Time-resolved Spectroscopy Science from BL15-2

SSRL Town Hall Meeting

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Oct 8th 2021

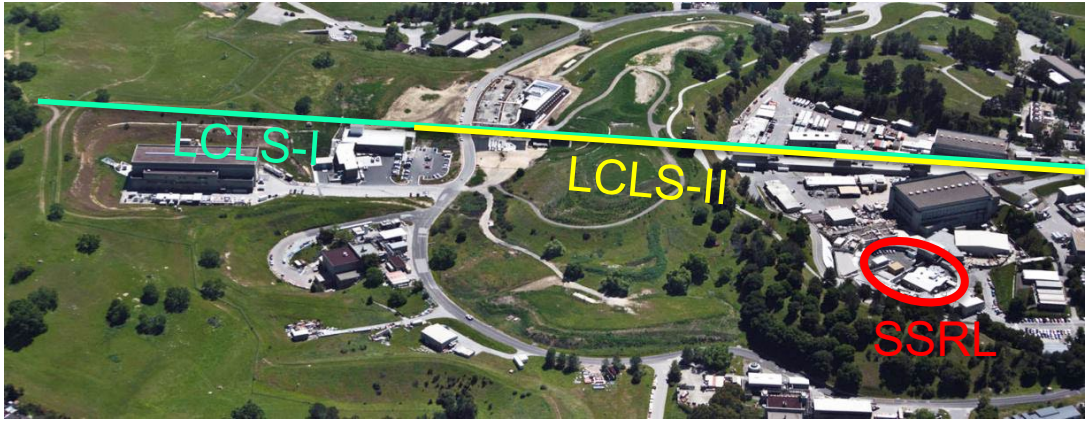
U.S. DEPARTMENT OF ENERGY | Stanford University

