, and the fusion energy physics communities for many years to come.

Comparison of relative photoexcitation oscillator strengths of two of the strongest X-ray lines in neon-like Fe^{16+} measured using the FLASH-EBIT at the LCLS and calculated using various theoretical methods. These results have been submitted to Nature and sent out for review (Bernitt et al, 2012).

4.1.2. Intense x-ray science at LCLS II

Lou DiMauro, Ohio State University

The LCLS XFEL is allowing the first experimental realization aimed at addressing intense x-ray-matter interactions. The initial experiments are unrivaled in scientific discovery but, equally important, they also provide a preview of transformational science whose objectives can be met by LCLS II. One obvious frontier is defined by intensity. The combination of ultrafast duration, high pulse energy and excellent spatial mode has allowed the LCLS to generate intensities that surpass all known laboratory x-ray sources by seven-orders of magnitude. In fact in this regard LCLS is equivalent to state-of-the-art amplified optical lasers, easily achieving electric field strengths in excess of an atomic unit (50 V/Å or an equivalent intensity of 3.5×10^{16} W/cm^2). This raises the obvious question: where is the strong-field non-perturbative limit for x-ray frequencies? At these intensities, matter interacting with optical lasers produces a plethora of non-perturbative, nonlinear behavior, both nonrelativistic and relativistic.

In 1965, Keldysh [1] established an important strong-field metric by extending the dc-tunnel formalism to include ac-fields. He defined an adiabaticity parameter, γ, as the ratio of the tunnel time to the optical period. In the limit where $\gamma << 1$, the ionization is tunneling and non-perturbative. It has been pointed out that $\gamma << 1$ is a necessary but not sufficient condition for a non-perturbative interaction [2]. A more complete set of metrics are defined by the intensity parameters for the bound-state, z_1, and continuum-state, z. The former parameter describes the distortion of the atomic structure by relating the energy characterizing the electromagnetic field to

an energy associated with a bound state. One implication is that in the non-perturbative regime the bound-state power broadening $|E \bullet r| \sim Ea_o$ (where a_o is the Bohr radius) becomes comparable to the single photon energy. This parameter can be expressed as $z_1 = (E/\omega)^2/I_p$ where ω is the laser frequency and I_p the electron's binding energy. The intensity dependence of the continuum-state, z, is defined as the ratio of the quiver energy to the photon energy and can be expressed as $I/4\omega^3$ where I is the laser intensity. A non-perturbative treatment of the atom-field interaction requires that $\gamma < 1$, and z and $z_1 < 1$.

The scaling laws discussed above show that the non-perturbative condition is strongly wavelength dependent. Figure 1 scales the bound, z_1, and continuum, z, intensity parameters into the x-ray regime. In the figure the $z_1 = 1$ curves are plotted for both the K-shell (blue line: core) and L-shell (blue dash-dot: valence) electrons of neon. Not surprisingly, the differential frequency scaling of z_1 and z results in the core-state distortion dominating over the continuum-state above 500 eV photon energy. This is in sharp contrast to the usual picture at optical frequencies of a quivering continuum wave packet. Within this picture, entrance into the strong-field regime will require intensities of nearly 10^{20} W/cm^2, which are beyond the performance of the LCLS. However, the total bound-state contributions (core + valence) result in a dichotomy in this definition since the strong-field limit defined by these states are clearly at odds. The breakdown of the perturbation theory may happen at significantly lower intensities than expected and within capabilities of the LCLS II operational parameters. The physics involved in the perturbative breakdown will be unique to the x-ray regime since it will involve many-body interactions, not seen in the optical regime.

The demands to access this new frontier in x-ray physics are within the design parameters of the LCLS II. Assuming 10 mJ pulse energy, 1 fs pulse duration and 1 μm^2 beam cross-section at 1 keV, the LCLS II will produce 10^{21} W/cm^2 intensity. Non-perturbative behavior should be readily apparent since the LCLS II will reach 170 *au* field strength. The requirements on energy and beam focus area are not particularly challenging, but the need for reproducible pulses of 1 fs duration will benefit from seeded-XFEL operation. Finally, the ability to vary the LCLS II photon energy from low, e.g. 0.25 keV, to higher, e.g. several keV, will enhance the ability to explore the change in ionization dynamics using the scaling laws as a crude roadmap.

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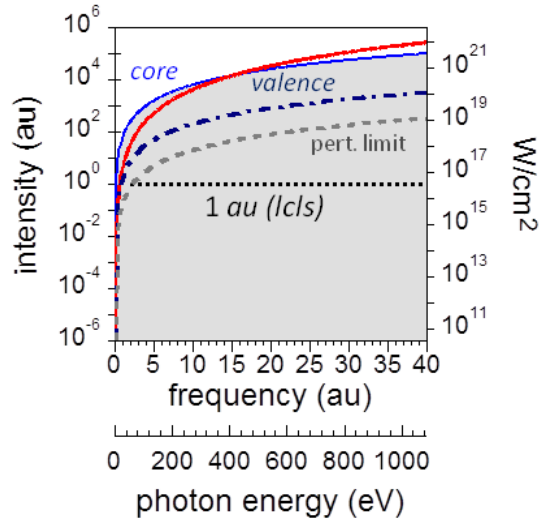
Figure 1: A plot of the z (continua-state: red line) and z_1 (neon K-shell state: blue line) intensity scaling parameter in the x-ray regime as a function of intensity. The lines are for the z-parameters equal to unity and the axis are plotted in atomic units (*au*) and standard units. The situation is very different at x-ray frequencies compared to optical since the distortion of the bound-state dominates and defines the breakdown of perturbation theory. The blue dash-dotted line shows the z_1 parameter for the neon valence L-shell which distorts at much lower intensity than the core. The grey dotted line is the perturbative limit defined as 10% of the L-shell z_1-parameter. Thus, the breakdown of perturbation theory may occur at a lower intensity since single-electron approximation, often used in the optical regime, may be inappropriate.

4.1.3. Creation of Photo-Ionization Pumped x-ray Lasers at Various Photon Energies

Richard A. London

Lawrence Livermore National Laboratory, April 20, 2012

Recent experiments at the Linac Coherent Light Source have demonstrated a photo-ionization pumped atomic x-ray laser (XRL) operating at 849 eV (Rohringer, 2012). This laser works by focusing the x-ray free electron laser (XFEL) into a cell containing neon gas, to establish a population inversion in a long cylindrical volume. Spontaneous emission from atoms near the front end of the gas volume gets strongly amplified in traveling down the axis of the cylinder, resulting in bright XRL radiation co-propagating with the XFEL beam. This laser is expected to have high brightness, narrow bandwidth, and short duration. It is expected to be useful for research in high-resolution spectroscopy, in nonlinear x-ray optics, and, in combination with the XFEL light, as a two-color pump/probe source.

It should be possible to generate XRLs with a variety of photon energies by using other atomic or molecular species pumped with appropriate energies. The anticipated properties of LCLS-II would make it an ideal source to develop and apply such lasers. We present estimates of the required properties of the XFEL radiation to produce lasers using the same pumping scheme as

the neon laser, namely K-shell ionization of the neutral species, which results in lasing of the K_α line of singly ionized species.

We estimate the required XFEL intensity to create photoionization pumped x-ray lasers of various energies. The dominant parameter that determines the output of such mirrorless lasers is the gain-length product (gL). The output grows exponentially with gL up to the point of

saturation. In practice, a gL-value of 20 produces strong output, at or near saturation. The gain is proportional to the oscillator strength of the transition times the population inversion density divided by the line width (Jaegle, 2008). For the K-shell systems under consideration, the oscillator strength is roughly constant, the inversion density is proportional to the photo-ionization rate divided by the Auger rate that depopulates the upper state, and the line width is proportional to the Auger rate. We assume that the photon energy of the XFEL pump is set at a value slightly larger than the K-shell ionization edge, which is in turn slightly larger than the laser energy. We further assume that the length of the laser scales like the attenuation length of the pump radiation. We use published data for the photoionization cross sections (Verner and Yakovlev 1995) and the Auger rates (Walters and Bhalla, 1971). We find the following scaling laws to achieve a fixed gain-length product: $I_{FEL} \sim (h\nu)^{3.6}$ for $h\nu < 1$ keV and $I_{FEL} \sim (h\nu)^{2.2}$ for $h\nu > 1$ keV.

element	$h\nu_{XRL}$ (keV)	$\Delta\nu/\nu$ (10^{-4})	I_{FEL}/I_{FEL_Ne}	$h\nu_{FEL}$ (keV)	E_{pulse} (mJ)	d_{focus} (μm)
C	0.277	1.6	0.02	0.30	0.25	14
Ne	0.85	3.2	1	0.91	0.25	2
Ar	2.96	4.6	17	3.4	1	1
Ge	9.86	6.5	280	11.7	2.5	0.4
Kr	12.7	7.0	493	15.0	2.5	0.3

Table. Properties of photo-ionization x-ray lasers and XFEL pump parameters

Using the scaling laws for intensity and the parameters determined for the neon XRL, we present a table of properties of the x-ray laser and the required XFEL pump for a sample of atomic systems, ranging from C to Ge. The listed pulse energies and focal spot diameters are examples of how the required intensity can be achieved. The energy estimate assumes a pulse length of 40 fs. The XFEL energy is set at 5% above the K-edge energy.

Other elements might be used to obtain intermediate XRL energies. In practice it would be easier to use elements that are available in gaseous form near atmospheric pressure. Noble gases would be the easiest to use. Molecules containing the desired elements might also be used, but they would likely require higher pump energies, due to smaller line strengths. Several conclusions can be drawn from the Table. First, it should be possible to create low energy XRLs, such as 0.277 keV in C, using the soft x-ray beam-line of LCLS-II. The creation of higher energy XRLs appears possible with the hard x-ray undulators. This would require higher XFEL pulse energies and a smaller focal spot than what was used for the neon XRL experiments in AMO endstation at LCLS.

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4.1.4. AMO physics: Controlling inner-shell electron dynamics

A.M. March, C. Buth, G. Doumy, R. W. Dunford, E.P. Kanter, B. Krässig, P. Ho, A. Picón, D. Ray, S. H. Southworth and L. Young

AMO Physics Group, Argonne National Laboratory

Intense, tunable, short-pulse x-rays provide the opportunity to exert control over inner-shell electron behavior, in a manner analogous to that used to control valence electron motion with optical lasers. The motivation to do so arises from the innate challenge of the problem and also from the notion that one might be able to mitigate x-ray induced damage in quantum systems. Studies so far have shown the electronic response to the femtosecond high-fluence LCLS pulses to be largely governed by sequential single photon absorption/ionization events [1], but that upon hitting strong resonances, the dynamics can evolve beyond that described by simple rate equation models to include phenomena such as Rabi cycling [2]. These studies have all been conducted with SASE (self-amplified spontaneous emission) pulses, and the limitations of these chaotic pulses for precision control experiments have been clearly shown. Experiments to date are quite rudimentary, having used only stand-alone SASE pulses, but earlier work has shown the ability to trap inner-shell electrons using a combination of x-ray and optical fields [3,4].

With LCLS-II, we propose advancing beyond these early experiments, as the limitations arising from chaotic SASE pulses are removed, as "self-seeded" pulses [5] for both soft and hard x-rays are expected to produce nearly transform-limited pulses with focused intensities approaching 10^{22} W/cm^2. The further addition of a synchronized optical (or other) field will open many other possibilities to manipulate inner-shell electrons on their natural timescales. Below we describe a few potential avenues of study.

Exploring the high-intensity x-ray regime. LCLS-II opens the door to ultraintense x-rays around 10^{22} W/cm^2, which will allow one to pioneer the next frontier in x-ray AMO physics. Nonlinear x-ray processes set LCLS apart from ultrafast, low-intensity synchrotron sources such as laser-slicing sources. At LCLS-I simultaneous two-photon absorption [6] and Rabi flopping [2] were identified. These processes were, however, still weak and experiments were hampered by the chaoticity of SASE pulse. For LCLS-II, the impact of such processes will be sufficiently strong for them to be studied in detail benefitting tremendously from self-seeded pulses. Atoms and molecules under so extreme radiation are mostly still uncharted terrain. The results are fundamental for many other experiments at LCLS such as matter under extreme conditions and will have considerable impact on astrophysics (e.g., x-ray bursts in supernovae) that rely on accurate data from laboratory research. Additionally, LCLS-II will have the potential to reach the strong-x-ray-field regime. Estimates indicate that the first observation of strong-field processes with x-rays for highly-charged ions should be within reach. This allows one to transfer the powerful field of optical strong-field physics, that has spawned attoscience, to x-rays. However, due to the relatively small x-ray induced quiver motion, one can expect that the physics would be quite different from that in an optical field. Many landmark experiments can be conceived that investigate basic effects in x-ray quantum optics, study the properties of highly-charged ions to test fundamental interactions, and to provide essential data to applied research. Ultraintense hard

x-rays offer prospects for nonlinear x-ray processes with inner-shell electrons of elements beyond the first and second rows (high-z) of the periodic table. Much higher x-ray intensities compared with light elements are necessary due to drastically shortened core-hole lifetimes compared with light elements. As this has never been tried experimentally, fundamental insights will be gained and novel effects may reveal themselves.

Understanding and controlling electronic damage. The interpretation of many experiments at LCLS depends on an accurate understanding of the interaction of x-rays with the target. In bio-imaging and condensed matter studies frequently the target structure will be measured and the relevance of destructive processes that blur the data need to be understood to be incorporated into the analysis. Absorption of x-rays creates (multiple) inner-shell holes that may decay in cascades of electron and photon emission. Damage to the samples arises locally from the disintegration of atoms due to decaying inner-shell holes. On a larger scale around the decaying atom, further destruction occurs from the emitted electrons and radiation that lead to secondary ionization. In addition to the disruption of the electronic structure of the system and thus the measured signal, nuclear dynamics leads to dissolution of the structure and eventually to an explosion of the target. LCLS-II will allow one to reduce x-ray absorption in low-Z materials with intense hard x-rays that have a substantially higher energy than their K-edge. This apparent increase in x-ray transparency at higher photon energies, however, is accompanied by an increased importance of Compton scattering and a decreasing signal strength in coherent scattering. Thus, understanding of damage inflicted by ultraintense radiation is crucial, and AMO physics is the key discipline providing accurate methods for the investigation of the interaction of x-rays with atoms and molecules. Based on the information gained, damage can be controlled by choosing favorable experimental conditions such as pulse duration, pulse energy, peak intensity, and x-ray photon energy.

Optical control of x-ray interaction. An optical laser has offered exciting perspectives to influence the interaction of x-rays with atoms and molecules in synchrotron studies of electromagnetically induced transparency (EIT) with x-rays [3,4] and weak-x-ray laser-dressed Auger decay at LCLS [7]. Furthermore, high-order harmonic generation (HHG) enhanced by x-rays [8] was predicted recently to occur at high x-ray intensities and there are many two-color effects yet to be discovered for ultraintense x-rays. None of the studies [3,4,7,8], however, have been carried out for ultraintense x-rays at LCLS. Specifically, ultrahigh intensities pose exciting questions about the competition between nonlinear x-ray processes, e.g., Rabi flopping, and nonlinear optical processes that can be time resolved exploiting ultrashort x-ray pulses. Ultraintense hard x-rays in conjunction with an intense optical laser offer prospects for optical control of inner-shell electrons of high-Z elements. Paired with increasing Rabi frequency for the resonant coupling of deep core holes to Rydberg states, an increase of the impact of an optical laser on the system is required in order to apply existing two-color schemes [3,4,7,8]. This can be achieved in two ways. First, the optical laser intensity is increased, e.g., for EIT, with x-rays [3,4] and intense-x-ray laser-dressed Auger decay in conjunction with singly charged ions that can sustain such optical laser intensities without significantly ionizing. Second, nonlinear mixing effects of x-rays and optical light such as high-order harmonic generation (HHG) enhanced by x-rays [8] depend on the fact that the core hole survives approximately a cycle of the optical light. Therefore, in order to utilize core holes of high-Z elements that promise attosecond pulses in the multi-kiloelectronvolt regime, one needs to employ shorter optical wavelengths with a correspondingly shorter cycle period. Above all, an optical laser provides, via streaking, an accurate measure of time of ultrafast processes that can be used to time decay cascades of deep inner-shell holes in atoms and molecules and to "film" the changing electronic structure of the system.

Pass-through, shot-to-shot pulse characterization. Little is known about LCLS pulses [7,9]. Simulations of the x-ray lasing in the undulators do not adequately predict the actual pulse properties (energy, duration, peak intensity, substructure) available in actual experiments. However, these characteristics are essential in order to interpret LCLS data as they decisively determine the outcome [1,2]. AMO physics with its rich set of methods is heavily engaged in providing diagnostic tools [7,9] but much effort is still required to develop a reliable shot-to-shot diagnostic of LCLS pulses. For soft x-rays, electron detectors are available that have been used in x-ray pump/laser probe experiments. Specifically, an optical laser is used to dress Auger or photo-electrons emitted after x-ray absorption and the average pulse duration of long LCLS pulses could be determined for selected cases [9]. For ultrashort (femtosecond) x-rays this approach can be extended in the so-called streaking regime [10] but is limited by the timing jitter between x-ray and laser pulses. Recently terahertz (THz) streaking [11] was employed in which the long electric field ramp of the THz light allows one to extract both timing and pulse duration information. Due to limited THz field strengths, this method has not yet been capable of detecting the substructure of LCLS pulses, which remains a challenge. The success of AMO physics-informed methods to analyze soft x-rays is, however, not matched yet by diagnostics for hard x-ray LCLS pulses for which only photon detectors are provided. We are implementing schemes based on x-ray (resonance) fluorescence to overcome this deficiency [12] by using fluorescent x-rays instead of electrons to provide the information. As in previous schemes [7,9,10], optical or THz light will provide timing information. Resonance fluorescence further promises to provide the x-ray peak intensity. The ultimate goal of a LCLS pulse diagnostic is an upstream or downstream tool that informs experimenters about the properties of each LCLS pulse that impinges on their targets to remove the many unknowns associated with current LCLS data. Finally, the ability to run parasitic experiments on LCLS-II could accelerate the development of such techniques.

