

# First experiments for LCLS-II

## NEH 1.1 - LAMP

### **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 will operate in a soft x-ray range (250eV to 1.5 keV), and will use seeding technologies 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 areas of science in which the unique capabilities of LCLS-II, offered at the NEH 1.1 LAMP instrument, 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 systems in strong fields; matter in extreme environments:** The strong fields generated in a focused X-ray laser beam are of particular fundamental interest on the molecular scale. Ordinary sunlight or conventional X-ray sources interact with molecules fairly weakly, by the simple measure that the motion initiated by absorption of a single photon is completely concluded before the next absorption event. X-ray lasers break this routine. The collective effect of multiple X-ray photons concentrate the energy so that the extreme conditions in the target can mimic the interiors of large planets or stars. They also lead to nonlinear processes such as photon harmonic generation.

**Photo-catalysis, coupling of electronic and nuclear dynamics:** Energy from the sun powers most of the earth, and the intelligent use of sunlight for our energy needs will be a critical component in addressing urgent challenges in energy production, transformation, and storage – with reduced impact on the environment. Making viable carbon-neutral fuel from sunlight with sufficient energy efficiency and selectivity involves a myriad of complex processes spanning many orders of length and time scales – down to atoms and femtoseconds. These include light harvesting, electron hole separation, charge localization and migration, catalysis driven by electrons or by heat, energy conversion and storage. The capabilities of LCLS-II for time-resolved, in-situ, element-specific and interface-sensitive studies will transform our ability to study many phenomena associated with these grand challenges in catalysis and photocatalysis. Understanding natural systems and man-made catalysts under their normal operating conditions, and across broad time- and length-scales will be critical to the design of robust, chemically selective, earth abundant and effective catalysts that will help us to meet pressing energy and environmental challenges.

## Typical first experiments in 1.1 (LAMP) - Femtosecond and Attosecond Photophysics and Photochemistry:

(\* = early science candidate)

1. **\*Probing structural dynamics of electrons and nuclei in the vicinity of conical intersections:** Time-resolved x-ray absorption spectroscopy allows for the unique opportunity to follow the electronic and nuclear dynamics of a gas phase molecule in the vicinity of a conical intersection simultaneously. A prototypical example is the photoinduced cis-trans isomerization of the molecular switch azobenzene.

Azobenzene can be photoexcited to an  $n\pi^*$  state yielding a prominent pre-edge feature in the nitrogen-edge near-edge x-ray absorption fine structure (NEXAFS) spectrum. The instant change of the character of the occupied electronic state during internal conversion through a conical intersection back to the ground state is visible in the disappearance of the pre-edge feature. The accompanying cis-trans isomerization of the molecule is simultaneously detectable in the structural information from the nitrogen edge extended x-ray absorption fine structure (EXAFS) features

- **Importance:** Understanding and controlling molecular dynamics in the electronic excited state remains a fundamental science challenge, in large part because we lack the requisite tools to probe these processes – simultaneously at the atomic level and on natural femtosecond time scales. The class of experiment described here will focus on the investigation of the interplay between dynamics of electrons and nuclei in the vicinity of a conical intersection during ultrafast photochemistry.

Dynamics are key to addressing this question, since excess photon energy must be rapidly channeled to desirable pathways (e.g. coordinated rearrangement of specific chemical bonds or migration of electrical charge) or else it will be dissipated into undesirable or even destructive channels. Thus, detailed knowledge of the concerted motion of electrons and nuclei that occurs in the electronic excited state on the fundamental time scale of femtoseconds is essential to understanding, and ultimately controlling these processes.

Experiments going into the direction of disentangling correlated nuclear and electron dynamics have been already performed at LCLS I using ion detection and high energy electron detection. The increased flux and repetition rate of LCLS-II will allow for a number of improvements over the previous measurements. These improvements include: the identification of orders of magnitude more subtle changes in electron spectra, electron-electron and electron-ion coincidence measurements, and spectroscopy at multiple edges in the soft x-ray range simultaneously.