SLAC NATIONAL ACCELERATOR LABORATORY

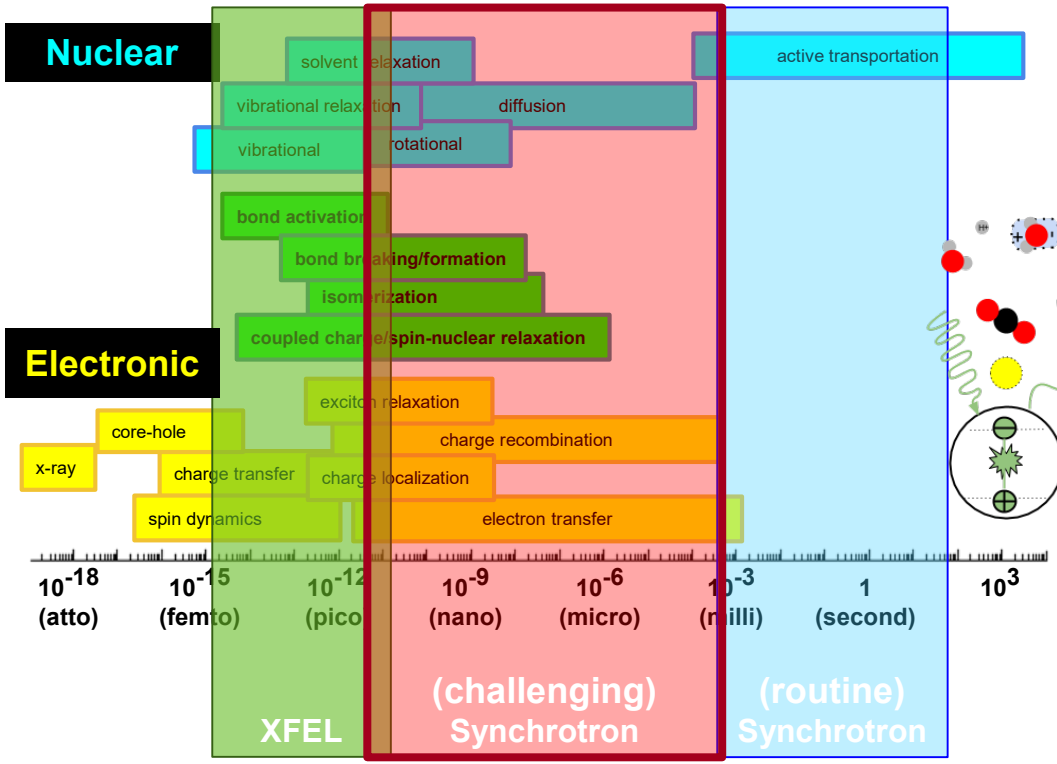
Vision and Strategy

- SLAC aims to maintain a world-leadership in x-rays and ultrafast science via its premier light sources: **SSRL** and **LCLS**

- The close partnership between **SSRL** and **LCLS** has been a unique SLAC strength for the growth of the science programs, development of capabilities, and exchange of expertise

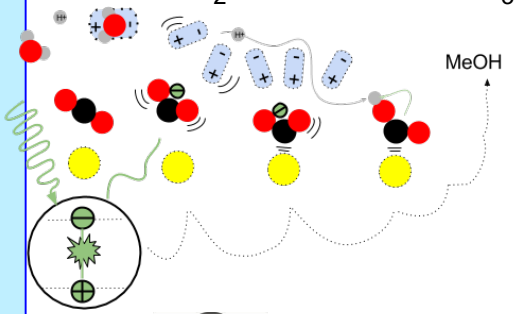


Science across broad timescales

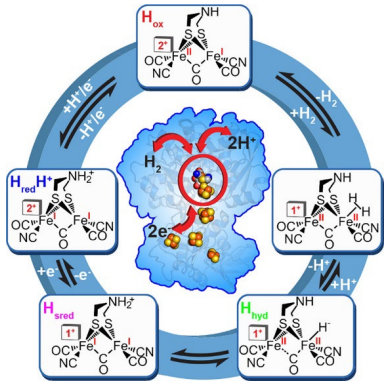


$CO_2 + h\nu + H \rightarrow$ alcohol

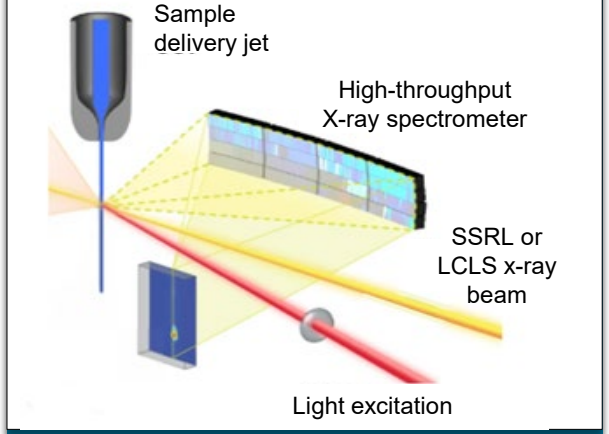
$N_2 + h\nu + H \rightarrow NH_3$



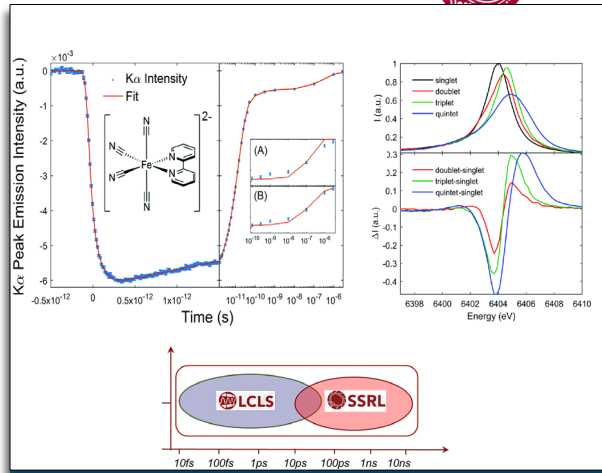
Chemical Reactivity: From Photoexcitation to Products (or Fuels)