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4.1.5. Clusters structure and dynamics studied with X-ray FEL pulses

T. Möller, TU-Berlin

Clusters of atoms and molecules can be regarded as a novel state of matter on the nanometer scale.[1,2] For example, different structural and chemical properties can be realized within the same material by just changing the particle size. This covers electronic properties such as the band gap[3], magnetic properties, as well reactivity and catalytic activity.[1,4] As an example, in semiconductor nanocrystals the band gap and thus the colour can be tailored by the size of the particles.[3] A key parameter for understanding cluster properties and function is the detailed knowledge of their size, shape and geometry. A wealth of information is obtained by spectroscopy with light ranging from IR to X-rays. The recent progress in laser technology opens the door to explore light-induced dynamical phenomena far beyond the analysis of ground-state properties of clusters[2]. Furthermore, x-rays offer the unique chance to gain unprecedented insight into the properties of single isolated clusters in the gas phase. X-ray structure determination of

small particles, e.g., macromolecules, clusters and nanocrystals, is directly linked to radiation damage.[5] Thus, understanding light matter interaction at X-ray wavelength is essential for imaging experiments of nanoparticles. The dynamics induced by intense light pulses are strongly wavelength dependent. Experiments with soft-X-ray lasers (FLASH) [6, 7, 8] and also at the LCLS[9] give a flavour of the very rich many-body physics underlying the ionisation processes, subsequent relaxation and disintegration of clusters.

With LCLS II a new regime of x-ray-matter interactions will be accessible. The following fundamental question of light-matter interaction can be addressed and are linked to cluster structure determination:

What are the dominant ionisation processes at x-ray energies?

Which atomic charge states are formed inside highly ionized clusters?

How does the removal of deep inner-shell electrons affect the electron dynamics and photoabsorption?

What is the effect of secondary electrons cascades, e.g. due to Auger electrons?

How does the chemical composition affect the ultrafast dynamics (covalent bond/metal)?

What is the time scale of electron removal from the cluster atoms?

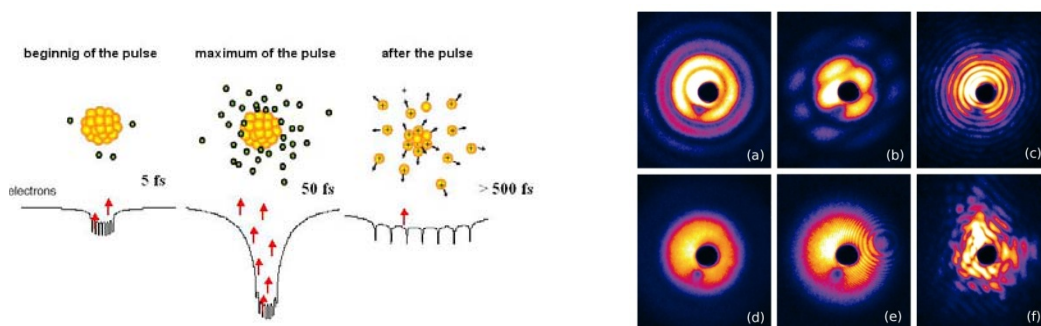How is x-ray scattering structure determination affected by the various ionisation processes?

Fig. 1.a Left: Schematic illustration of the ionisation dynamics of clusters in intense light pulses[7]; 1.b Right Single-shot scattering patterns of large Xe clusters: (a) a single cluster; (b) two clusters in direct contact; (c) a single large cluster; (d) an ensemble of many clusters (more than 10) in the focus; (e) two clusters separated by a large distance; (f) a complex pattern from an ensemble with unknown geometry.[7]

The strongly wavelength-dependent interaction between intense light pulses and clusters proceeds in three steps (Figure 1.a). So far, virtually nothing is known about the interaction of intense x-ray pulses with nanometer-scale matter at power densities which allow imaging of single particles with atomic resolution. X-ray pulses from the LCLS II focussed to a few hundred nm spot will open the door to this completely new regime where all electrons are stripped from the individual cluster atoms, at least for low Z elements. At these power densities, high quality scattering patterns of single clusters can be recorded which allow precise structure determination of clusters and nanocrystals, ultimately with atomic resolution. So far scattering patterns of clusters give only low resolution (~10 nm) information on their shape (Figure 1.b). Especially for individual, mesoscopic nanoparticles, getting precise structure, approaching atomic resolution will be a breakthrough. The structure of single, individual clusters and nanoparticles important for many applications can be revealed for the first time in this way. An understanding of the relationship between x-ray induced electron dynamics as well as nuclear dynamics and their x-ray scattering

response is essential to achieve this goal. The methods of choice will be time resolved experiments based on x-ray/x-ray and IR/x-ray pump–probe schemes.

With this approach important new areas of research can be entered. First, it will allow the study of ionisation and plasma dynamics of size-selected particles. Even more importantly, phase transitions in clusters, especially time-resolved studies of liquid-solid transitions, for example, surface melting, become feasible. LCLS II will provide a unique chance to study the geometry and shape of nanocrystals. Presently this in a completely open field since only a few model systems, e.g., rare gas clusters, could be studied so far. Heterogeneous clusters, core shell structures as well as fractal clusters are of particular interest. Experiments with advanced cluster sources will allow the study of mass-selected cluster ions with almost exact number of atoms and precise control of temperature. An important aspect will be the study of surfaces of clusters and nanocrystals that play a key role in many catalytic processes.

Requirements:

- Direct beam with maximum power, 250eV – 3/6 keV, > 10 mJ small focus, 100 nm, variable pulse length 5- 200 fs

- Synchronized lasers and THz pulses (electron streaking) IR-laser 50 fs pulse length, a few mJ pulse energy single cycle THz pulses

- X-ray split and delay unit (1st and 3rd harmonic) 3rd harmonic more than 1%, energy dispersive pixel detector

- Flexible experimental chamber, endstations decoupled from beamline

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4.1.6. Amplification of spontaneous emission and impulsive Raman scattering of x-rays in atomic and molecular gases

N. Rohringer

The construction of XFELs opens the possibility to transfer non-linear spectroscopic techniques from the optical to the x-ray regime. At 3rd generation synchrotron sources, X-ray spectroscopic techniques are limited to the linear interaction of photons with matter, such as photo-electron, Auger or photo-absorption spectroscopy (XANES, EXAFS). Photon in/photon out techniques such as resonant inelastic x-ray scattering (RIXS) [i] and its radiationless counter part of resonant Auger-spectroscopy [ii] became widely used tools to study the correlation between manifolds of excited states in solids [iii,iv] and molecules [v]. RIXS is a spontaneous process, with relatively small cross section and the time-resolution is usually limited to the core-hole lifetime [vi].

With intensities achievable at XFELs, stimulated processes in the x-ray regime become important. This was demonstrated in a recent experiment, where pulses from the LCLS pumped an inversion of an atomic inner-shell transition in neon, which resulted in the first realization of saturated amplification of spontaneous emission in the x-ray regime [vii]. Along these lines, it should therefore be possible to study stimulated inelastic x-ray scattering with XFELs. Even more appealing would be, to transfer concepts of coherent Raman spectroscopy [viii] and four-wave mixing techniques [ix] to the x-ray regime, which creates a pathway to study coherent wave-packet dynamics and charge-transport in molecules and solid state systems. Atomic and small molecular systems in the gas phase, as well as nanometer scale clusters form a test bed, based on which new non-linear spectroscopic techniques in the x-ray regime can be developed. We identify this as one goal of the soft x-ray beam lines at LCLS II – the development of new, coherent, non-linear spectroscopic techniques in the x-ray regime.

Generally, non-linear coherent x-ray spectroscopic techniques require several phase-stabilized x-ray pulses of different frequency and fs to sub-fs duration, which even with LCLS II will be beyond reach. To circumvent this problem, less complex, non-linear spectroscopic techniques have been suggested, in particular the x-ray analogy of impulsive Raman scattering [x,xi]. For these experimental techniques, a control of the spectral properties of the x-ray pulses is indispensable. The first experiments will focus on small test systems, i.e., the study of time-dependent wave-packet dynamics in small molecules in the gas phase. These first experiments will be tailored to study the details of the excitation (pump) process, assess competing (loss) mechanisms and develop different probe and measurement techniques. Ultimately, the scheme can be extended to study coherent charge transfer in complex systems. The molecular gas-phase experiments will serve as a test bed to develop stimulated x-ray Raman techniques for surface science, catalysis and chemical reactions in solution.

In contrast to all optical pump-probe techniques, impulsive Raman scattering in the x-ray domain is element specific, see Fig. 1. The incoming x-ray pulse is assumed to have a spectral bandwidth which covers a range of valence excitations, hence a typical bandwidth of ~10 eV. This means that both the pump (photon in) and the probe (stimulated photon out) wavelength is provided in the same pulse. The wavelength regime would span from the Carbon K edge (~ 280 eV) to the lighter transition metal L edges (< 3 keV). With LCLS II the broad bandwidth could be achieved by broadband SASE pulses or by sub-fs transform limited x-ray pulses. By tuning the x-ray photon energy close to a core-excited resonance of a specific atom in the molecular complex, an electronic and vibrational wave packet will be launched. In a first series of experiments the transmitted spectrum through an optically dense gas sample will be monitored, which will give insight into the nature of the created wave packet. An additional diagnostic could be Auger-

electron spectroscopy, which would specifically give information of the intermediate core-exited states. A reproducible, controlled spectrum of the incoming x-ray pulse, i.e., a wavelength jitter free source of well-defined width, or a non-destructive measurement would be indispensable for these experiments.

Impulsive Raman scattering is also of interest in dense atomic gases. A recent theoretical study in the VUV regime suggests that a sub-fs resonant VUV pump pulse would induce four-wave mixing and lasing without inversion in an atomic system [xii]. These techniques have the potential of creating attosecond pulses in the VUV regime. The parameter regime for which these higher-order non-linear processes become accessible in the x-ray regime, is being investigated for simple atomic systems [xiii].

Another class of experiments would focus on high-resolution self-stimulated x-ray scattering in molecules. In these experiments, a high-intensity x-ray pulse at small bandwidth (< 1eV) would be tuned across core-excited resonances, or above the element specific K-edge of a molecular gas. In analogy to the atomic inner-shell x-ray laser, a few spontaneously inelastic scattered x-ray photons would drive an avalanche of stimulated scattering events, thereby creating additional intense, red-shifted x-ray beams co-propagating with the XFEL pump beam. This self-stimulated RIXS method could be used to study continuum resonances in molecules [xiv]. It can also serve to create high-intensity two-color x-ray pulses. A dense gas sample would serve as the mixing cell, in which a second x-ray color is produced. At the exit of that gas cell, a second gas sample could be studied by stimulated RIXS. The dynamics of continuum-embedded resonances could be studied by optical pump, stimulated RIXS techniques.

Theoretical studies of these x-ray pump-probe schemes for small molecules are on the way. A first feasibility study indicates [xv], that with typical design parameters of LCLS II (self-seeded soft x-ray pulse of photon energy of 410 eV, pulse duration 5 fs, pulse energy 1 mJ) it should be possible to achieve saturated x-ray amplification on inner-shell transitions in molecular nitrogen, by core-ionization. The emitted x-ray frequency will be discretely tunable, depending on the frequency of the pump relative to the K-edge and the shape resonance. Detailed simulations indicate, that at the point of saturation of amplification it is possible to induce vibrational wave packets (see Figure 2) in the intermediate state manifold. These wave packets are induced by interplay of electronic Rabi flopping and vibrational dynamics and could be probed by Auger-electron spectroscopy.
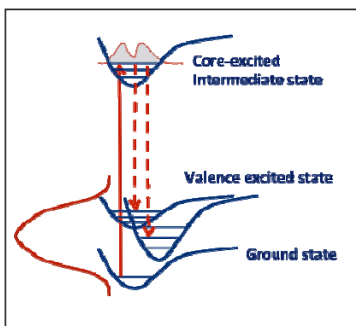

Figure 1: Schematic picture of the impulsive Raman effect. The incoming x-ray pulse has a spectral width spanning over several valence excitations, typically ~10 eV. This corresponds to a pulse duration (temporal coherence) of ~0.3 fs for a transform limited (SASE) x-ray pulse. The main frequency is tuned on a resonance of a core-excited state, thereby specific elements can be selected. The impulsive Raman effect will excite valence and vibrational wave packets in the molecule.
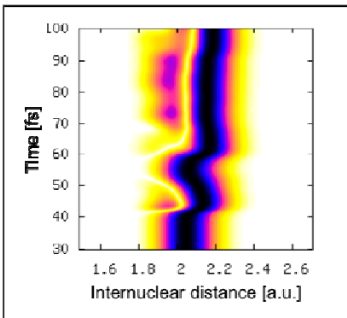
Figure 2: Nuclear wave packet in the core-ionized $^2S_u^+$ state of N_2 created by saturated self-amplified spontaneous x-ray emission following a strong 5 fs XFEL pump pulse [xviii]. X-ray stimulated scattering has the potential of inducing both, electronic and nuclear wave packets in the intermediate core-excited and final valence excited manifold.
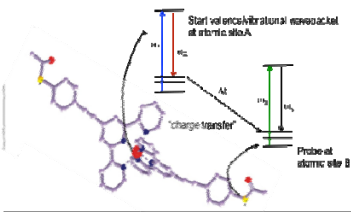

Figure 3: Sketch of an impulse Raman pump/probe process to study coherent charge transfer in a molecule. An electronic/vibrational wavepacket is launched specifically at atomic site A, which could be a photoreaction center of a molecule, and is successively probed at atomic site B with a broad-band pulse tuned to an element specific core-resonance of atom B

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4.2. Materials Sciences and Chemistry

4.2.1. X-ray four-wave mixing: Transient grating measurements of nano-scale thermo-elastic responses

Felix Hofmann, Keith A Nelson

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA

Characterizing and modeling thermal transport over short length scales is a substantial challenge. In insulators thermal energy is primarily transported by phonons. As the length scale of thermal transport is reduced and approaches the mean free path (MFP) of heat carrying phonons, thermal transport deviates from the macroscopic diffusive regime and ballistic transport becomes important. In silicon at room temperature (RT) ~35% of phonons contributing to thermal transport have MFP greater than 1 μm [1]. Since features in microelectronics are now routinely on the ~100 nm length scale, quantitative understanding of non-diffuse thermal transport is essential for thermal management in these structures [2]. In thermoelectric materials nano-structuring can be utilized to minimize thermal transport, whilst maintaining good electrical conductivity [3]. To be able to optimize the performance of these materials detailed knowledge of thermal transport over nm distances and interfaces is required.

At optical wavelengths transient grating (TG) techniques provide a powerful tool for the excitation and monitoring of thermal gradients and acoustic phonons [4, 5]. They rely on the generation of a spatially periodic, temporally transient excitation grating by overlapping two femtosecond laser beams in the sample (Fig. 1a). Absorption of the pump light produces a periodic temperature grating and a transient periodic stress profile. The latter launches two counter-propagating coherent acoustic waves with wavelength equal to the TG period. The phonon-induced changes in strain and the periodic temperature profile couple to changes in the material refractive index that can be detected by the

Figure 1: a) Schematic of transient grating created by crossed pump beams in the sample and probe light path [50]. b) Transient grating diffracted probe signal, Ti film on Si substrate, 0.76μm grating period. Inset: Spectrum of the phonon signal [6]. c) Hard X-ray split-and-delay device [9]. d) X-ray beam crossing schematic using phase gratings. Schematic of high energy grating (lower left) and SEM image of grating (lower right) [10].

scattering of probe light. For example a trace of diffracted intensity as a function of time for a Ti film on a Si substrate, excited with a TG period of 0.76 μm, shows a number of oscillations with ~5 GHz frequency superimposed on an exponentially decaying background [6] (Fig. 1b). The oscillations are due to the counter-propagating longitudinal acoustic phonons (spectrum inset in
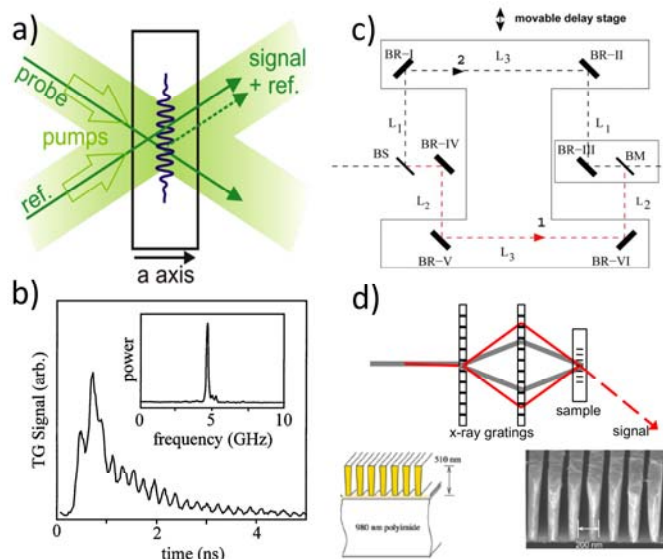
Fig. 1b). The slowly decaying background is due to the decay of the transient temperature grating as thermal energy is transported from peaks to nulls. From this decay the effective thermal conductivity of the material specific to the length scale of the grating period can be extracted. In the Nelson group we have applied TG measurements to energetic materials, thin films, nanoparticles, etc. [5, 7, 8]. The key benefits of the TG method over alternative methods are its non-contact nature and the ease with which different grating periods can be studied. However, at optical wavelengths only TG measurements for grating periods larger than ~700 nm are possible. Clearly this means that we miss the most significant part of our region of interest from a few μm to a few nm.