- **Measurement:** Time-resolved NEXAFS spectroscopy has been performed in the gas phase at LCLS-I by high energy Auger electron detection. Two full 12hr shifts were needed to collect a dataset of the essentially background-free pre-edge features with with 0.5 eV resolution and appreciable signal-to-noise by scanning a ~20 eV range of x-ray photon energies around the edge. To accompany the electronic structure information about the conical intersection with transient nuclear structure information from photoelectron scattering, the scanning range has to be considerably increased to >100 eV into the post-edge EXAFS range. Transient EXAFS features are 1-2 order of magnitude less intense than the NEXAFS features and have significant background from the static EXAFS spectrum.
- **Requirements:**
  - Self-seeding for x-ray beam, bandwidth of < 0.5 eV (determines NEXAFS spectral resolution)
  - X-ray energy scanning over ~150 eV
  - High energy (1 keV) electron spectrometer for Auger electron detection
    1. Energy resolution: 0.5 eV
    2. Energy window: 200 eV
      - a. Achievable by windows of ~10% of the pass energy
  - X-ray rep rate 100kHz to 1MHz
  - Optical excitation (800 nm, 400 nm, and 267 nm), sub-30 fs pulse duration
  - Optical excitation (UV-Vis), sub-50 fs pulse duration
  - 10 fs UV-x-ray timing synchronization would be useful, but measurement (cross-correlation) is also possible since experiments will be recorded on a single-shot basis and can be time corrected
  - $10^3$  mJ/cm<sup>2</sup> for optical excitation
  - Sample Delivery: Samples should be in gas phase, but various delivery methods could be required.
    - Molecular beam for gas phase samples
    - In-vacuum oven for example experiment, sample densities of  $\sim 10^{12}$  cm<sup>-3</sup>

## 2. \*Time-resolved multi-edge photoelectron-photoion covariance spectroscopy:

- **Importance:** This technique(s) allows for unprecedented mechanistic access to ultrafast molecular reaction dynamics at multiple sites. A prototypical example is the ultrafast photodissociation of the atmospheric chemistry compound nitrobenzene: The reaction is believed to proceed via an ultrafast roaming-type mechanism. In this proposed mechanism, as a first step the N-C bond between the phenyl ring and the NO<sub>2</sub> group breaks and an O-C bond is formed instead. In a second step, an NO fragment is released from the molecule. This proposed sequence of steps can only be verified by site-specific spectroscopy simultaneously at multiple sites in the molecule. An ideal method is time-resolved x-ray-photoelectron spectroscopy, due to its local sensitivity to the bonding environment. The carbon,

oxygen, and nitrogen edges can be probed simultaneously with an x-ray pulse of a photon energy well above all three edges. Since the molecule contains multiple oxygen and carbon sites, the full time-dependent structural information is only available by measuring the photoelectrons along with ionic fragments either in coincidence or covariance. The covariance technique elucidates correlations in highly fluctuating signals, which are typically lost in a conventional averaging procedure. In order to most effectively use the covariance technique the dataset must have sufficient fluctuations. When coupled to a high repetition rate source, the measurements can be made with finer resolution.

- **Measurement:** This measurement requires correlated detection of covariant photoions and high energy photoelectrons.
- **Requires:**
  - High energy electron spectrometer/analyzer
    - Electron energies up to 500 eV
    - Kinetic energy window of  $\sim 150$  eV (cover at least two of the K edges of carbon, nitrogen and oxygen simultaneously)
    - 0.5 eV energy resolution of this window.
  - Ion spectrometer
  - Self-seeding for x-ray beam, bandwidth of  $< 0.5$  eV
  - X-ray rep rate 100kHz to 1MHz
  - Optical excitation (800 nm, 400 nm, and 267 nm), sub-30 fs pulse duration
  - Optical excitation (UV-Vis), sub-50 fs pulse duration
  - 10 fs UV-x-ray timing synchronization would be useful, but measurement (cross-correlation) is also possible since experiments will be recorded on a single-shot basis and can be time corrected.
  - Sample Delivery: For covariance experiments a low-density effusive jet is required.

### 3. Coherent electron dynamics in valence excited-states probed by high energy electron spectroscopy (Auger or multi-edge XPS)

- **Importance:** Photochemistry always begins with electron motion, but the fundamental dynamics of electron motion is often too fast to detect. This class of experiments will follow the flow of charge through the creation of superpositions of valence excited molecular states. In analogy to the optical domain, where stimulated Raman scattering is used to create rotational and vibrational wavepackets, impulsive stimulated X-ray Raman scattering (ISXRS) can be used to create valence-excited electronic wavepackets in molecular systems. Thus allowing us to explore the very important role of electronic coherence, electron-electron correlations, and electron-nuclear coupling in chemical reactions. To continue the analogy between the optical and x-ray domain further, multi-dimensional optical

spectroscopy has proven so valuable to physical chemistry over the past few decades, and similar techniques can be exploited in the x-ray domain.