Study sequential multi-step processes in chemical energy transformations across multiple timescales



Advanced x-ray spectrometers at SSRL and LCLS enable speciation of chemically active metal sites of catalysts with unprecedented sensitivity



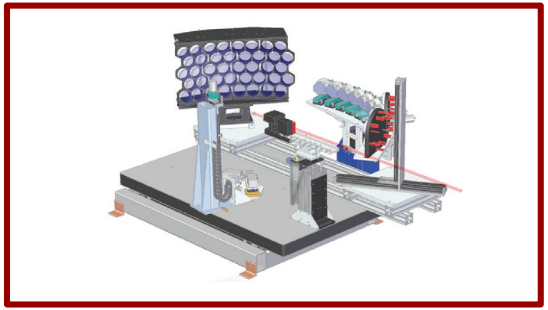
Complementary timescales of LCLS and SSRL (fs to μs) enable holistic studies of photocatalytic dynamic/kinetic phenomena upon light excitation

Complementarity of SSRL and LCLS accelerates advances in fundamental knowledge and applications for chemical energy transformations

High Resolution X-ray Spectroscopy at SSRL

6-2b

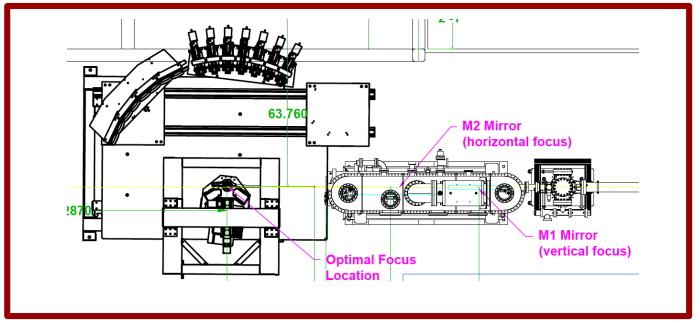
4.5-18 keV: XES, XAS, RIXS



15-2

4.2-25 keV: XES, XAS, RIXS

2020



BL15-2: Project Completion

- **BL6-2 end station has been integrated at BL15**
  - Multicrystal spectrometers
  - Sample environments
  - Detectors
  - Data acquisition and controls

- **All instruments/techniques commissioned and operational**
  - X-ray emission/HERFD/RIXS/X-ray Raman

- **BL15-2 is up and running**
  - Regular User Program has been resumed
  - 23 user experiments performed in 2021
  - 2 peer review publications are out and several more submitted

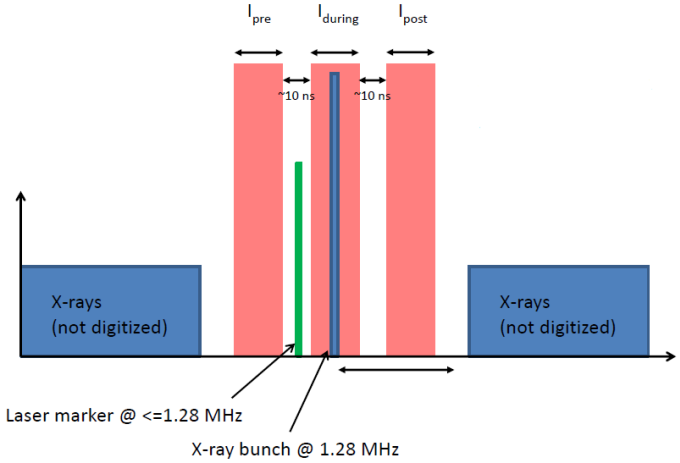
BL15-2 - New Opportunities

- **100% beamtime**
  - Enhancing the capacity of the existing successful science program
  - Expanding our capabilities to address further high impact research topics
- **Focused beam**
  - Long KB mirrors
    - **High rep-rate time-resolved studies (Overlap pump laser + x-rays)**
    - High pressure studies (Diamond Anvil Cells for transition metals, actinides)
    - Liquid mixing (microfluidics) and thin streams (low sample consumption)
- **Higher energies**
  - Up to 25.5 keV (unfocused)
    - High-Z Actinides (Am, Cm, Bk, etc.)
    - 4d Elements (e.g. Mo, Ru, Rh, Pd)