Extending TG measurements to hard X-ray wavelengths (8-10keV) would allow the TG fringe spacing to be varied from the nanometer range to molecular and μm length scales. This includes the mesoscopic length scales containing essentially all condensed matter correlation lengths, including those associated with phase transitions, intermolecular structure in disordered or partially ordered materials (ordinary or supercooled liquids, polymers, structural or dipolar glasses, incommensurate or rotator crystals, etc.). Our central objective in the proposed work for LCLS II is therefore to extend TG measurements to hard X-ray wavelengths (8-10 keV) for the direct measurement of condensed matter thermal transport on mesoscopic (nm) length scales, of collective structural dynamics on picosecond time scales, and of the high-wavevector acoustic phonons that are involved in both.

In practical terms we envision the following setup: The incident beam would be split into a pump and time-delayed probe using a split-and-delay device similar to that shown in Fig. 1c [9]. The pump beam would be separated into two beams and recombined on the sample by a set of two X-ray phase gratings as shown in Fig. 1d. Pump and probe beams would enter the splitting device non-collinearly, such that they would overlap in the sample with or without the presence of the X-ray grating. Hence the scattered signal and any transmitted pump light will be spatially separated for detection. Using efficiency values from the literature for the X-ray optics [9, 10] we can estimate a requirement of 3×10^{13} photons with energy of 8.4 keV per pulse with $\Delta E/E$ of 10^{-4} and duration of ~40 fs. To maximize the flux available to us within a narrow bandwidth, seeded operation of the LCLS II is highly desirable.

Whilst we initially intend to focus on thermo-elastic measurements, one should recognize the huge general potential of X-ray four wave mixing (XFWM) [11]. At optical wavelengths four-wave mixing (FWM) techniques are a cornerstone of ultrafast nonlinear spectroscopy. Formally speaking, FWM includes most of the time-resolved techniques used to investigate isotropic materials, ranging from the commonplace pump-probe spectroscopy to a wide variety of more exotic techniques. Developing these tools for hard X-ray wavelengths will permit a broad range of nonlinear spectroscopy with hard X-rays, just as FWM has enabled an extraordinary range of nonlinear optical spectroscopy. As such we feel it is vital that X-ray four–wave mixing (XFWM) be on the LCLS II roadmap.

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4.2.2. Fast switching in multiferrorics

Steve Johnson (ETHZ), Urs Staub (PSI)

Multiferroics are a broad class of materials that simultaneously display different kinds of ferroic order parameters, typically ferroelectricity and either ferromagnetism or antiferromagnetism. Among other potential applications, they show great promise for new types of low-power consumption memories that use electric fields to change magnetic states [1, 2]. The advantage over more traditional magnetic storage or spin injection schemes is that no electrical current must actually flow through the device in order to set the state, reducing energy consumption and heat dissipation issues.

While it seems clear that the general idea of using electric fields to control magnetism in multiferroics for memory devices is a realizable goal [3-11], one critical issue that has not been much addressed is the time scale required for such switching. Resonances called electromagnons, strongly coupled excitations of an IR active phonon and a spin wave [12], may hold the key to fast switching. Typical frequencies for these excitations range from 0.3 to 3 THz, suggesting that the fundamental limit to magnetoelectric dynamics is many orders of magnitude faster than for conventional Oersted switching of ferromagnets. Recent theoretical work by Mochizuki and Nagaosa predict that a sufficiently strong, short pulse of THz radiation can switch magnetic order on a time scale of a few picoseconds [13].
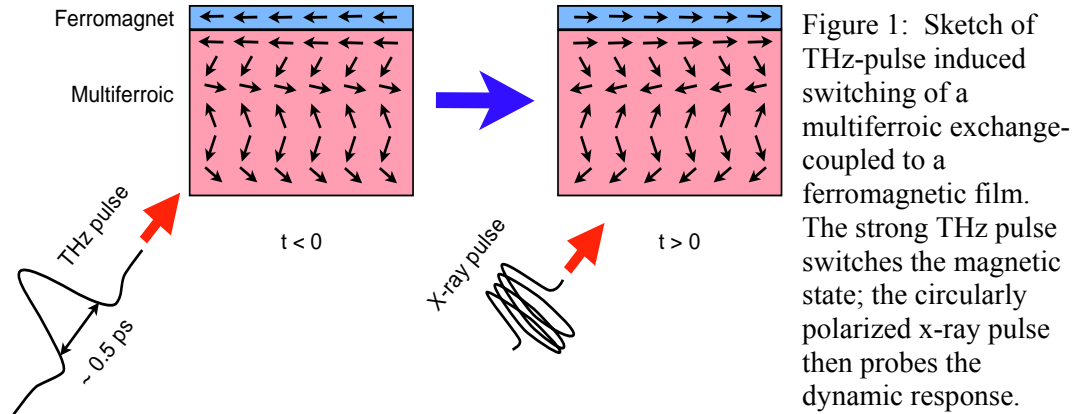

Figure 1: Sketch of THz-pulse induced switching of a multiferroic exchange-coupled to a ferromagnetic film. The strong THz pulse switches the magnetic state; the circularly polarized x-ray pulse then probes the dynamic response.

A key to successful control of dynamic magnetism in multiferroics is an unambiguous, quantitative measurement of the magnetic order parameter with a time resolution of at least 50 fs. Resonant magnetic scattering with x-rays has proven to be enormously successful in static studies of multiferroics [8, 14-16], and recent success with resonant magnetic scattering at the LCLS has shown that these methods can applied in pump-probe experiments with femtosecond time resolution [17]. Currently LCLS is limited in several important ways that preclude the full exploitation of the capabilities of an XFEL source to study this type of problem.

Key requirements for a broad range of experimental capabilities for studying dynamics in multiferroics include:

X-ray photon energies from 400-1500 eV to cover the L- and M-edges of the relevant elements involved in multiferroics.

X-ray photon range from 4-12 keV for non-resonant or K-edge studies, particularly for short-period ordering wavevectors that are inaccessible for longer wavelengths.

Full polarization control of the incoming x-rays. The magnetic spiral structures in many induced multiferroics can be characterized by the differences in magnetic scattering for the different helicities of incoming x-ray radiation. In addition, differences in the scattering as a function of linear polarization angle give information on the direction of the magnetic dipoles.

High-field, carrier-envelope-phase stable THz-frequency pump radiation synchronized to the XFEL beam. Switching in mutiferroics may require a peak field of more than 10 MV/cm for 2-5 cycle long pulses at frequencies of 1-10 THz.

A flexible sample environment that allows for sample temperatures of 5-400 K, static magnetic fields > 1 T, and electrical biases via electrodes. This is required to adequately explore the thermodynamic phase space where multiferrocity is present in a variety of materials.

Effective time resolution of 10-50 fs. Although the THz pump cycle period is longer (100 fs for 10 THz radiation), much of the interesting dynamics will take place on time scales significantly less than this.

The above instrument parameters will enable comprehensive experimental studies of the dynamics of magnetic coupling not only in multiferroics but in any material with magnetic order. With the right instrumentation, LCLS-II could make major scientific contributions to how we understand the dynamics of magnetism in modern materials.

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4.2.3. High-Resolution Inelastic Hard X-ray Scattering

Wei-Sheng Lee, Shibing Wang, Wendy L. Mao, Zhi-Xun Shen, and Chi-Chang Kao

Scientific Challenges

Physical properties of matter are mainly determined by symmetry and low-lying excitations. High resolution momentum-resolved spectroscopy can measure low energy excitations of spin, charge, and lattice encoded with symmetry information in the same data set, providing significant insight into microscopic behaviors of the emergent novel quantum phases. One established case is the angle-resolved photoemission spectroscopy (ARPES) [2], which can measure the momentum-energy dispersion of single particle excitations, providing rich information about the band structures and Fermi surface topology of correlated materials. Another case is the inelastic neutron scattering (INS) [3], which can measure the spin correlation function and phonon spectral function, providing essential information on collective spin excitations and phonons. While single particle spectra, spin excitations and phonon spectral functions can be measured by ARPES and INS, the crucial low energy charge excitations in the momentum-energy space is still missing, making the phenomenology of correlated materials incomplete. In principle, these low energy charge excitations can be measured by inelastic X-ray scattering (IXS) [4]. Although current state-of-the-art IXS instruments can measure phonon spectral functions with an energy resolution of few milli-electron-volts (meV) [5], it cannot resolve low energy collective charge excitations due to insufficient photon flux with similar energy resolution.

An unprecedented high flux and high resolution IXS instrument is possible using self-seeded X-ray FEL at the LCLS-II. Recent preliminary tests at LCLS and supporting simulations indicate that a saturated, self-seeded X-ray FEL beam at LCLS should have a factor of 10 more average flux in ~0.5 eV bandwidth than current 3rd generation sources. Further, it may be possible to improve the self-seeding bandwidth by a factor 10, and also to increase the effective repetition rate by a factor of 10. Combining these revolutionary features, we estimate that the LCLS-II photon flux to be ~10^{13} photons/meV/sec, 1000 times brighter then IXS instruments on current 3rd generation synchrotron light sources. Furthermore time structure of the LCLS-II provides unique opportunities to combine the IXS with extreme sample environments, such as high magnetic field and high pressure. With the high photon flux and extreme sample environments, this proposed instrument will make LCLS-II the world-leading facility of inelastic X-ray scattering, which can address a range of important problems.

Important Problems for IXS

Comprehensive high quality phonon mapping: The phonon spectral function can be mapped out with finer grid in the momentum space, crucial to identify subtle phonon anomalies that may be associated with the electronic degrees of freedom. Furthermore, since the momentum resolution of X-ray scattering measurements is generally much higher than that of INS, the line shape of phonon spectral function can be reliably analyzed, providing richer information about how lattice coupled to other degrees of freedom as well as some of the underlying symmetry properties of exotic orders that are hard to detect by other means. Importantly, IXS can be performed on a small amount of sample, allowing the phonon mapping on novel materials that are prohibited from INS measurement due to the difficulty of synthesizing large single crystal.

Search for novel low energy collective charge excitations: It becomes possible to resolve novel low energy collective charge excitations, such as the collective modes of d-wave superconductivity [6], amplitude and phase modes of charge ordering states, and pseudogap states. Furthermore, since IXS measures the dynamic structure factor $S(q,\omega)$ of charge degree of freedom in the momentum-energy space, one can obtain the partial frequency-integrated spectral function near zero frequency, which is a sensitive quantity to quantum criticality in correlated

materials [8]. As an example, this quantity can be applied to identify fluctuating stripe in cuprates (Figure 1 (a)), which may be crucial to understand high temperature superconductivity. [7, 8]

Charge excitations under extremely strong magnetic field: By taking advantage of the low repetition rate and ultrafast X-ray FEL pulses, IXS instrument can be ideally combined with pulsed high field magnet to create extremely high magnetic sample environment (> 40 T), which is otherwise impossible to be built in a high repetition rate machine, such as a synchrotron light source, due to inevitable magnet heating problem. The magnetic field dependence of charge and lattice excitations can then be uniquely studied at the LCLS-II. In most of the correlated materials, the spin degree of freedom usually exhibits mysterious interplay with the emergent novel quantum states. Furthermore, it is of great interest to study magnetic field induced phase transitions and the associated quantum critical phenomena [9, 10, 11, 12] (see Figure 1, for an example). This high magnetic field related phenomena are at the forefront of condensed matter physics research. Undoubtedly, IXS measurement under high magnetic field will open a new chapter in correlated material research.

IXS applications on other disciplines: In addition to correlated materials research, the proposed IXS instrument at LCLS-II also brings new opportunities to other fields of research. For example, it can be used to determine high frequency collective dynamics in disordered system, such as Hydrogen-bonded liquids, glass formers, quantum liquids and even biological materials. Another example is the possibility of performing phonon spectral function measurements and x-ray Raman scattering measurements for materials under very high pressure (> 100 GPa) and temperature (> 3000 K) by combining pulse laser heating with the LCLS [13-14]. These measurements will provide critical information on the sound velocity, electronic structure and chemical bonding for materials under conditions relevant to Earth and Planetary sciences for the first time.
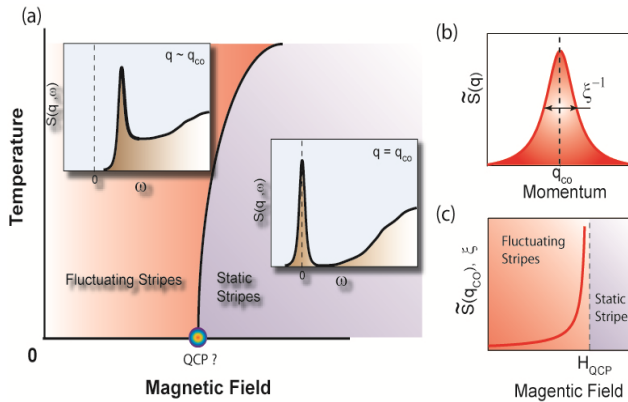

Figure 1 (a) A thought experiment for high resolution IXS measurement to identify a quantum critical point (QCP) in the magnetic field and temperature phase diagram, motivated by a recent magnetic field-induced charge order in a high temperature superconducting cuprates [12] and a theoretical proposal for identifying a QCP [8]. While static stripe states can be measured by x-ray diffraction, the fluctuating stripe phase can be detected by the proposed high resolution IXS instrument, which measures low energy charge dynamics structure factor $S(q,\omega)$. One expects to observed a soft mode and possibly, a gap in the $S(q,\omega)$ spectral function. (b) The measured high resolution $S(q,\omega)$ can be used to obtain partially integrated $S(q)$ near the zero frequency, and the correlation length, z. Both $S(q_{co})$ and z are expect to diverge near the QCP when the magnetic field is varied.

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4.2.4. Time-and Momentum-Resolved RIXS on Correlated Materials

Wei-Sheng Lee, Yi-de Chuang, Andrew Wray, Robert W. Schoenlein, Chi-Chang Kao, Thomas P. Devereaux, Zhu-Xun Shen, and Zahid Hussian

Scientific Challenges

Grand challenges of correlated materials remain at the forefront of modern condensed matter physics. Many fascinating phenomena exhibited by correlated materials are known as "emergence", in which electrons form a variety of exotic quantum phases bearing little resemblance to the expectations derived from the constituents of the materials alone. These exotic phases, including unconventional high temperature superconductivity (HTSC), charge/spin/orbital ordering, fractional quantum Hall effects, colossal magnetoresistance (CMR), and multiferroicity, to name a few, are derived from strongly intertwined spin, charge, orbital, and lattice degrees of freedom and such interplay enhances their sensitivity to external perturbations, yielding rich phase diagrams as functions of chemical compositions and externally applied fields [1]. The proximity of various phases in the phase diagrams, especially near a quantum critical point, can partition the material into electronically distinct domains which experience temporal and spatial fluctuations over many time and length scales. The key challenges to the correlated materials research could be summarized in two different aspects: (1) understanding the underlying organizing principle of the emergence, and (2) controlling the properties and/or even the emergence of these novel quantum phases.
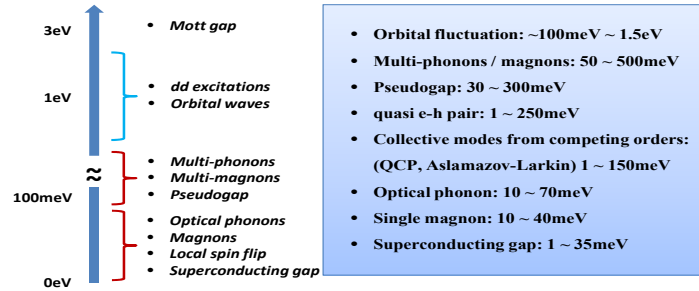
Figure 1: Energy scales of important excitations that can be studied by RIXS.

Time-and momentum-resolved RIXS at LCLS-II

LCLS-II presents a unique opportunity to realize the time- and momentum-resolved high-energy resolution resonant inelastic soft X-ray scattering. In the initial phase of LCLS-II, the RIXS measurements with a moderate resolving power of 5000 can be performed using the SASE X-ray FEL. Later when the seeded soft X-ray FEL becomes available, RIXS measurements with a higher resolving power can be carried out. When self-seeded beams are available, the source will be ideal for spectroscopy measurements with small photon cross section, such as RIXS, in which accumulated (instead of shot-by-shot) data acquisition to minimize the readout and statistical noise is often necessary. Furthermore, the narrow bandwidth of seeded X-ray pulses improves the photon flux by a factor of 10 – 100 over SASE beams, allowing soft X-ray RIXS measurements at a resolving power of $\sim 3 \times 10^4$, which is comparable to current state-of-the-art RIXS instruments. Previous experimental experience suggests that detection efficiency of scattered photons observed in low energy RIXS (at L-edge of transition metal elements) scattering channels from a single spectrometer is approximately 10^{-9} for mid-transition metals (10^{-5} from the solid angle of measurement [14], and 10^{-4} from intrinsic cross sections), making RIXS measurement feasible for *single day* experiments at the LCLS-II. Therefore, combining the superior temporal resolution and unprecedented brightness of LCLS-II, soft X-ray RIXS instruments at LCLS-II will enable us to measure the low energy spin, charge, and orbital excitations in energy, momentum, and time domains for the first time. Here, we elaborate some of the important experiments.

