First experiments for LCLS-II
NEH 2.2 - RIXS & LJE

Overview:

LCLS-II will be a transformative tool for energy science, qualitatively changing the way that X-Ray imaging, scattering and spectroscopy can be used to study how natural and artificial systems function. It will enable new ways to capture rare chemical events, characterize fluctuating heterogeneous complexes, and reveal quantum phenomena in matter, using nonlinear, multidimensional and coherent X-Ray techniques that are possible only with X-Ray lasers. This facility (endstation) will provide access to the "soft X-Ray" regime (250 eV to 1.6 keV) to provide fully coherent X-Rays in a uniformly spaced series of pulses with programmable repetition rate and rapidly tunable photon energies.

In the following, we briefly summarize two broad areas of science in which the unique capabilities of LCLS-II, offered at the NEH 2.2 experimental beamline, will be essential to address critical knowledge gaps at the new scientific frontiers of matter and energy. A complete description of these science opportunities can be found in the report: New Science Opportunities Enabled by LCLS-II X-Ray Lasers (SLAC-R-1053)

Quantum Materials:

Strong coupling between charge, spin, orbitals, and lattice motion in quantum materials gives rise to collective modes that determine the macroscopic material properties of profound interest such as high-temperature superconductivity, colossal magnetoresistivity, and topologically protected phases. Momentum-resolved resonant inelastic X-ray scattering (q-RIXS) has emerged as a powerful tool to characterize collective excitations for comparison with fundamental theoretical models based on the Kramers-Heisenberg approach. Because the ground states of quantum materials arise from a subtle balance among competing interactions, the relevant emergent collective modes appear at modest energies, typically up to a few hundreds of meVs but with a number of excitations lying below 100 meV, where the required combination of photon flux and energy resolution press the limits of modern X-ray sources and spectrometers. The high repetition rate of LCLS-II will offer transformative capabilities – for both characterizing collective modes and excited states (energy and momentum dependence across the Brillouin zone), and for following their response to tailored external stimuli to disentangle coupled phenomena in the time domain. For example recent studies have shown that broadband THz pulses can selectively couple to electronic order, and thereby transiently decouple charge and lattice modes. Such approaches can also trigger phase transitions and create new phases that are inaccessible in thermal equilibrium. Tailored ultrafast vibrational excitation has been shown to drive insulator-to-metal phase transitions in colossal magnetoresistant (CMR) manganites, and enhanced superconductivity is claimed to result from transiently-driven nonlinear lattice dynamics. These novel photo-induced phenomena are ultimately related to the emergent properties in equilibrium and are a key step

towards active control, yet a clear interpretation and characterization of the collective modes in the transient regime is still lacking.

First experiments at LCLS-II will provide crucial pieces of information by time- and momentum-resolved RIXS (*q*-RIXS instrument, NEH 2.2). In cuprates, Cu *L*-edge RIXS will map the evolution of magnetic excitations and phonons in time, energy, and momentum to provide a more complete microscopic picture about the transient superconducting phase. The time-evolution of charge-stripe order, a co-existing state in superconducting cuprates, and its associated excitations can be simultaneously monitored. This will provide new insights into the much-debated issue of the role of charge order in high-T_C superconductivity, as well as provided quantitative assessment of the strength of spin fluctuations and electron-phonon coupling as candidates for a superconducting pairing mechanism. This approach is applicable to many other outstanding problems in quantum materials, such as the relation of recently discovered collective modes near the zone center and the role of magnetic fluctuations in the electron-doped cuprates, as well as more generally to excitations in multi-ferroics, topological spin liquids, and understanding battery cathodes.

Typical first experiments in 2.2 - Quantum Materials Topical Areas

(*= early science candidate)

1. *tr-RIXS correlated materials
    - **Importance:** How do magnetic excitations in the cuprates couple to electronic and phononic perturbations?
    - **Measurement:** Time-evolution of the magnon dispersion
    - **Requires:**
        - <50 meV resolution
        - Q-resolution to map the dispersion
        - Incident x-ray energy tunability: for complete RIXS mapping
        - Incident and scattered x-ray polarization control: to isolate sigma and pi
        - Phonon pumping at ~80 meV (15 microns, 20 THz), Mid-IR OPA, optical (1.55 eV) and THz (0.1 - 2) wavelengths
        - 30 fs FWHM optical pulses in the visible range. Tunable FT-limited pulses in the Mid-IR
        - Fluence up to ~10 mJ/cm^2
2. *tr-RIXS correlated materials
    - **Importance:** Dynamics of dispersive CDW excitation and phonon coupling in Bi2212
    - **Measurement:**
        - Time-evolution of the CDW dispersive excitation