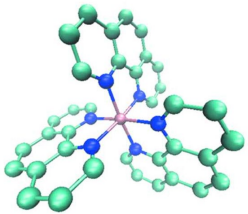
BL15-2: MHz repetition rate pump-probe ultrafast spectroscopy

- BL15-2 has developed a MHz rep-rate *laser pump x-ray probe* time-resolved capability
  - X-ray absorption (XANES and EXAFS)
  - X-ray Emission Spectroscopy
  - Resonant Inelastic X-ray Scattering
  - Unprecedented Detection sensitivity

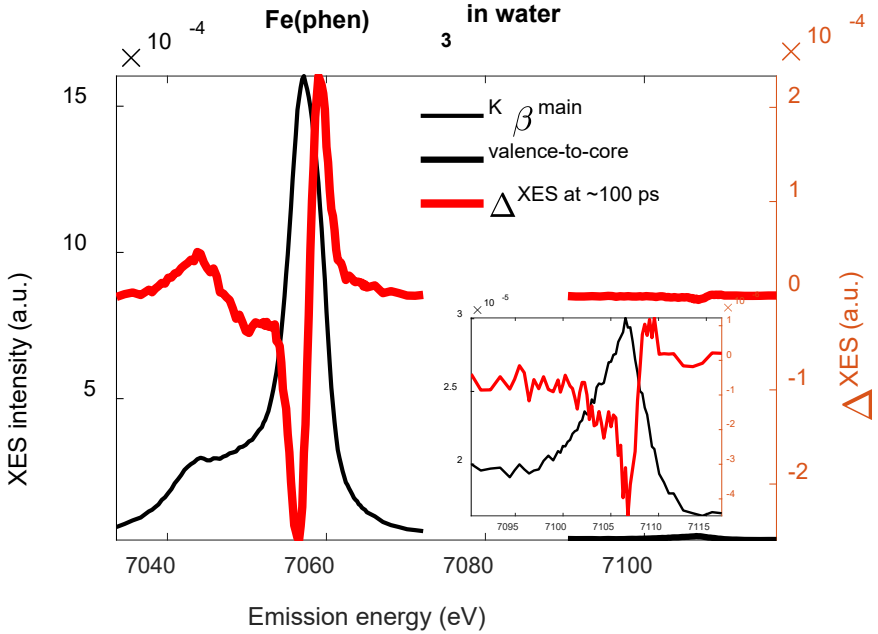
- Timing mode based on
  - 20mA camshaft (**~70 ps**, 10^{12} ph/s, 1.28MHz)
  - 50W Ytterbium-doped fiber laser
  - APD detectors with ns-response

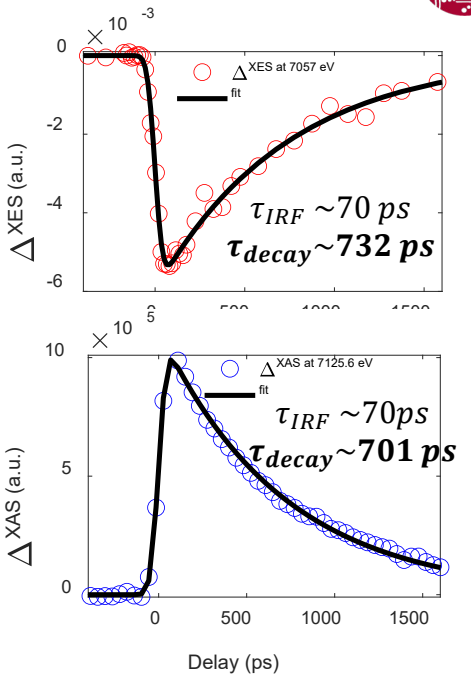


SSRL BL 15-2: Characterizing metastable high-spin states in solvated spin-crossover compounds