• *Experiments with a moderate R.P. ~ 5000:*

The emergence of the charge, spin, and orbital ordering states reflected in high energy excitations: Charge, spin, and orbital ordering states are commonly observed in complex materials and the fluctuating orderings, such as dynamic charge stripes or frustrated CE-type orderings, are often associated with the aforementioned emergent properties such as HTSC or CMR. Despite their importance to these emergent properties, our current understanding on their underpinning physics is limited by the lack of methods to experimentally observe how electronic ground states evolve on a nanometer scale to form the repeated structural units. Signatures of charge localization through orderings could be reflected in the "high-energy" excitations. For example, it has recently been shown by L_3-edge RIXS that the intrasite *dd* excitations (a valence excitations where particle-hole both reside at the transition metal 3*d* orbitals) of $Pr_{0.5}Ca_{0.5}MnO_3$ exhibit a temperature dependence which tracks the CE charge/orbital ordering transition ($T_{CO/OO}$) [12], while the intersite *dd* excitations revealed by K-edge RIXS show an opposite trend that is caused by charge localization into the CE orderings [13]. By choosing between different RIXS resonances that have "direct" (L_2/L_3 resonance) and "indirect RIXS" (L_1 resonance) scattering processes, one can probe excitations that reside mostly on a single atom or are more delocalized.

The proposed RIXS instrument, when combined with the existing tr-REXS setup, can become very informative in addressing the open questions of how dynamical spin/charge/orbital fluctuations, representing the 'functional' electronic environment felt by the mobile charges,

evolve after selective perturbations and the real-space progression of charge, spin and orbital configurations towards a known ordered ground state.

Temporal evolution of many-body wave functions: In complex materials, the strong Coulomb interaction mixes these single electron wave functions into entangled states, from which novel phenomena such as superconductivity and magnetism emerge. A lack of knowledge of the many-body state at this level is one of the major unanswered issues in all of physics, impacting both fundamental and applied questions of physics. Substantial information about the wave function can be extracted from momentum-resolved RIXS via the selection of initial, final, and intermediate states accessed by tuning incident and scattered photon momenta, energies, and polarizations.

This takes on greater significance when looked in the time-domain. The intrinsic correlated nature of these states leads to non-trivial temporal evolution of the wave function, governing the way in which the individual electrons may un-tangle when driven by external potentials. Upon photo-excitations, a new set of RIXS processes can then be explored, accessing different excited state dynamics and charge relaxation pathways, revealing the temporal evolution of the many-body wave function. With the proposed RIXS instrument, such evolution of the wave function can be mapped out.

The photo-induced suppression of the Mottness:

Many emergent quantum states of interest, such as HTSC, stripe states, and pseudogap states are generated by doping charge carriers into antiferromagnetic Mott states. For these systems, the Mott correlation gap often retains significance, and remains the largest energy scale of direct relevance to the emergent phenomena. While RIXS measurements have been performed to study the doping dependence of Mott gap and in-gap states in thermal equilibrium, it is still unclear how exactly the incremental loss of the Mott physical regime (loss of "Mottness") should be considered with respect to emergent quantum states. Driving the system out of equilibrium via photon pumping can disentangle the dynamics associated with Mottness from the specific ordered structures of novel quantum states in the time domain. Materials can thus be probed by the proposed tr-RIXS instruments in transient regimes that retain Mott correlations but lack more delicate spatial correlations such as charge stripes, providing new insight on their mutual interplay.

• Experiments with a high R.P. > 10,000:

Characterization of fundamental interaction as a function of time: As an example, the spin exchange interaction is one of the fundamental interactions that are believed to be important ingredients of many novel quantum states, such as high temperature superconductivity, magnetism, etc. The strength of spin exchange interaction can be reliably extracted from single magnon's momentum-energy dispersion through momentum-resolved RIXS spectroscopy. It is of great interest to use RIXS to monitor the change of this spin exchange interaction when the system is perturbed by photon pulses. This information could be linked to the emergence of photo-induced superconductivity and lead to a new pathway of further enhancing superconductivity. A similar notion can be applied to the lattice degrees of freedom. The electron-phonon coupling strength can be directly characterized by multi-phonon excitations seen in the RIXS spectrum. Thus, using the proposed time-resolved RIXS technique, the electron-phonon coupling variation can be probed as a function of time when the system is perturbed by laser excitations. Since electron-phonon coupling is often a crucial factor to induce electronic stabilities for a phase transition, the information could further lead to control of emergence in complex materials using light (see Figure 2).

Importantly, specific momentum positions where these fundamental excitations exhibit unusual behaviors could also be identified, revealing subtle, yet important, signatures of electronic coupling at finite momentum, which is otherwise insensitive to optical spectroscopy probes.

The emergence of charge, spin, and orbital ordering states in the time-energy-momentum domain: The low energy dynamics of these electronic orders contain crucial information of the underlying mechanism of how they form out of intricate interplays between different electronic degrees of freedom. At LCLS-I, time-resolved resonant elastic X-ray scattering spectroscopy (tr-REXS) have been performed to reveal the temporal evolution of electronically ordered structures via superlattice Bragg reflections and their response to selective ultrafast optical perturbations. However, information in the energy domain (inelastic channel) remains unexplored. With the proposed RIXS instrumentation, one can performed time-resolved RIXS measurements at the characteristic wave vectors associated with these electronic orders to track their formation in the energy-time domain. The "soft mode" of fluctuating orders or oscillations of collective modes could be observed during this emergence process. This information critically completes the phenomenology of non-thermal dynamics of the electronic orders.

The photo-induced suppression of Mottness: In addition to monitoring the temporal evolution of Mott gap structures with a moderate energy resolution, low energy in-gap states could be directly modified through the addition of photo-induced charge carriers and they can be studied with a high resolution RIXS instrumentation. According to equilibrium state RIXS measurements at the *L*-edges of transition metal elements, these in-gap states appear when the Mott state is suppressed by charge dopants, and have strong momentum-space characteristics [13]. For example, hole (electron)-doped in-gap states in the superconducting copper oxides are enhanced around Q~ (p,0) ((p/2,0)) [13]. The proposed high-resolution tr-RIXS instrument will be uniquely suitable for studying these in-gap states. By exploring their momentum space structure at different delay time after photo-excitation, one can further elucidate the nature of in-gap states and their interplay with correlated electron physics.

Summary and Beam parameters:

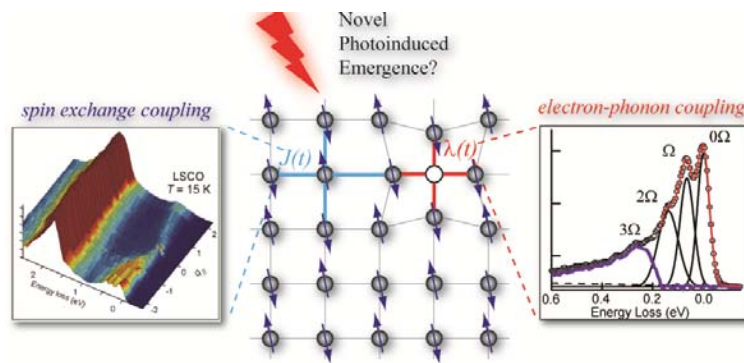Time and momentum resolved RIXS at FEL light sources such as the LCLS-II will provide the

Figure 2: Time- and momentum-resolved RIXS can be used to characterize fundamental interactions, such as spin exchange coupling and electron-phonon coupling in momentum-energy space as a function of time. Spectra of spin and phonon excitations are from Ref. [7] and [11], respectively.

first opportunity to observe collective charge dynamics in the time-momentum-energy domain. It has the potential to greatly enrich our understanding of correlated quantum materials and multi-step electronic processes such as photovoltaics and artificial photosynthesis, and will provide a key missing piece to interpret the time resolved structural information currently obtained from

techniques such as tr-REXS. Ultra-high X-ray fluence at the LCLS-II also has the potential to take the RIXS technique into new regimes of application that will require both theoretical and experimental investigations to properly explore its potential as an incisive tool for studying many body interactions in complex materials. A strong electric field provided by the intense FEL electromagnetic wave can be used to drive Rabi-like oscillations of the core hole state, and potentially dramatically enhance the excitation of low energy states at energies within the beam resolution through auto-stimulation.

Science	Wavelength range	Band-width	Photons per pulse	Pulse duration	Polarization	Focus size	Sample environment	Detector needs
tr-qRIXS	400-2000 eV	0.02%	10^{12}	30 - 100 fs	Variable	<30 x 300 μm[4]	High vacuum	Spectrometer (roll-up)
tr-qRIXS	400-2000 eV	0.002 %	10^{12}	30-100 fs	Variable	<10 x 300μm[4]	High vacuum	Spectrometer

(1) Photon energy covers the *L*-edge of *3d* transition metal elements and the *M*-edge of *4f*-rare-earth elements.
(2) A high resolution monochromator may be needed, if the bandwidth of the seeded X-ray FEL is larger than these numbers.
(3) The pulse duration is consistent with the required bandwidth, if the x-ray FEL is transform limited.
(4) Vertical direction is assumed to be the dispersion direction of the spectrometer, crucial for achieving high resolution.
(5) High resolution spectrometer needs a resolving power of $\leq 2 \times 10^4$ and a full q-resolved capability without breaking vacuum. This may be achieved with a 5-7 m long spectrometer utilizing a CCD detector with 5 μm pixel size.

Other requirements:

Permanent facility: It is very time-consuming to achieve the optimal alignment of high resolution RIXS instrument. The proposed high resolution RIXS instrument should be a permanent instrument. In addition, it is important to have sufficient space to rotate the spectroscopy to different angle to perform momentum-resolved RIXS measurement.

Laser pumping capability: In addition to the most common pump laser in the optical wavelength (e.g. 400 and 800 nm), Mid-IR to THz (1 to 30 THz) is strongly desired. With Mid-IR and THz pumping, one can pump the system resonantly with the collective mode energy, adding the ability of manipulating and control of the emergent novel phases in correlated materials.

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4.2.5. Structure and Dynamics of Water in its Various Forms

Anders Nilsson

Water is the key compound for our existence on this planet and it is involved in nearly all chemical, biological and geological processes. Access to clean water is also one of the most challenging questions for mankind in the coming century, in particular with the prospect of climate change. Furthermore, water is involved in several energy related chemical transformations and is the key in many environmental processes. Although water is the most common molecular substance it is also the most unusual with many peculiar properties such as increased density upon melting, decreased viscosity under pressure, density maximum at 4°C, high surface tension and many more (1). Water properties are also affected by various solutes and are fundamental to biological activity (2).

One of the most essential questions to address for a microscopic understanding of water is: *What is the structure and dynamics of the hydrogen bonding (H-bonding) network in water that gives rise to all these unique properties?* This question has been discussed intensively for over 100 years and has not yet been resolved. Recently there have been indications that we need to derive a new understanding of the structure of water and aqueous solutions based on various synchrotron radiation experiments (3). This has caused an intense world-wide debate (4). In order to gain new information regarding the structure of the H-bond network in water, it is essential to develop new experimental techniques. With the development of fully coherent x-ray sources a new era in structural determination will evolve where we will use ordered beams to study disordered materials. Using ultrashort x-ray beams we can also take structural snapshots of the liquid where pulses are shorter than the dynamical rearrangement of the hydrogen bonding network.

Currently the most direct way to obtain structural information on a liquid is via x-ray and neutron diffraction experiments to extract the pair correlation functions (3). However, to obtain additional information on the liquid we need to obtain higher order correlations that allow also angular information that is hidden in the pair correlation functions.

Using a fully transverse coherent source allow the derivation of higher order correlation from the coherent diffraction pattern. Figure **1** shows a speckle pattern from a colloidal glass obtained at ESFR (5). The left part of the figure shows plots of angular correlations between speckles at a fixed Q value. There are hidden symmetries that become apparent from these angular variations in speckle correlation that varies also at different Q-values.
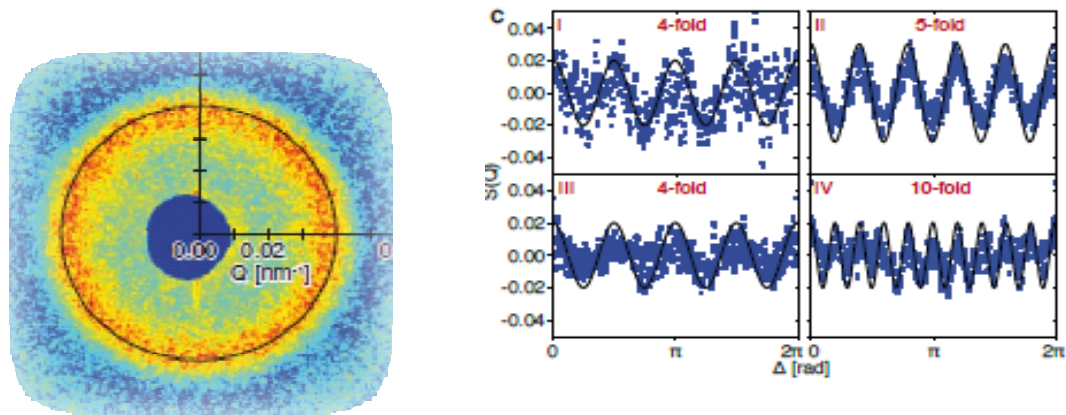
Figure 1. (right) Coherent scattering image showing a typical intensity spectrum with speckle structure of a colloidal glass **(**left) Experimental results after applying the cross-correlator C_Q(D) to the data in *right* at different Q values (5).

Using LCLS II at higher photon energies around 20keV we can obtain a speckle pattern that extend to higher Q values. This will increase the information content and the accuracy of the various higher correlations. Since a liquid will be frozen on the time scale of a single pulse from LCLS we expect to observed speckles. Although the speckle pattern will be weak but the angular correlations can be determine for each individual x-ray pulses and by adding many correlation patterns enough statistics can be obtained. Using Reverse Monte Carlo techniques to fit the higher order correlations at many Q values and also angular correlations between different Q we anticipate that the structure of water and aqueous solutions can be derived to an unprecedented level and can revolutionize our view of water. This can also be combined to obtain temporal information with x-ray correlation spectroscopy and thereby derive the dynamics of the hydrogen-bonding network. There exists hidden dynamic heterogeneities in water that are essential for the understanding of its unique properties.

The mysterious properties of water become even more extreme in the supercooled region below the freezing point (6-8). Figure 2 shows the temperature dependence of the isothermal compressibility, heat capacity and the thermal expansion coefficient. Characteristic for all three is that they are related to fluctuations in the liquid and that these show a minimum where beyond they *increase* upon cooling contrary to expectation for normal, simple liquids. What is even more dramatic is that the temperature dependence of these properties when fit to a power law seems to diverge to infinity at a mysterious temperature of -45 °C (6). In addition, water seems to exist in at least two rather different amorphous forms, low-density amorphous (LDA) and high-density amorphous (HDA) ice, with a density difference of 20% between them (4,5). A possible explanation of these experimental observations is that there exists a second liquid-liquid critical point (LLCP) (5,6), which has been proposed, where the separation between two liquid phases, known as low-density liquid (LDL) and high-density liquid (LDL), would vanish and a fluctuating mixture of local structures resembling the two proposed liquid phases would give rise to the anomalous behavior of liquid water, see Figure 3 (8). However, the temperature where the thermodynamic properties diverge is located in the so called "*no man's land*" where the liquid is

unstable and homogeneous ice nucleation takes place at relatively short time scales, which has so far prohibited a direct experimental study of the liquid under these conditions.
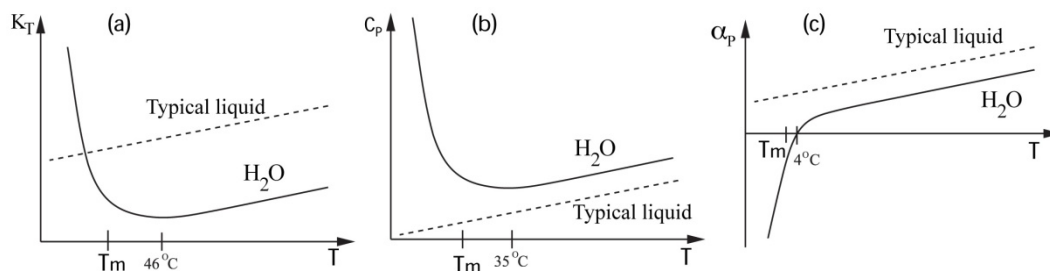

Figure 2. Comparison of thermodynamical response functions for H_2O water (full line) with that of typical liquids (dashed) showing the onset of anomalous behavior already at ambient temperatures and pressure. The melting point is indicated by Tm. (**a**) Isothermal compressibility, κ_T, which shows a minimum at 46 °C. (**b**) Isobaric heat capacity, C_P, with minimum at 35 °C and (**c**) coefficient of thermal expansion, α_P, which becomes negative at 4 °C. (Figure adapted from ref. (6)).

LCLS opens up completely new capabilities for water studies in no-mans land. In particular, it is now possible to access the "*no man's land*" from two directions, high temperatures above and low temperatures below the "*no man's land*". This can be achieved from above by using fast cooling of room temperature micron-sized droplets and from below through ultrafast single-shot probing using x-rays and laser heating to induce a glass to liquid transition of thin amorphous ice films followed by ultrafast probing with x-rays before crystallization occurs. In a recent LCLS experiment it has been demonstrated that the first route into the "*no man's land*" can be attained. Furthermore, LCLS also opens the study of the early stages of ice nucleation. LCLS will permit experiments using X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) methods, to derive the local structure and fluctuations in the liquid around local configurations on various length scales from room temperature and all the way down into the "*no man's land*". Another essential task is to obtain information regarding the timescale of the structural fluctuations in liquid water. Although the dynamics of breaking and formation of H-bonds is on the order of 1-2 ps (9), little is known about the time scale of the fluctuations of larger units in liquid water. This can be addressed by exploiting x-ray correlation spectroscopy (XCS) at LCLS, where an x-ray pulse is split into two pulses separated by an adjustable time delay. The speckle patterns from the two x-ray pulses can then be correlated in time, allowing for dynamics to be probed on time scales from 100 fs to several ns.