        - Temperature evolution: CDW signatures up to 240 K; relation to spins and pseudogap (nickelate analogy)

    - **Requires**:
        - <50 meV resolution
        - Q-resolution to map the dispersion
        - Incident x-ray energy tunability: for complete RIXS mapping
        - Phonon pumping at ~80 meV (15 microns, 20 THz), Mid-IR OPA, optical (1.55 eV) and THz (0.1 - 2) wavelengths
        - 30 fs FWHM optical pulses in the visible range. Tunable FT-limited pulses in the Mid-IR
        - Fluence up to ~10 mJ/cm^2

3. *tr-RIXS correlated materials
    - **Importance:** Dispersion of phase and amplitude CDW modes measured via time-resolved diffuse x-ray scattering

    - **Measurement:** Time-evolution of the diffuse x-ray scattering following ultrafast perturbation

    - **Requires:**
        - <50 meV resolution
        - Q-resolution to map the dispersion
        - Incident x-ray energy tunability: for complete RIXS mapping
        - Phonon pumping at ~80 meV (15 microns, 20 THz), Mid-IR OPA, optical (1.55 eV) and THz (0.1 - 2) wavelengths
        - 30 fs FWHM optical pulses in the visible range. Tunable FT-limited pulses in the Mid-IR
        - Fluence up to ~10 mJ/cm^2

4. XPCS of fluctuating charge/spin dynamics
    - **Importance:** Ground state dynamics of density wave orders throughout the phase diagram of the transition metal oxides measured via XPCS

    - **Measurement:** X-ray correlation spectroscopy via the split-pulse method, covering dynamics up to nanosecond range

    - **Requires:**
        - Extension of split pulse machine operation with variable pulse delay: from 0 to dozens of ns (requires R&D effort)
        - High speed/low noise x-ray camera for photon-counting data collection
        - Q-resolution to capture superlattice reflection

- Large sample-detector distance to alleviate small x-ray spot constraints.
- Incident x-ray energy tunability

First experiments that require low-to-moderate overall resolving power:

5. *tr-RIXS correlated materials
    - **Importance:** Ultrafast dynamics of the Zhang-Rice singlet in 1D spin-chain cuprate $CuGeO_3$

    - **Measurement:**
        - Time-evolution of Zhang-Rice singlet state and charge-transfer excitations
        - Evolution with temperature, above and below the spin-Peierls transition

    - **Requires:**
        - <300 meV resolution
        - Phonon pumping at ~80 meV (15 microns, 20 THz), Mid-IR OPA, optical (1.55 eV) and THz (0.1 - 2) wavelengths
        - 30 fs FWHM optical pulses in the visible range. Tunable FT-limited pulses in the Mid-IR
        - Fluence up to ~10 mJ/cm^2
        - Incident x-ray energy tunability: for complete RIXS mapping

6. *tr-RIXS correlated materials
    - **Importance:** Electron-phonon coupling in the light induced Superconductivity in K_3C_{60}

    - **Measurement:**
        - Time-evolution of the T_{1u} phonon dispersion following resonant excitation
        - Evolution with temperature, above and below transition temperature

    - **Requires:**
        - <200 meV resolution
        - Phonon pumping at ~80 meV (15 microns, 20 THz), Mid-IR OPA, optical (1.55 eV) and THz (0.1 - 2) wavelengths
        - 30 fs FWHM optical pulses in the visible range. Tunable FT-limited pulses in the Mid-IR
        - Fluence up to ~10 mJ/cm^2
        - Incident x-ray energy tunability: for complete RIXS mapping

The 2 experiments listed above could be performed with the existing portable X-ray Emission Spectrometer, providing a RP ~2,000

Photo-catalysis and Coordination Chemistry

Understanding the fundamental processes of photo-chemistry is essential for directed design of photo-catalytic systems for chemical transformation and solar energy conversion that are efficient, chemically selective, robust, and based on earth-abundant elements. The central events of excited state chemistry critically influence the performance of photo-catalysts since stable charge separation, transport, and localization are mediated by strong interaction between electronic and nuclear structure. New tools that enable direct observation of these central events, on fundamental time scales, and with chemical specificity, will qualitatively advance our understanding of chemical dynamics in photo-catalytic systems, and advance the development of design principles for directing molecular and materials synthesis. The high repetition rate of LCLS-II combined with advanced instrumentation for time-resolved resonant inelastic X-ray scattering, RIXS (NEH 2.2) will map the energy distribution and evolution of occupied and unoccupied molecular orbitals of model complexes and functional photo-catalysts in operating (liquid) environments.