Zhan *et al.*, *Journal of Synchrotron Radiation* 24, 4, 818-824 (2017)



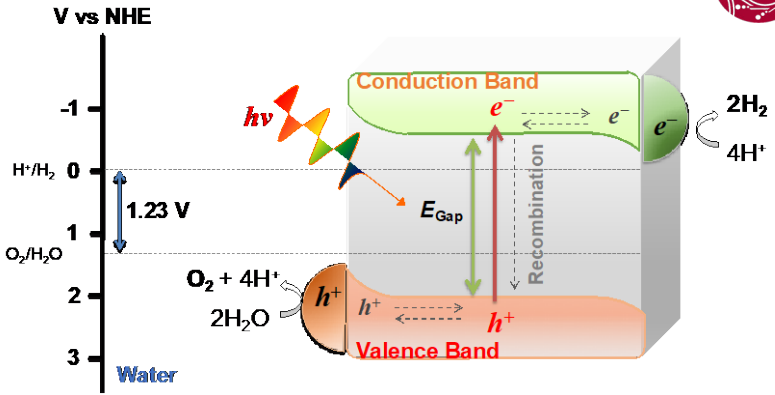


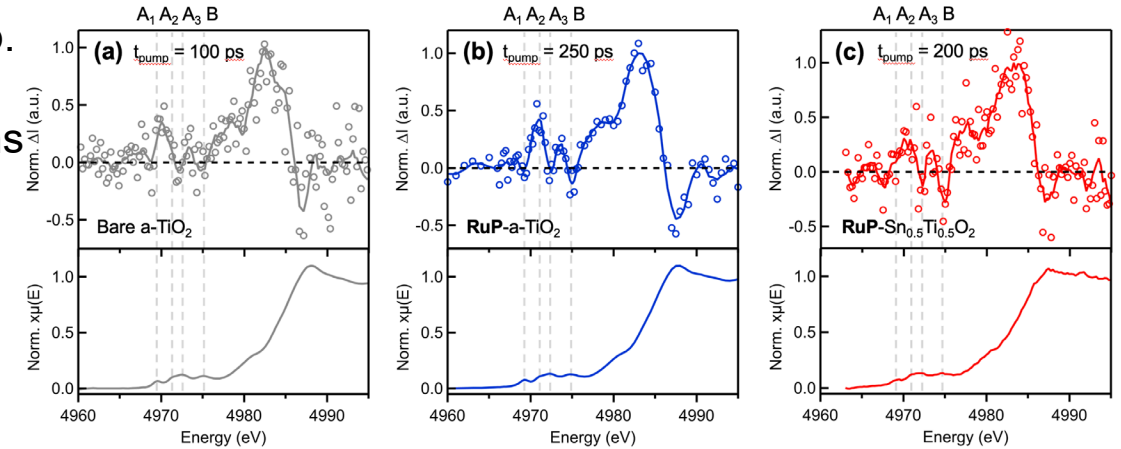
Metastable high-spin states of spin crossover transition can be followed with Kβ XES
High-throughput time-resolved capabilities at **SSRL can now also enable v2c XES**

Unpublished research

SSRL BL 15-2: Studying photocarriers dynamics in heterogeneous photocatalytic systems

- Sustainable production of solar fuels requires appreciable improvement of solar-to-fuel efficiency
- Understanding and improving solar photoabsorbers quantum efficiency (=conversion of solar photons to usable charge carriers) is a key step.
- Ability to follow charge trapping paths can enable us to