There is a large uncertainty in the pressure at which the LLCP occurs –if it exists (8). It would be necessary to develop a droplet system that can operate under pressure for the LCLS experiments. Since LCLS is a 120 Hz pulsed source it is possible to apply the pressure in pulsed manner when the x-ray beam is arriving at the sample. It would be possible to go to the hypothesized LLCP and see huge critical fluctuations at many different length and time scales as expected in the vicinity of a critical point.

It would also be advantageous to conduct pump-probe experiments where the probe represent the full arsenal of the above mentioned x-ray techniques. Here it would be essential to pump the hydrogen bonding vibrations using THz radiation in the 1-10 THz region.

The understanding of water at various interfaces is essential for many processes related to energy transformations, environmental science and various water cleaning technologies. It is important to probe how the interaction at various interfaces influences the fluctuations between LDL and HDL, which may be important to understand the properties of interfacial water. With

LCLS-II there will exist possibilities to probe the structure and dynamics of interfacial water using the above described x-ray techniques.
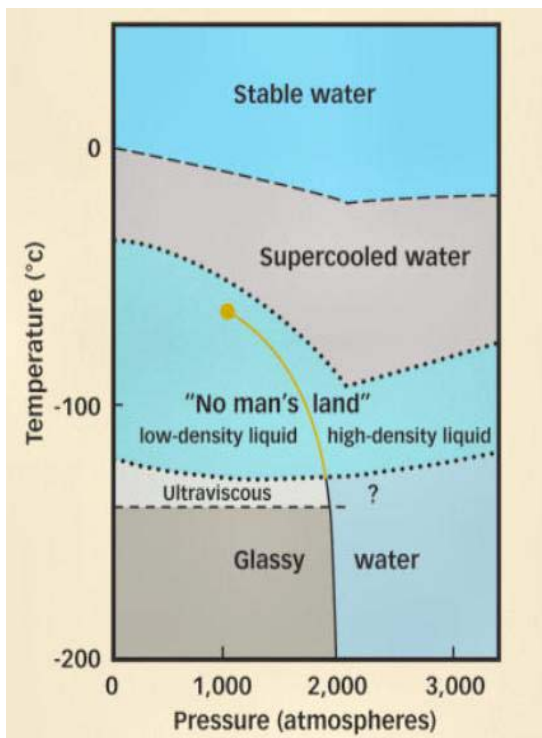

Figure 3 Schematic drawing of the hypothesized phase diagram of water in presence of a liquid-liquid critical point. The glassy water is comprised of LDA (grey) and HDA (blue). The Widom line extends from the critical point.

Water research at LCLS-II should be performed at several different instruments to obtain complementary information. It is essential to develop a detector at the CXI instrument that have a very uniform and linear response to detect weak diffusive scattering. This is, in particular, essential to obtain higher order correlations where the modulations in angle could be less then 0.1%. It would also be essential to go out to Q=10 Å^{-1} with either photon energies of 20-30 keV or large angle detection. In order to detect single shot weak scattering in the low Q region we would need to have higher fluence with energy of the pulse larger then 10mJ. X-ray correlation spectroscopy should cover timescales from femtoseconds to milliseconds. The development of an instrument that can incorporate higher pressures will be essential. It is important to develop a dedicated liquid jet end station for soft x-ray XES measurements. In particular if new schemes using stimulated emission were to be developed. The interfacial science instrument can be combined with the surface science instrument for catalysis.

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4.2.6. Chemical Energy Storage as a Challenge for Surface Chemistry

Martin Wolf (FHI)

The growing demand of the world economy for electrical power, fossil fuels and chemical products implies not only economic problems due to the steadily rising prices of crude oil but also the risk of severe climate changes as a result of the rising CO_2 concentration in the atmosphere. This poses the challenge to transform our future energy supplies from fossil fuels to renewable energy while still enabling economic growth. In principle, a clever combination of photovoltaics, thermosolar-, wind- and hydro-power could satisfy all energy needs of the world if the demand for storage and flexible transportation of these energy resources can be solved. In particular, mobility and transportation, e.g., airplanes or trucks, require the combustion of fuels with high energy density, which can be easily stored and distributed. This defines the challenge to convert renewable energy by electro-chemical and catalytic processes to chemicals, which can serve as feedstock for "solar fuels", see Fig 1. Figure 2 defines such a scheme based purely on renewable energy and refinery processes using CO_2 and hydrogen obtained by electrolysis of water. Such a scenario could fully employ the existing infrastructure and technology for fossil fuels while recycling the CO_2 produced by combustion. However, a key challenge for such chemical energy storage is the development of efficient heterogeneous catalytic processes to convert CO_2 selectively into the desired products.
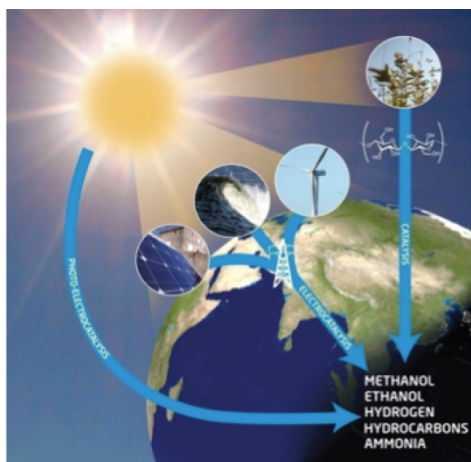

Fig. 1 Illustration of the essential role of catalysis in the production of "solar fuels" (courtesy, SUNCAT center for interface science and catalysis, SLAC)
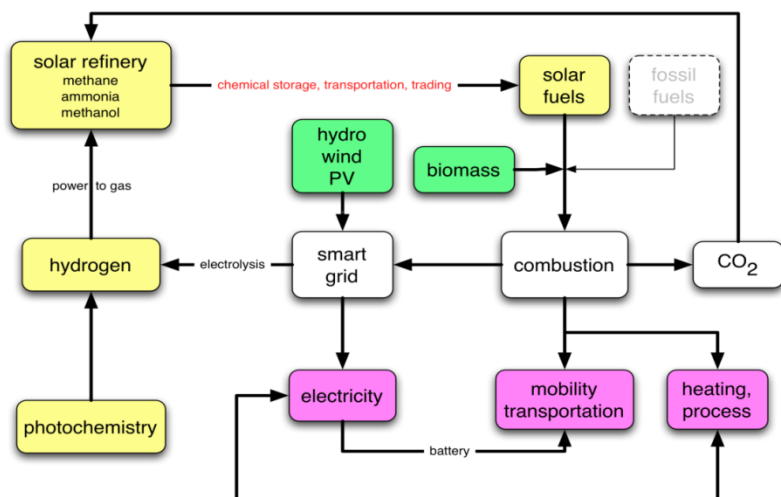
Fig. 2 Concept of future energy supply based on renewable energies and solar fuels produced from hydrogen and CO_2 (courtesy R. Schlögl, FHI Berlin)

Heterogeneous catalysis is a key process in the production of chemicals and energy, which are basic for our daily life. Such catalytic reactions involve typically a complicated sequence of reaction steps at surfaces and a microscopic understanding of catalysis therefore requires an in-depth knowledge about the dynamics of the underlying elementary surface processes. The atomic motion in surface reactions occurs typically on a picosecond-or femtosecond time scales. This provides the challenge to identify short-lived reaction intermediates and to obtain direct information about the key process of making and breaking of chemical bonds. Although time-resolved surface studies have yielded some insights in the past, e.g., about diffusion or desorption processes, the "holy grail" of probing the time evolution of a real chemical reactions, i.e., dissociation and formation of chemical bonds directly at the surface, has not been realized so far. We stress that LCLS-II provides a completely new ultrafast tool to follow chemical reaction on surfaces in real time, see Fig. 3. X-ray techniques allow us to visualize the dynamics of electronic structure changes in connection to bond making and breaking during catalytic reaction.
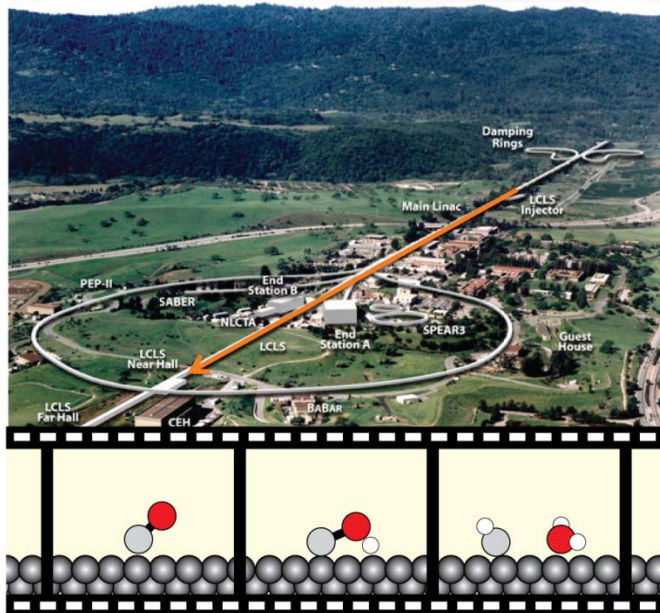
Fig. 3 LCLS-II delivers coherent ultrashort x-ray down to 1 fs that will allow the usage of atom specific spectroscopy and diffraction to follow catalytic reactions in real time.

4.2.7. Ultrafast in-situ surface chemistry

Hirohito Ogasawara (SLAC), Jerry LaRue (SLAC), Martin Wolf (FHI), Martin Beye (HZB), Wilfried Wurth (Hamburg) and Anders Nilsson (SLAC)

Heterogeneous chemistry plays many vital roles in our world, from the thermocatalytic, electrocatalytic and photocatalytic conversion of chemicals, to protecting the environment by removing unwanted and often toxic byproducts, to creating renewable forms of energy such as liquid fuels. Heterogeneous chemistry functions by reactions on surfaces that provide alternative mechanisms for the making and breaking of chemical bonds, which can lead to more efficient and selective reactions. In order to follow the individual reaction steps in real time, which take place on the femtosecond time scale, it is necessary to probe the reactions using ultrafast methods. The capabilities of LCLS-II have the potential to vastly expand what is possible today.
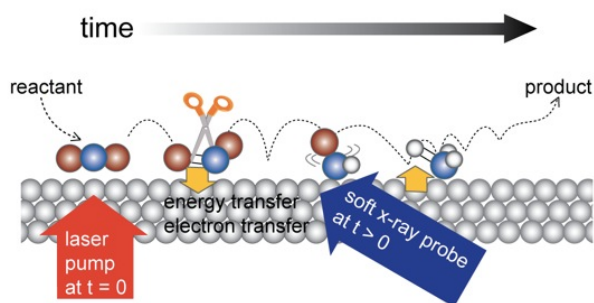

Figure 1: Using a laser pump, soft x-rays can be used to probe the time evolution of the reactants, intermediate states, and products during the course of a reaction.

Soft x-rays provide the opportunity to probe not just element specific atoms on surfaces, but also elements populating intermediate states during chemical reactions, which are usually short lived. Figure 1 shows how reactants, intermediate states, and products evolve in sequential manner during a typical catalytic process on the surface of a catalyst. Intermediate states may be present only as spectators or as species that are directly participating along the reaction pathway. These intermediate states are populated transiently, so it is critical to use femtosecond pump-probe techniques to monitor them. Soft x-ray emission spectroscopy (XES) provides a way to probe changes in electronic structure during the course of a reaction. The occupied electronic structure of the reactants, intermediate states, or products can be selectively studied by tuning the x-ray energy to resonantly excite the state of interest.

The first XES demonstration experiment at LCLS showed that XES in the soft x-ray region is a suitable technique to probe surface dynamics of submonolayer amounts of light elements, such as oxygen, nitrogen and carbon on metal surfaces [Dell'Angela et al., to be submitted]. We propose to utilize LCLS-II as a tool to understand reaction mechanisms on the ultrafast timescale and to determine parameters to control the surface reactivity under catalytically relevant conditions. Some of the most catalytically important insights in the reaction mechanism that we need to obtain are related to the active state of the catalyst and the potential intermediates during operating conditions. Since XES is based on photon-in/photon-out spectroscopy, these experiments can be carried out in-situ under ambient pressure, which approaches catalytically relevant environments.
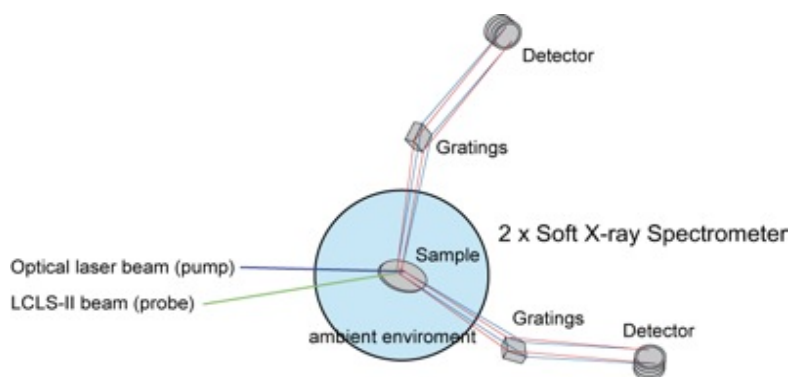
Figure 2: Schematic of the experimental in-situ XES setup. Two soft x-ray spectrometers are used to obtain polarization dependent information of the chemical bonds under ambient condition.

In probing these types of reactions, we support two major improvements to the existing LCLS setup: (1) an intense monochromatic seeded soft x-ray beam and (2) a highly efficient x-ray spectrometer setup. Because the x-ray emission signal is weak due to a small cross section of the radiative core hole decay, it is important to increase both the x-ray probe intensity and the detection efficiency. Using LCLS, we have demonstrated that the LCLS pulse after the monochromator is not destructive to the adsorbate. Therefore, the current experiments are still flux limited, and a high intensity source of x-rays are needed to collect enough data to obtain good signal-to-noise ratios. The self-seeding option of LCLS-II, which will deliver Fourier-limited monochromatic x-rays with high intensity, would result in experiments with x-ray emission signals orders of magnitude above what is achievable today. With this increase in signal, multiple surface reactions could be probed. Tunability of the incoming x-ray polarization is also important to enhance the selectivity of the excitation process. The polarization dependent x-ray emission signal projects information about chemical bonds in a given symmetry, which can be acquired simultaneously using multiple high efficiency x-ray spectrometers.

Finally we like to point towards other exciting opportunities to develop alternative ways to pump chemical processed on surfaces. Femtosecond visible laser pulses are currently used to initiate surface reactions with optical excitations at $t = 0$ and the time evolution is then probed using the LCLS x-ray pulse. The ultrafast visible laser pulses produce short lived and highly excited (hot) electrons and holes at the surface. Thermally excited catalytic reactions are driven either directly or indirectly by the heat generated through phonon coupling of hot electrons and holes. These thermal excitations include phonons (substrate lattice vibration), frustrated vibrational motion of molecular adsorbates, and translational and rotational motion of molecular adsorbates in the adsorption potential well. When chemical bonds either break or form during reactions, the excitation of these vibrations is necessary to mediate the nuclear motion along the reaction coordinate.

Here we consider the direct excitation of phonons, as well as frustrated rotational and translation motions of molecular adsorbates, by mid to far IR radiation without going through the hot electron mechanism as in the case of optical laser pumps. Since atoms and molecules in the gas phase do not have these excitations, access to the thermally induced phenomena via IR radiation is constrained to the surface. With a laser or accelerator based, time-synchronized source, the combination of IR and X-ray spectroscopy offers a unique possibility for FEL facilities to study ultrafast chemistry at surfaces, as shown in Figure 3.
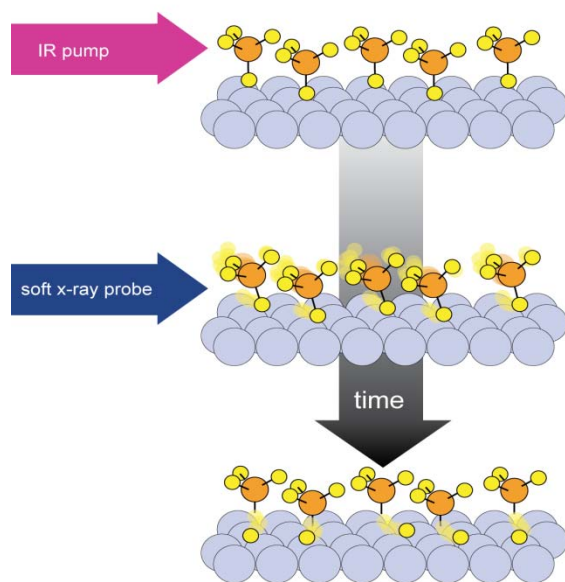
Figure 3: Schematic sketch of the IR pump and X-ray probe experiment. The molecular motion at surfaces to initiate the reaction is optically triggered by the IR radiation. Time evolution of the reaction is probed using an ultra-short x-ray pulse.

By combining a seeded, intense, and monochromatic x-ray pulse with high efficiency x-ray spectrometers and an IR pump source, LCLS-II will have the resources necessary to probe and understand the most fundamental and important surface catalysis issues facing the heterogeneous catalysis community today. This will help pave the way for advancements in cleaner energy, renewable fuels, and more efficient industrial production of chemicals.