- **Measurement:** Observing charge migration in aromatic compound para-aminophenol ( $\text{NH}_2\text{-C}_6\text{H}_4\text{-OH}$ ). An intense broad bandwidth soft x-ray pulse tuned to the oxygen (or nitrogen) near-edge resonances in aminophenol creates a coherent superposition of valence excited-states via ISXRS. The initial wavepacket will be localized either at the oxygen (or nitrogen) site.

This coherent superposition is probed by a second time-delayed x-ray pulse. The dynamics can be probed through x-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES). Trade-offs can be made between resolution and collection efficiency with the improved rep. rate available from LCLS-II. The rep. rate can also be exploited for correlation measurements.

- **Requirements:**
  - X-ray pump/ x-ray probe capabilities:
    - Two-color x-ray pulses, with  $\sim 100$  eV energy separation (different atomic edges for pump and probe).
    - Broad bandwidth x-ray pump pulse ( $\sim 5\text{-}10$  eV bandwidth, with few femtosecond duration). The coherent bandwidth of the pump pulse directly controls the states that can be excited (energetically). Shorter pulse (sub-femtosecond) durations would enable study of a larger set of molecular systems.
    - The time delay between the x-ray pulses should be synchronized (or measured) to the sub pulse-duration level. Reduced resolution would make resolving dynamics tricky.
  - High energy electron spectrometer (decreasing priority)
    - Collection of high energy electrons, upto 1 keV.
    - Large collection window ( $\sim 200$  eV): Ability to collect photoelectrons or Auger electrons from different atomic edges which are separated by  $\sim 100$  eV. Can be achieved through scanning multiple windows.
    - Energy Resolution of Electrons:  $\sim 0.5$  eV
    - Angular Distributions: The angular distribution of emitted electrons contain a great deal of information on the symmetry of the excited state. Correlations in the electron angular distributions may provide a sensitive probe of the charge dynamics.
  - Single-shot Detection: Single-shot ability will open up the opportunity for correlation analysis of electron spectra. Correlation analysis allows for separation of different channels. Single-shot detection is also required if x-ray pulse synchronization can not be maintained to sub-femtosecond precision, i.e. if the delay has to be measured and the data rebinned.

- X-ray repetition rate: 100 kHz or higher. The Raman excitation fraction is expected to be only a few percent at best. Repetition rate will give the necessary statistics to disentangle the Raman signal.
- Sample Delivery: Samples should be in gas phase, but various delivery methods could be required.
  - Molecular beam for gas phase samples
  - In-vacuum oven for solid or liquid samples

#### 4. \*Time Domain Correlation Spectroscopy

- **Importance:** We can make use of the randomness which is inherent to SASE pulses to study the time-domain dynamics of molecular systems. By correlating electron kinetic energy spectra measurements with the time-domain substructure of a sequence of random SASE pulses, it is possible to reconstruct the time-evolution of the molecular system. We will use this technique to study the complex interplay between electronic coherence and nuclear motion in small molecular targets.
- **Measurement:** Time Domain Correlation will be used to resolve x-ray initiated dynamics in NO. When exposed to few-femtosecond (or sub femtosecond) x-ray pulses, the molecule will undergo rapid charge and molecular rearrangement. This rearrangement can be “probed” by a second sub-spike in the same SASE pulse. By correlating the measured electron kinetic energy spectra with the x-ray pulse profile, it will be possible to discern the complex charge and molecular motions.

Single-shot photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES) in coincidence with a measurement of the x-ray pulse temporal profile.

- **Requirements:**
  - High-energy electron spectroscopy (decreasing priorities)
    - Single-shot capability
    - Collection of high energy electrons, upto 1 keV.
    - Large collection window (~200 eV): Ability to collect photoelectrons or Auger electrons from different atomic edges which are separated by ~100 eV. Can be achieved through scanning multiple windows.
    - Energy Resolution of Electrons: ~0.5 eV
    - Angular Distribution: The angular distribution of emitted electrons should depend critically on the state of the molecular system.
  - Single-shot information about the temporal profile of the x-ray pulse (angular streaking, XTCAV) is preferred
  - For the correlation analysis, the data must be taken in a single shot method.
  - Higher repetition rates (>100 kHz) are useful to obtain a sufficiently diverse set of incident x-ray pulses for correlation analysis.

**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.