Whereas LCLS studies have demonstrated the ability of time-resolved RIXS to map frontier molecular orbitals, the low repetition rate limits these experiments to coarse ligand dissociation process of simple model complexes at high concentrations. First experiments at LCLS-II will map frontier orbitals and charge-transfer dynamics in 3*d* transition metal donor-bridge-acceptor complexes that seek to link efficient light harvesters directly with a catalytic active site. The development of such complexes, and optimization of their functionality through tailored ligand structures, is a promising approach for solar energy conversion and related applications. A detailed understanding of the coupled ultrafast changes in electronic and atomic structure provided by LCLS-II will be indispensable for guiding design and synthesis efforts.

One important example from nature that illustrates the potential for this new class of science at LCLS-II is the site for water oxidation (Mn_4CaO_5 cluster) that acts as a charge storage device in the reaction center of photosystem II (PS-II). Tremendous progress has been made in the structural characterization of this catalytic center in its resting state, with record atomic resolution and damage-free room-temperature results provided by XFELs. However, a major knowledge gap is the transient electronic configurations of the metal sites and the flow of charge within the catalytic center during all four steps of the reaction cycle, and particularly the electronic structure of the metastable S4 state, where O-O bond formation occurs. Time-resolved RIXS experiments at LCLS-II will provide the first mapping of the transient electronic structure of the Mn_4CaO_5 cluster under operating conditions.

Typical first experiments in 2.2 - Condensed Phase Chemistry Topical Areas

(*= early science candidate)

1. *tr-RIXS - condensed phase chemistry
    - **Importance:** Understanding critical photocatalytic and electrochemical reactions like CO_2 and N_2 reduction and H_2O oxidation that involve multiple electron or proton transfer steps

- **Measurement:** PS-II Oxygen evolving complexes covering dynamics out to the millisecond range

- **Requires:**
  - <500 meV resolution
  - Moderate resolution (R~2,000) VLS or TES spectrometer
  - Excitation at 527 nm, 250 ps FWHM optical pulses
  - Incident x-ray energy tunability: for complete RIXS mapping
  - Increased spectral resolution from soft x-ray self seeding techniques

2. *tr-RIXS - condensed phase chemistry
   - **Importance:** Connecting excited state electron density dynamics to the catalytic activity and the charge transfer excited state lifetime

   - **Measurement:** Probing electron density dynamics occurring in charge transfer excited states in iron-based complexes containing polypyridyl, cyano, and carbene ligands

   - **Requires:**
     - <500 meV resolution
     - Moderate resolution (R~2,000) VLS or TES spectrometer
     - Excitation in the visible regime, 20 fs FWHM optical pulses
     - 10 fs FWHM optical laser to X-ray synchronization
     - Incident x-ray energy tunability: for complete RIXS mapping

3. *tr-RIXS - condensed phase chemistry
   - **Importance:** Ligand control of charge transfer and excited state relaxation in 3d transitions metal complexes

   - **Measurement:** Understanding how to manipulate electronic excited state relaxation in Fe and Co complexes with changes in molecular structure by tracking charge and spin dynamics with femtosecond resolution x-ray fluorescence and by monitoring the impact of spin state on photochemical activity with ultrafast RIXS

   - **Requires:**
     - <500 meV resolution
     - Moderate resolution (R~2,000) VLS or TES spectrometer
     - Excitation in the visible regime, 20 fs FWHM optical pulses
     - 10 fs FWHM optical laser to X-ray synchronization
     - Incident x-ray energy tunability: for complete RIXS mapping

Logistical Synopsis for executing experiments: In conjunction with the TTO plan laid out by the LCLS-II Project, early science experiments occurring in the abovementioned timeframe will be led by LCLS staff, with significant contribution from relevant users in the community. Experiments will serve as a bridge between technical commissioning and the start of general user access.

Initially, equal access will be split between photon operations (LCLS) and the Accelerator Directorate for machine development (MD). Typical photon experiments will range from 24-36 hours, with equal time given back to the MD program. Technical changes between early science experiments will be severely limited and strictly enforced. Only minimal changes to the instrument's baseline scope will be considered.