4.2.8. Emergence and control of magnetic order

Theo Rasing, Radboud University Nijmegen

"How do complex phenomena emerge from simple ingredients?" has been named one of the six grand challenge areas for condensed matter and materials physics for the next decade [1].

Introduction

Though all properties of matter are based on quantum electrodynamics and its two main constituents, electrons and photons, it is their collective response that determines the rich variety of optical, magnetic, and (super) conducting properties that emerge at a length scale of several unit cells or mean free path, i.e. nanometers, and on a time scale in which electrons or photons traverse those, i.e. femtoseconds. Understanding the interaction of electromagnetic radiation with matter has not only led to the development of quantum theory, and subsequently of solid-state physics, electronics and lasers, but also to laser cooling and "coherent control" of atoms and molecules, allowing such spectacular observations as Bose-Einstein condensation [2], the control of chemical reactions [3], the realization of q-bits and the first steps to quantum computers, such developments being honored by Nobel prizes in 1997, 1999, and 2001. These advances naturally lead to the question: "would it be possible to achieve full optical control of condensed matter systems?" **Emergence and control of magnetic order**

In recent years it has been demonstrated that the influence of magnetic fields on light, leading to the well-known Faraday and other magneto-optical effects, has a counterpart in an inverse Faraday effect: the change of magnetization with light. This work has led to the demonstration of all-optical reversal of magnetic domains by femtosecond (fs) laser pulses [10].

These intriguing observations have triggered intense experimental and theoretical efforts to understand the fundamental processes behind such ultrafast laser-induced dynamics [4]. Yet, one must conclude that the dynamics below 1ps is currently hardly understood, due to two problems:

1) Most experiments use fs all-optical pump-probe techniques and magneto-optical effects; however, the interpretation of the latter is ambiguous.

2) In the field of ultrafast dynamics, theoretical developments lag behind experimental ones.

The problem with optical probing is that laser radiation in the visible and near-infrared probes mostly the electronic and magnetic properties of the d-electrons. However, it is often the interplay between d- and f-states, and between the spin and orbital degrees of freedom that is responsible for the rich variety in properties of these magnetic and strongly correlated systems [5,6]. Even if state-of-the-art theoretical studies incorporate non-equilibria between different baths of electrons, spins and lattice [7], they are still performed under the assumption of quasi-equilibrium and thus inapplicable for describing strongly non-equilibrium states.
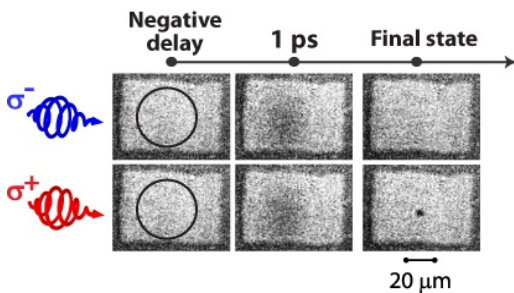

Figure 1. Single shot magneto-optical imaging of thin magnetic FeGdCo film after excitation with circular fs laser pulses (adapted from Ref. 8). At a delay of 1ps, top and bottom images display a similar paramagnetic state as evidenced by the grey contrast. However, the final state displays an oppositely oriented white (top) or black (bottom) domain. How does magnetic order emerge and why can it be controlled?

A clear example of the limitations of present techniques and understanding laser-induced switching of the magnetization is illustrated in Fig. 1, showing some single-shot magneto-optical microscopy pictures taken at time intervals after a thin magnetic film is brought into the paramagnetic phase using optical excitation with circularly polarized fs laser pulses. The magneto-optical microscopy images at a delay of 1ps are practically identical and show a fully demagnetized state for both polarizations of the excitation. Why and how does one disordered system (bottom) evolves in a magnetically ordered but reversed state and the other (top) returns to the original ordered state? The final state is clearly determined by the pump polarization, though this excitation was only of 100fs duration. How does the fully disordered system remember this? Along which path does the state at 1ps develop into a magnetically ordered final state? It is obvious that to answer these questions one requires the application of a technique that can probe magnetic order on a much smaller scale than the micron resolution of the present experiment, but without sacrificing the temporal resolution!

Fs X-ray scattering: probing at fs time and nm length scales

X-ray Magnetic Circular Dichroism (XMCD) is a well-established spectroscopic technique to probe the spin and angular contributions to the magnetic moments in an element specific way. A recent breakthrough was made at the Femtoslicing facility of the Helmholtz-Zentrum Berlin, where the modulation of the synchrotron radiation with a fs laser pulse has led to the generation of fs X-ray pulses [9, 11]. We have used this opportunity to probe laser-induced magnetization dynamics in FeGd by measuring the XMCD changes with circularly polarized 100 fs X-ray pulses at the Fe L_3 absorption edge and at the Gd M_5 edge. At these energies the dynamics of the 3d magnetic moment of Fe and the 4f moment of Gd can be probed, respectively, because of the

non-ambiguous relationship between the measured XMCD signal and the elemental magnetic moments given by the sum rule [12]. To our great surprise these experiments revealed distinct demagnetization dynamics of the Fe and Gd magnetic moments on the sub-picosecond time scale. This element-specific demagnetization subsequently led to a *transient ferromagnetic state despite the strong anti-ferromagnetic coupling* between the Fe and Gd sub-lattices [Rad2011]. While groundbreaking, these experiments suffer from a very low photon yield (slicing effectively uses only a very small fraction of the beam flux) and poor spatial resolution that is no better than optical (a few microns).

The new Free Electron based X-ray facilities such as the LCLS at Stanford solves both shortcomings. Starting from an intrinsic fs electron bunch, the XFEL offers a high photon flux of tunable X-ray radiation, allowing element specific scattering experiments that yield, via the inverse of the scattering wave vector, spatial information down to nm resolution. The fs pulses can be used both in single shot and in a pump-probe mode. Combining this with the use of XMCD provides a totally unique experimental tool that will allow a combined nm spatial (via the scattering wave vector) and fs temporal (via the intrinsic pulse structure of the XFEL) resolution of the charge, spin and orbital correlations.

Challenges

1. Understanding angular momentum transfer at fs time scales
2. Understanding magnetic phase transitions at fs time scales
3. Understanding nucleation of stable magnetic domains at nm length scales

Approach

Emergence of magnetic order and spontaneous symmetry breaking initiated with a fs pulse

For the *initial nucleation dynamics*, time resolved soft X-ray scattering need to be used, as this can simultaneously give information about the magnetic ordering via XMCD and the length scale at which this happens via the scattering angle. We have performed the first ever experiment with access to these microscopic dynamics last year at the LCLS: time-resolved resonant soft x-ray scattering of an optically laser pumped FeGd structure. The results are tantalizing and show nucleation and growth of the ordering of Gd spins occurring in specific regions on the length scale of 10 nm. At first this new technique will be applied to a simple ferromagnetic structure like Fe, which can be brought suddenly into its paramagnetic phase via an intense fs optical laser pulse. In a second step we want to study the nucleation dynamics in the well-known alloy FeNi and in FeGdCo. Using the element specificity of XMCD, the ordering dynamics of the individual moments of Fe and Ni can be probed, as well as the correlations and possible angular momentum transfer between them.
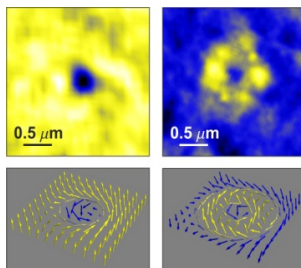

Figure 2. SNOM images and corresponding spin structures in a TbFe film after excitation with single linearly polarized fs laser pulse for two different laser fluences (left: 5mJ/cm^2; right: 7mJ/cm^2).

Skyrmion-like structures.

A particularly intriguing and challenging goal is to understand the formation of the skyrmion-like structures that are formed by fs optical excitation of a TbFe film (see Fig. 2). These structures appear above a certain fluence threshold and changing the laser fluence can reproducibly vary their structures. They can be created by both circularly and linearly polarized light and they are absolutely stable over time.

Questions: How are these structures created? How do they nucleate and how do they subsequently evolve to their final state?
Their stability make these structures very interesting for storage applications. How are these soliton-like structures created? What determines their final shape*?*

In the model systems mentioned above, the ordering takes place by cooling from the high temperature paramagnetic to the low temperature ferromagnetic phase. Complementary to these systems we would like to study materials like TbFeCo or FeRh, where a fs heating pulse brings the system *from a low temperature paramagnetic or antiferromagnetic to a high temperature ferromagnetic phase, respectively.* In TbFeCo this transition is accompanied by a first-order structural phase transition from an amorphous to a crystalline phase. By simultaneously measuring XMCD and the corresponding X-ray Bragg peaks, a full dynamical picture can be obtained of this fascinating emergence of both magnetic and crystalline order.

Application perspectives

Magnetic recording and processing magnetically stored information is a multibillion dollar (33.4B$ revenue in 2010) industry, which, on the one hand, has a huge world-wide market and, on the other, is based and strongly dependent on novel technological concepts. Presently, the density and speed of one-bit-recording is facing a fundamental and technological gap. Therefore, the search for advanced materials and novel concepts of ultrafast control of magnetism on the nanoscale has become an issue of vital importance for magnetic data storage and information processing.

All-optical switching is a potentially viable technique for the next generation magnetic storage. For this to become reality, all-optical switching has to be demonstrated at sub-100nm length scales and on materials where the thus written domains remain stable. This requires the investigations of new materials that have to combine magnetic hardness (for the high density) and optical switchability. We have recently shown that all-optical switching can occur by a heat pulse alone in ferromagnetic materials [13,14]. The new concepts to develop hybrid, synthetic ferrimagnetic materials and to use laser-generated femtosecond pulses of effective magnetic field and/or heat for magnetization reversal go well beyond the state-of-the-art in magnetic storage and information processing technologies. It may deliver solutions to the need of the ever-increasing density and speed of data storage and manipulation as well as initiate a development of novel technology for unprecedented fast THz magnetic recording and information processing. This will require further research on these new materials that combine sub-picosecond dynamics with nanometer resolution, something that can only be done at the LCLS.

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4.2.9. Stimulated X-ray Scattering: Towards imaging the low-energy excitations in complex magnetic materials on the mesoscale

Andreas Scherz

The advent of the x-ray free-electron laser (XFEL) has opened the door to nonlinear spectroscopic techniques at x-ray wavelengths. Recent examples of nonlinear X-ray matter interactions include the realization of an atomic x-ray laser [1] based on a photo ionization scheme in Ne, the observation of Rabi cycling in a resonantly excited two level system [2] and reports on stimulated X-ray Raman scattering observed with coherent x-ray diffraction [3]. These results signify the feasibility of studying charge transfer dynamics in molecules, chemical reactions, and phase dynamics in complex materials at unprecedented temporal and spatial resolutions. In the optical regime, stimulated Raman scattering, coherent anti-Stokes Raman scattering (CARS), four-wave mixing and transient grating spectroscopy are essential concepts of ultrafast nonlinear spectroscopy. The potential and prerequisites for time-resolved, nonlinear x-ray Raman spectroscopy at LCLS II have been addressed previously in more detail [4]. Here, we devise a technique based on coherent diffraction imaging (CDI) for obtaining structural information on low-energy excitations in complex magnetic materials.

Understanding, tailoring and ultimately controlling emergent phenomena in complex materials is one of the forefront grand challenges in condensed matter physics. The strong local interplay of spin, charge, orbital and lattice degrees of freedom leads to novel phases on the mesoscale that govern the macroscopic properties of the materials such as magnetism, colossal magnetoresistance and high temperature superconductivity. Understanding of such ordering and phase kinetics on relevant length and time scales is important for tailoring and exploiting material properties in nanotechnology. Conventional resonant inelastic x-ray scattering (RIXS), the x-ray analog of resonant Raman scattering, has emerged over the last decade as a powerful new tool for the study of low-energy excitations (meV-eV) in solids [5,6]. However, time-resolved or even spatially-resolved studies are presently out of reach at third-generation synchrotrons due to small x-ray cross sections.

We propose coherent diffraction imaging of low-energy excitations in complex magnetic materials based on an optical pump / resonant stimulated x-ray Raman probe. Conventional resonant CDI and resonant elastic x ray scattering (REXS) reveal the lateral structure of charge, orbital, and spin ordering in materials on nanometer length scales with element-, shell- and chemical specificity [7]. The CDI technique itself is capable of obtaining femtosecond single shot images with X-ray lasers, and time-resolved experiments allow for studying transient electron and spin dynamics triggered by ultrashort optical excitation [8,9]. The CDI contrast relies on the sample refractive index, $n = (1 + \chi^{(1)} + \chi^{(3)} E^2 + \ldots)^{1/2}$ and is proportional to the first order susceptibility, $\chi^{(1)}$, (~10^{-2} at soft X-ray resonances) because of the much smaller spontaneous inelastic scattering cross section. Aside from coherence requirements, the small inelastic cross section nearly precludes imaging of the fundamental excitations that underlie the ordering phenomena. This can be overcome with stimulated x ray Raman at sufficiently high x-ray intensities, $I \sim E^2$: Theoretical studies in the soft x-ray regime for the Carbon K edge [10] and the Co metal L edges [11] show that $\chi^{(3)}$ at x-ray wavelengths is of the order of $10^{-22} m^2/V^2$, similar to the electronic polarizability to third order in the optical regime [12]. At moderate fluences and femtosecond duration x-ray pulses, supplied at LCLS with SASE and seeded schemes, stimulated x-ray Raman would give sizable, nonlinear contributions to the refractive index. The scalability of stimulated X-ray Raman holds the key for probing fundamental excitations with CDI.

We envision the following instrumentation, cf. Fig. 1: For stimulated X-ray Raman, ideally two seeded XFEL pulses of narrow bandwidth and corresponding short pulse duration are required. The pulses of same polarization (linear or circular) should have different main carrier frequencies with a variable energy separation ranging from 0.1eV up to a few eV. An x-ray spit-and-delay device will separate and then spatially and temporally recombine the pulses on the sample. Both the primary and stimulating pulse mix at the interaction point and diffract coherently onto separate detectors. The two diffraction patterns contain complementary information on the lateral variations of the linear ($\chi^{(1)}$) and the non-linear ($\chi^{(3)}$) refractive index representing the underlying low-energy excitation spectrum. By taking the sum (~ $\chi^{(1)}$) and the difference (~ $\chi^{(3)}$) of the two CDI patterns, one can separated the two contributions for image reconstruction.
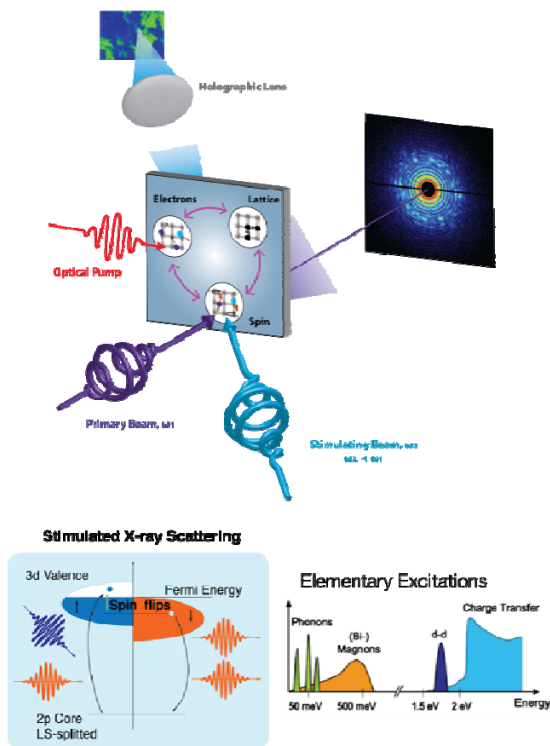
Figure 1: Experimental setup for optical-pump stimulated X-ray Raman probe for studying transient state dynamics and excitation spectra on the nanoscale. An optical pump pulse triggers the nonequilibrium dynamics that is probed by two x-ray pulses of different frequencies coincident on the sample. Two array detectors record the coherently diffracted beams. Images of the transient state and the underlying excitation spectrum are obtained by combining the two complementary diffraction patterns.

Initially, one can consider exploiting impulsive stimulated X-ray Raman, where a broader bandwidth pulse (with the potential of using ultrashort (~fs), transform limited pulses) is split into two pulses instead having two seeded XFEL pulses. This approach would require the spectral properties of the pulse to be recorded. In this geometry, the two CDI patterns would carry identical information and the linear and nonlinear contributions could not be disentangled and therefore only a composite image reconstruction would be possible. A spectrometer could replace one of the imaging detectors as it becomes obsolete, in order to characterize the spectral properties of the stimulating pulse behind the sample.

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4.3. Biology

4.3.1. Watching proteins function on the chemical time scale

Philip Anfinrud, Friedrich Schotte, and Hyun Sun Cho

Laboratory of Chemical Physics/NIDDK

National Institutes of Health

Bethesda, MD 20892

Proteins make life happen. Of the more than 20,000 protein-coding genes found in the human genome, some code for enzymes that catalyze the making and breaking of chemical bonds, a task that is accomplished with remarkable selectivity and efficiency. The amino acid side chains surrounding the catalytic site in an enzyme tend to be highly conserved, and create the environment necessary to properly execute the protein's function. Though the turnover rate can be slow, the actual bond breaking/making event and associated structural changes occur on the chemical time scale of ~100 femtoseconds (~10^{-13} s). To understand how enzymes work, it is crucial to characterize the correlated structural changes that accompany the catalytic process, i.e., we wish to watch a protein as it functions on the chemical time scale. Structural changes in proteins have been tracked with < 2 Å spatial resolution on time scales as fast as ~100 ps using the pump-probe method: a laser pulse triggers a structural change, and an x-ray pulse probes the protein structure via diffraction [1]. The time resolution achievable with this technique is limited by the duration of the x-ray pulse, which is ~100 ps at third generation synchrotron facilities. The LCLS-II aims to exploit self-seeding to generate narrowband (~0.05%) ultrashort (~20 fs) x-ray pulses with unprecedented pulse energy (several mJ) and stability. This source would be ideally suited to investigate protein structural changes in enzymes on the chemical time scale.
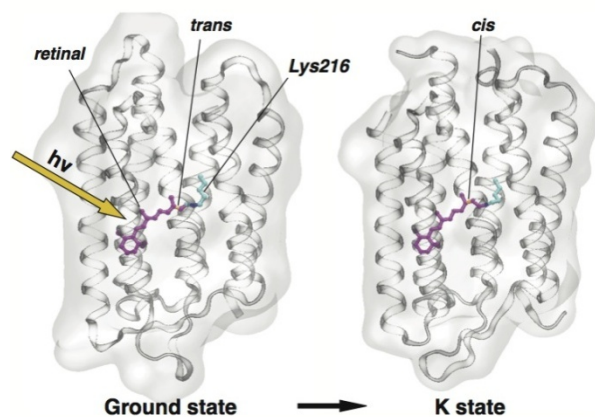
Fig 1. Structure of bR in all-*trans* and 13-*cis* (cryo-trapped) states. The retinal (magenta) is linked to Lys216 via a protonated Schiff base. The C13=C14 double bond is colored yellow.

Time-resolved crystallography depends on our ability to synchronize the structural changes occurring within the x-ray illuminated volume of the protein crystal. The only practical way to achieve synchronization on the chemical time scale is with light. Therefore, we focus our attention on biological processes that are light driven, or can be triggered by a pulse of light. An ideal model system for studying ultrafast structural dynamics in proteins is bacteriorhodopsin (bR), see Fig. 1, a light-driven proton pump found in *Halobacterium halobium*, an archaebacterium that thrives in the harsh environment of salt marshes. This 26 k-Da protein contains a retinal chromophore that, upon absorbing a visible photon, undergoes selective isomerization from all-*trans* to 13-*cis* with 2/3 efficiency. How does this protein achieve such high selectivity and efficiency, and could the protein be engineered to achieve even higher efficiency? Clues to the efficiency are found in the excited state relaxation, which was found to be biexponential [2]. Interestingly, the faster of the two pathways (240 fs) has 2/3 of the amplitude and correlates with the appearance time of the *cis* isomer, the photoproduct responsible for pumping protons. The slower pathway (750 fs) has only 1/3 of the amplitude and evidently returns to the all-*trans* ground state. To understand how this protein functions at the mechanistic level, it is crucial to track the atomic coordinates of the retinal and the surrounding protein side chains during isomerization.

To make a movie of atomic motion on the chemical time scale, the pump-induced change in structure factor amplitudes must be determined with high accuracy and precision. Since partiality introduces the largest source of systematic error when acquiring monochromatic still images, we propose to record the diffraction pattern before and after laser excitation and compute the ratio of the measured structure factor amplitudes. This approach mitigates the effects of partiality, but also requires that the x-ray pulse be non-destructive. With the specified x-ray parameters, see Fig. 2, a 35 μm crystal would be sufficiently large to produce high dynamic range diffraction images while limiting the x-ray pulse-induced T-jump to about 10 K. This T-jump is large enough to influence the structure factor amplitudes in the subsequent image. Extrapolation of the first two images predicts the structure factor amplitudes of the third image without laser excitation. The pump-induced change in the structure factor amplitudes in the third image can therefore be determined accurately by computing the ratio of the measured to extrapolated structure factor amplitudes. What about radiation damage? The 200 ns period of time between the first and third x-ray pulse is too short for radical-induced radiation damage to compromise the diffraction of the crystal. Therefore, the dominant effect of x-ray dosage would be a temperature jump, which should be well characterized by the first two images. The crystalline sample could be mounted in a photocrystallography chip [3] or delivered via a liquid column injector [4]. If delivered by an injector and moving at 5 m/s velocity, the distance traveled in 200 ns would be only 1 μm, which is small compared to x-ray focus. Time-resolved diffraction data acquired in this fashion would provide unprecedented information

regarding how proteins achieve high efficiency and selectivity, and would provide answers to fundamental questions regarding how life happens.
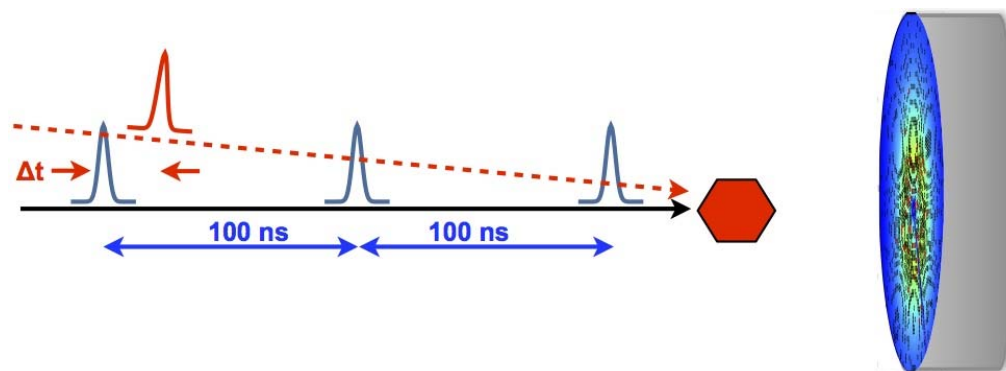

Fig 2. Data collection protocol. A protein crystal diffracts three x-ray pulses (blue) spaced by 100 ns. The diffraction image generated by each x-ray pulse ($\sim 10^{11}$ photons; 12 keV; 80 μm^2 spot size) is imaged on a fast frame-rate camera (10 MHz). A laser pulse (red) triggers a structural change at a time Δt before the arrival of the third x-ray pulse.

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4.3.2. Imaging Biological Samples with Terawatt X-ray Pulses

Henry Chapman, Anton Barty, John Spence, Janos Hajdu

The imaging method of "diffraction before destruction" requires pulses containing enough photons to produce measurable diffraction patterns and short enough to outrun radiation damage [1,2]. The peak power provided by LCLS is already delivering new biological science: structure determination at a spatial resolution better than 1.6 Å has been verified using serial diffraction measurements of protein nanocrystals carried out at LCLS, and various proteins including previously unknown structures of proteins from the Trypanosoma brucei parasite have been solved by this method. Diffraction data have been collected with much higher signals per crystal than would be possible at a synchrotron, with doses to the sample in some measurements reaching over 100 times higher than tolerable by conventional methods. Unlike those conventional methods, diffraction data at LCLS are collected at room temperature. A biological imaging endstation on the terawatt-class LCLS-II is essential to reach the ultimate limits of the technique to study the most challenging biological samples.

Our experiments at LCLS have confirmed a model of the dynamics of the sample degradation, showing that the highest diffraction signals are achieved by increasing the pulse intensity, rather than pulse energy (number of photons) [3]. The incident X-rays cause the onset of sample disorder, which grows as a function of time. Although increasing pulse intensity causes the sample to disintegrate faster, the increase in the number of scattered photons during that time more than outweighs the increased destruction rate. We find empirically from our plasma physics model that the attainable scattering signal from the biological sample scales as the 2/3 power of intensity. This trend does not depend on the crystallinity of the sample—this general finding holds also for single molecules and viruses. As an example, consider a

3 mJ pulse of 60 fs duration (50 GW). At 9 keV this consists of 2×10^{12} photons. When focused to give a pulse of 10^{17} W/cm^2, we find that the sample survives only the first 30 fs, so the useful signal is generated from only about 1×10^{12} photons. Increasing the pulse energy by a factor of 2, to 6 mJ, by increasing the pulse length by the same factor gives the same pulse intensity and does not change the fact that only the first 30 fs contributes (again from 1×10^{12} photons). If, instead, we decrease the duration of the 3 mJ pulse to 30 fs the intensity and power are doubled, causing a more rapid disintegration time of 24 fs. Therefore the signal is generated by 1.6×10^{12} of the photons. That is, increasing the peak power from 50 GW to 100 GW gives a 1.6 times increase in signal. Increasing to 1 TW would give almost a 7.5 times increase (utilizing the first 8 fs). An 8 fs, 8 mJ (1 TW) pulse, focused to $(0.3 \ \mu m)^2$ would enable measurable diffraction from single particles at 3 Å resolution. At these intensities, additional radiation tolerance could be achieved by frustrated absorption [4].

The combination of higher pulse power and smaller spot size will give over a factor of 1000 increase in pulse intensity compared to prior LCLS protein nanocrystallography experiments at 2 keV. In those experiments diffraction was observed from crystals only 6 unit cells across, i.e., less than 300 total unit cells. The integrated Bragg signal scales linearly with total unit cells, giving confidence for obtaining measurements from single objects with the achievable factor of 1000. Note that the spot size cannot be smaller than the sample, which sets a limit to focusing as an intensity-increasing strategy.
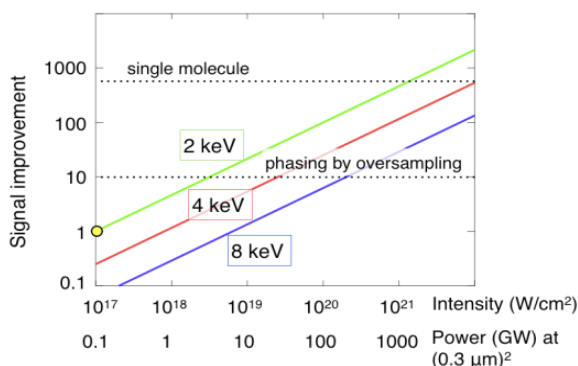

Figure 1: Improvement in signal relative to measurements at 2 keV with 10^{17} W/cm^2, where diffraction from 6x6x6 unit-cell crystals of photosystem I were observed. The improvement needed for single molecule measurements and phasing by "oversampling" [6] are indicated. As intensity increases the explosion occurs faster, but the increase in photons more than compensates. Scaling may be more favorable above 10^{20} W/cm^2 than indicated here due to effects such as frustrated absorption [4].

The absorption of a photon leads to photoionization, Auger decay or fluorescence, and a cascade of collisional ionizations, with about 200 ionizations per absorbed X-ray. The dynamics of these damage processes in a sample are generally dependent on the absorbed energy, and Cretin calculations show that the sample dynamics for different photon wavelengths depends solely on the dose rate. Since, away from absorption edges, absorption scales approximately as $\lambda^{2.7}$, the dose rate at 2 keV is over 40 times higher than at 8 keV for the same pulse intensity. However, the increase in scattering signal (λ^2) offsets the faster explosion [t $\sim (\lambda^{2.7})^{(-2/3)}$], giving a net advantage of a quadratic wavelength dependence on scattering signal since the number of photons per pulse also scales with λ, assuming a fixed detector efficiency. Since the diffraction-limited resolution is inversely proportional to wavelength, the implication is that measurements should be made at the longest possible wavelength that supports the desired (or achievable) resolution. These observation are summarized in Figure 1.

Photon energies at or above 2 keV can support resolution down to 4 Å with detectors arranged to collect diffracted light in all forward directions ($2\theta \leq 90°$). For single molecules, sample heterogeneity may limit resolution to about 4 Å. Higher photon energies to about 13 keV give access to absorption edges of

specific elements used for phasing by anomalous diffraction. The most useful edges to access are for sulfur (2.5 keV) and selenium (12.6 keV). Over 70% of all proteins contain one or both of the sulfur-bearing amino acids cysteine or methianine. Sulfur can be substituted for Se in these amino acids. Synchrotron-based S anomalous diffraction measurements are currently carried out at 4 keV to avoid the need for a complete vacuum path to the detector, reduce dose (and beam extinction), and give higher resolution with conventional detectors. Our in-vacuum serial diffraction approach solves the first two of these issues, as has been demonstrated by 2 keV nanocrystal experiments, and can accommodate improved detector arrangements for improved resolution. Anomalous diffraction signals are predicted to be significantly enhanced at high intensities [5].

In addition to structure determination from static and reproducible objects, as well as time-resolved structure studies by laser pumping or continuous-flow mixing, the use of fast pulses instead of freezing makes possible a kind of snap-shot chemistry, in which snapshot scattering from many identical proteins in solution is used to track biochemical reactions. These snapshots can be recorded at different positions along our jet as temperature and reaction coordinate change. Models based on molecular dynamics simulations are currently being used to match angular correlation functions to those of experimental patterns. The short pulses produce two-dimensional patterns showing correlated fluctuations, which contain more information than conventional SAXS patterns. Unlike single-shot, single-particle methods, this method provides a 100% hit rate, and will benefit from the increased intensity of LCLS-II for the same reasons that the single-particle work will benefit.

The above considerations lead to the proposal that a single particle diffractive imaging and nanocrystallography instrument is needed to utilize the high-power pulses available at LCLS-II, and which covers the very unfortunate void in available photon energy that currently exists at LCLS-I. This region is exactly in the optimal region for imaging macromolecular structures.   Given that the CXI station already covers energies above about 4.5 keV, the LCLS-II station should span 2 keV to as high photon energy as possible (given optics constraints). The LCLS-II station would accommodate the most challenging samples (nanocrystals down to uncrystallized objects). It should consist of a dedicated high-throughput structure determination station (utilizing low-flow liquid-jet injection with fast sample switching for protein solutions and protein nanocrystal suspensions) and a more general-purpose instrument that would include an aerosol particle injector. The detector requirements for the full-forward scattering geometry are challenging: tiles arranged on tiltable panels (at least in the direction perpendicular to the plane of polarization) and a total pixel count of 3k x 3k. Detectors must be low noise to enable single-photon detection at 2 keV. Focusing should be adjustable from 0.1 μm diameter to 10 μm. Additionally we propose high-numerical aperture optics for convergent beam diffraction. This allows a more complete integration of nanocrystal Bragg peaks for accurate structure factor estimation with significantly few diffraction patterns, as an alternative to using broader bandwidth pulses.

The priorities for bio-molecular imaging at LCLS-II are summarized as:

1. **Highest possible peak intensity.** The achievable diffraction signal scales with pulse intensity, not pulse energy, requiring a combination of the highest peak power pulses with focusing below 0.3 μm diameter.

2. **Dedicated endstation utilizing 2 keV to about 6 keV photon energy.** The highest signals are achieved at the longest wavelength that supports the resolution, which should be better than 3 Å. High-intensity sulfur anomalous diffraction requires photon energies above 2.7 keV. Additionally, the CXI instrument should be extended to photon energies above the 12.6 keV Se edge.

3. **Low-noise photon detectors, arranged for scattering up to 2θ = 90º**. Such a geometry is required to achieve high resolution at long wavelengths. Nanocrystal samples require up to 3k x 3k pixel counts.

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4.3.3. High-intensity beam lines for biological imaging with 0.5-2 and 2-6 keV X-rays

Filipe R. N. C. Maia[1,2], Max F. Hantke[1], Tomas Ekeberg[1], Gabor Bortel[3], Janos Hajdu[1,4]

(1) *Laboratory of Molecular Biophysics, Department of Cell and Molecular Biology, Uppsala University, Husargatan 3 (Box 596), SE-751 24 Uppsala, Sweden,* (2) *NERSC, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA,* (3) *Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, H-1525 Budapest, P. O. Box 49, Hungary,* (4) *European XFEL, Albert-Einstein-Ring 19, 22761 Hamburg, Germany*

The vast number of primary amino acid sequences that exist in biology take up a very small number of structural folds. Identical folds with different sequences can perform completely different functions. The number of different folds is estimated to be about a thousand (Chothia, 1992). This suggests that 3D structure is significantly more conserved in biology than sequence similarity. Connecting form to functionality will therefore require high-resolution structures on biological objects. Macromolecular assemblies populate the mesoscale, and the proposed imaging beam lines will allow high-resolution studies on mesoscale complexes.

The current LCLS is weak and this limits what can be studied with it. Test experiments on single macromolecules (Figure 1) show that an upgrade will be necessary to reach the goals in biomolecular imaging. The predicted and observed diffraction patterns of single RNA Pol II molecules are shown in Figure 1. RNA Pol II (Gnatt et al. 2001) contains about 31,000 atoms in 12 polypeptide chains and has a molecular mass of half a million Daltons. The protein used in the study shown on Figure 1 was labeled with 11 gold clusters of $Au_{102}(p\text{-MBA})_{44}$ to enhance the diffraction signal. We estimate there were about a hundred (or so) scattered photons in the measured pattern, and this is not enough for successful structural studies. Decreasing the focal spot size to 100 nm or below could, in principle, increase the required photon density for very small target systems, but this spot size is much too small for most other applications (discussed below), and excludes studies on mesoscale objects.
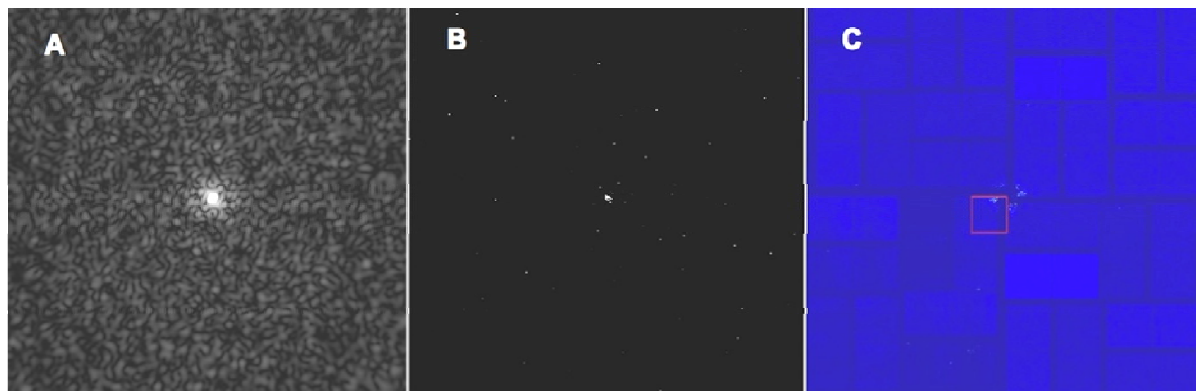

Figure 1. Predicted and observed diffraction patterns from an RNA Pol II molecule labelled with 11 gold clusters of of $Au_{102}(p\text{-MBA})_{44}$. (A) Section through the Fourier transform of a gold-labeled RNA Pol II molecule. (B) Predicted diffraction signal with 1 mJ LCLS pulses at 5 keV energy focused to a 1 micron spot. (C) Experimentally measured diffraction pattern from the CXI station (3.7 mJ pulse, 5 keV

X-ray energy, 2.2 micron focal spot diameter FWHM, and ~10% beam line transmission). Resolution at the edge: 4.3 Å.

The diffraction signal from a macromolecule can be divided into three main regions as a function of the scattering vector (Figure 2). The lowest resolutions part (region 1 in Figure 2) depends on the overall shape of the object, the medium resolution part (region 2) depends on the distribution of groups of atoms within the object, and the highest-resolution part (region 3) depends on the number and distribution of all atoms in the object (Bergh et al. 2008). Region 3 extends to the wavelength-dependent diffraction limit (Figures 2 and 3).

The black curve in Figure 2 shows the overall distribution of the scattered radiation for a nearly spherical macromolecule with the mass of RNA Pol II. The red curve represents scattered radiation for an equivalent ball of uniform density (i.e. no atomicity). The envelop of the scattered intensity from such a ball falls off with $1/d^4$ where d is the resolution length. Scattering by a real macromolecule (black) deviates significantly from scattering by the ball, especially at medium- and high-resolutions. At medium resolution, the scattered intensity can be approximated by a $1/d^3$ dependency (Shen et al., 2004), while the high-resolution region (region 3) gives a more or less flat resolution-dependency as seen in Figure 3.
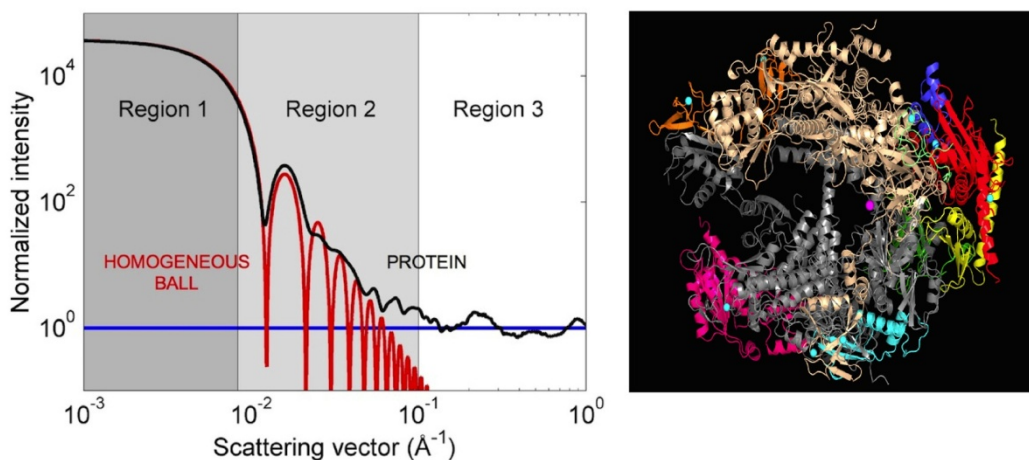

Figure 2. Intensity distribution in orientationally averaged and normalised diffraction patterns. The diffraction pattern represented by the black curve was calculated for a macromolecule of 500,000 Dalton mass with an approximately spherical shape (diameter: 12 nm). RNA Pol II (on the right) is such a molecule. The scattered intensity is normalised by the number of atoms. The blue line gives the incoherent sum of scattering from all atoms in the molecule (normalised to unity). The red curve shows the diffraction pattern of an equivalent ball with uniform density, i.e. no atomicity (Bergh et al. 2008).
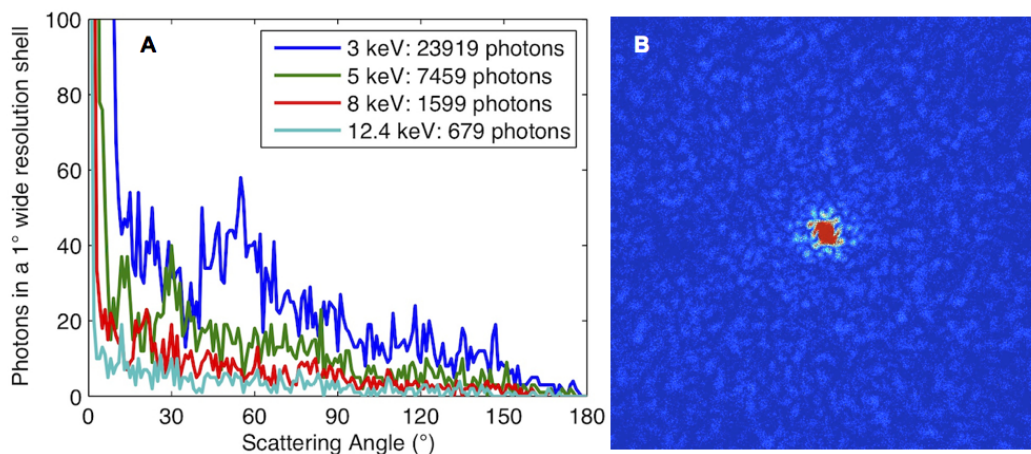
Figure 3. Expected signal from RNA Pol II with 10^{13} photons and a 500 nm focal spot. (A) The number of scattered photons is 23,919 at 3 keV (blue), 7,459 at 5 keV (green), 1,598 at 8 keV (red) and 670 at 12.4 keV (light blue). The wavelength-limited resolution (at full back scattering) is 2 Å at 3 keV, 1.2 Å at 5 keV, 0.8 Å at 8 keV, and 0.5 Å at 12.4 keV. (B) The expected diffraction signal from a single RNA Pol II molecule labeled with 11 gold clusters (5 keV photons, pulse energy: 3.5 mJ, 100 nm focus, 10% beamline transmission). The pattern contains nearly 60,000 photons. Resolution cutoff at the edge: 4.3 Å. This pattern was created with *spsim*, the single-particle diffraction simulator at http://xray.bmc.uu.se/hawk/?q=hawk/spsim.

High-resolution structures require more intense pulses from the LCLS than the pulses currently available. Figures 2 and 3 show that the scattered intensity in region 3 is uniformly strong all the way to the wavelength-dependent diffraction limit. If the signal is strong enough at the boundary between regions 2 and 3 of Figure 2, then it will also be strong enough all the way to the highest possible resolution. This is not the case in crystalline diffraction where the quality of the crystals sets the resolution limit. An analysis of the intensity distribution of the scattered radiation from single particles shows that with a fixed pulse intensity, X-rays of 3-5 keV energy give the strongest scattering signals while also providing high detail resolution (2 Å max. at 3 keV, 1 Å max. at 6 keV). The LCLS is blind in the 2-5 keV energy region today.

As the highest priority, we propose to establish a high peak-power intermediate-energy X-ray imaging instrument, operating with 2-6 keV photon energies for studies on mesoscale biological objects with Ångström resolution. Two end-stations will be needed in series for simultaneous operation, equipped with lasers, sample environments, and diagnostics. We also propose an additional beam line with two end-stations for studies at mesoscale resolutions on cells, cellular components and large viruses. Such studies would require access to the water window and to the phosphorous K edge, covering the 0.5-2.5 keV energy range.

Sample size and the size of the focal spot: There is a requirement to harmonize the beam size with the size of the sample. A 100 nm focal spot at the LCLS could approach the required photon density for certain target systems, but this spot size is much too small for most applications. In general, the diameter of the focus should be 5-10 times bigger then the diameter of the object in order to assure uniform illumination with a reasonably planar wave front (or with a wave front that is known). A 100 nm focal spot is good for samples that are not much bigger than about 10-15 nm. The total number of *different* proteins in this size domain is only about 100,000 in biology. Many of these have already been "done" as demonstrated by structures deposited in the Protein Data Bank.

Intriguing new biological structures are in the 10 nm - 600 nm size domain. The total number of different structures in this size domain is well over a billion (including all viruses and small living cells). Very few of these structures have been studied. Photon number, focus size, pulse length, and coherence properties

determine how big objects can be studied. The new instruments would bring mesoscale objects within the scope of detailed analysis for the first time.

Repetition rate is no substitute for a strong single-shot signal. Since heterogeneity is inherent to biology, any single exposure captures only one of many possible structural states of a biomolecule or biomolecular assembly. If each of the diffraction patterns contains only a few photons, then the information in these patterns will not be sufficient to separate structural differences on a realistic basis. According to Lanczos, "we should recognise the general principle that a lack of information cannot be remedied by any mathematical trickery" (Lanczos, 1961). One of the grand challenges in structural sciences is to determine experimentally the conformational phase-space of large macromolecules. More photons per pulse will bring us closer to this dream.

Experimental stations, general requirements

The requirements outlined above translate into the following instruments:

(1) The highest priority is to establish an experimental station for studies on mesoscale biological objects, including large macromolecules, macromolecular complexes, viruses and cell organelles. This requires variable focus (between about 0.3-3.0 micron diameter), 2-6 keV X-rays, and between 10^{13-14} photons per pulse with 120 Hz - 1 kHz repetition rate. The more photons we get per pulse the bigger objects we will be able to cover.

(2) Studies at intermediate resolutions require access to the water window and to the phosphorous K edge, and should span the 0.5-2.5 keV energy range.

Both instruments require high peak-power (TW) pulses, KB optics for achromatic focusing, low-noise and high-dynamic range detectors. Care should be taken to optimize the beamline transmission for the entire optical path from the undulators to these instruments. Continuous R&D leveraging the existing LCLS is required on sample delivery systems. Optical lasers are required for triggering dynamics in time-resolved studies and as a diagnostic for the sample injectors (eventually reaching the capability for particle tracking on the path to the interaction region).

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4.3.4. Time-Resolved X-ray Spectroscopy of Photosynthetic Water Oxidation

Junko Yano

Vittal Yachandra

Physical Biosciences Division, LBNL

In nature, the water oxidation reaction is accomplished effectively by the oxygen-evolving complex (OEC) in Photosystem II (PS II), a multi-subunit membrane protein of green plants, algae, and cyanobacteria, in which solar energy is used to couple the oxidation of water to oxygen. The OEC of PS

and energy storage potential. However, effective methods for water splitting have proven elusive, in part due to difficulties in managing the overall four electron, four proton redox chemistry. Given the role of PS II in maintaining life and the future vision of a renewable energy economy, understanding the structure of the Mn_4Ca catalyst and the mechanism of the water oxidation reaction is considered to be one of science's grand challenges.
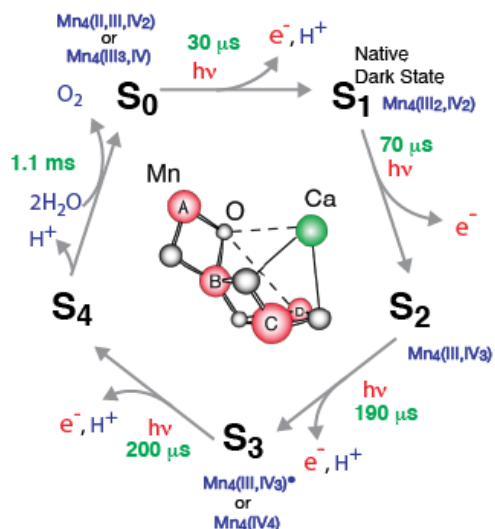

Fig. 1. The Kok S-state cycle for photosynthetic water oxidation and oxygen evolution. Proposed structure from single-crystal polarized X-ray spectroscopy is in the inset (Yano et al., 2006).

The detailed chemistry involved in the OEC has emerged slowly, and much of importance remains to be learned. The structure of the Mn_4Ca complex in the S_1 state is emerging from X-ray diffraction and X-ray spectroscopy studies, but much less is known about the structural changes in the Mn_4Ca cluster through the catalytic cycle, which are critical for understanding the mechanism of oxygen evolution. The intermediate S-states of the OEC, S_0 through S_3, have been studied to varying degrees using biochemical and spectroscopic techniques. However, almost nothing is known about the putative S_4 state, although experimental results, UV/Vis, EPR and X-ray spectroscopy indicate that there are some kinetically resolvable intermediate states present during turnover.

There are many proposed mechanisms for the photosynthetic water oxidation reaction and the formation of the O-O bond. The favored mechanisms for water oxidation by the OEC are (Fig. 2): A) reaction of a bridging/terminal Mn-oxo unit with predominant radical character with an oxo/hydroxo/water ligand of Ca/Mn or an exogenous H_2O, B) nucleophilic attack
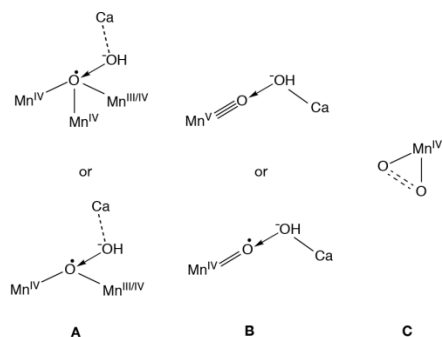

Fig. 2. Schematic showing three different proposals for the formation of the O-O bond during the S_3- [S_4] - S_0 transition.

on a Mn(V)≡O or Mn(IV)=O• terminal ligand by Ca bound water or hydroxide, C) involves an end-on peroxo ligand to a single Mn center.

We propose to study the geometric and electronic structure changes during each S-state transition of the catalytic S-state cycle (Fig. 1), and to detect any transient states that are present. The time-resolved experiments will be carried out in a pump-probe mode, where the Mn-OEC and other model systems are advanced with visible light laser pulses and the X-ray absorption or emission spectrum will be collected. The major objectives are (1) to detect the formation of the critical O-O bond, which is likely to occur at the stage associated with the formation of the transient S_4, and (2) to detect the electronic events (electron transfer and electronic structural changes) that trigger the structural changes in the Mn_4Ca catalytic center during each transition. These events occur within the range of ps/fs (electron transfer) to ms/μs (bond formation and breaking) time scale. We plan to develop time-resolved instrumentation at the LCLS that is applicable to PS II and other engineered photosynthetic systems that work in a wet and dilute environment. The challenge is to detect the weak signals from dilute samples, overcome the effects of radiation damage, and collect spectra within the time-scale of catalytic reactions. For this purpose, detection techniques and sample handling methods need to be further developed.

In one method, the reaction is initiated by a laser pulse, and the time-development of the X-ray spectrum is detected in the X-ray absorption near-edge structure (Mn K or L-edges) region, by stepping through the energy region point by point. The sample is injected in a stream to avoid sample damage because these studies will have to be conducted at or near room temperature. The time-resolved absorption spectrum is then constructed from these energy points. For a more complete analysis of the nature of intermediate states and to elucidate the order of oxidation-state changes, bond rearrangements, ligand movements, substrate binding/dissociation and other events in the OEC during the individual S-state transitions, it is necessary to record full XANES/EXAFS spectra in a time resolved manner. The challenge is to improve the detection technique and collect data within the threshold of the radiation damage at room temperature.

We will also use a different X-ray spectroscopic technique that avoids the necessity of scanning the X-ray energy. In particular, the plan is to collect the entire emission spectrum with either non-resonant excitation or the resonant inelastic X-ray scattering (RIXS) spectrum with resonant excitation. The major change to existing x-ray emission spectroscopy (XES) and RIXS studies of the OEC proposed is the employment of a new type of spectrometer based on wavelength dispersive optics. This will allow us to collect time-resolved spectra from a defined XES/RIXS energy region at any given time point without scanning the monochromator or crystal analyzers. X-ray emission spectra contain information about the electronic structure and the spin state of the specific element. Scattered X-rays from the sample are collected by multiple analyzer crystals, which are tuned to collect a desired X-ray emission region (for example, Mn Kα, Kβ, etc.). Using the Bragg diffraction of the analyzer crystals, the emitted X-rays are then collected by the detector. In a current setup, spherical analyzer crystals are used, and the entire emission spectra are collected by scanning the analyzer crystals. To achieve time resolved capability and collect the entire spectrum on each pulse, we will combine energy dispersive analyzer crystals and position sensitive detectors. For time-resolved studies, a wavelength dispersive setup in *e.g.* a von Hamos geometry is required. In such a setup, the analyzers are cylindrically curved and the XES spectrum is recorded on a position sensitive detector. Rather than scanning the instrument, the spectrum is acquired in a static setup. In principle, the time resolution of this method is limited only by the laser pulse, and the S/N is related to the concentration of the sample. We are exploring the next generation position sensitive detectors that are being developed expressly for spectroscopic experiments.

The higher flux provided by LCLS II will enable: (1) the observation of weak transitions such as valence to core levels (> 10 times weaker than Kβ), (2) polarized spectroscopy performed with separate columns of analyzer crystals, and (3) RIXS spectroscopy requiring a monochromator.