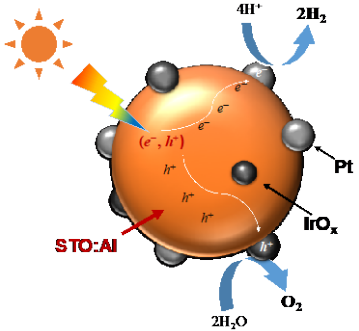


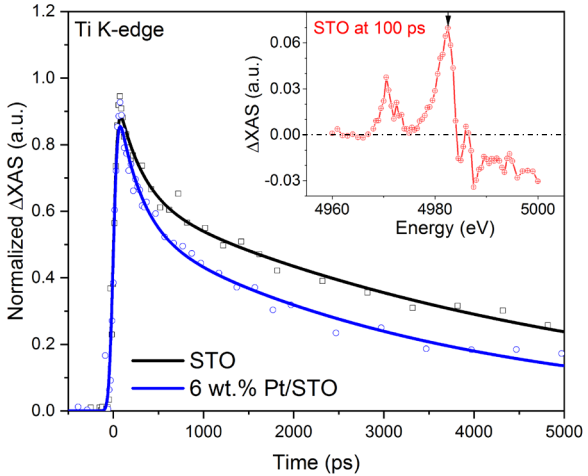
Unpublished research

J. Spies, Yale

SSRL BL 15-2: Studying photocarriers dynamics in heterogeneous photocatalytic systems

- Cocatalysts dramatically improve the solar-to-fuel conversion efficiency of heterogeneous photocatalytic systems not only by improving the catalytic TOF but also by forcing better charge extraciton
- Photocarrier dynamics and charge transfer rates across solid-liquid interfaces consists a major scientific topic beyond photocatalysis
- Example: Time-resolved XAS of bare SrTiO3 and SrTiO3 loaded with 6% of Pt 1-nm particles reveal different charge carrier lifetimes.
- Ability to measure actual semiconducting absorbers under realistic reaction environments is key

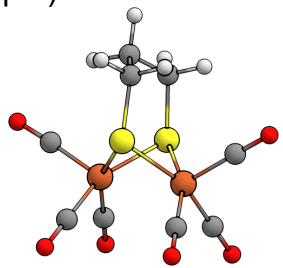


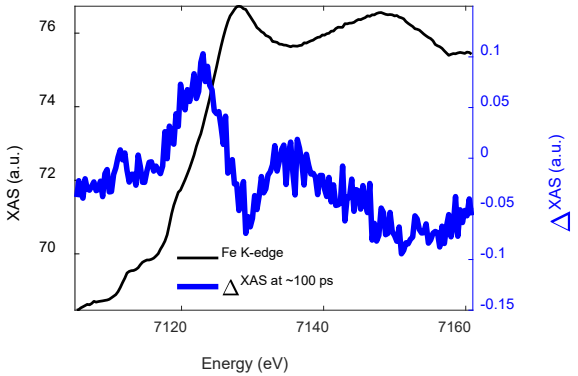


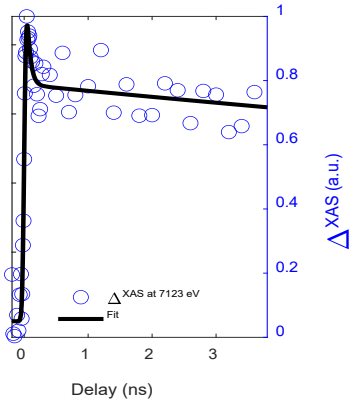
Unpublished research

SSRL BL 15-2: Towards studying reactive intermediates of hydrogenase model systems

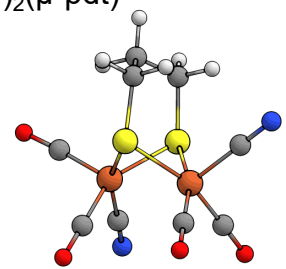
$Fe_2(CO)_6(\mu\text{-pdt})$

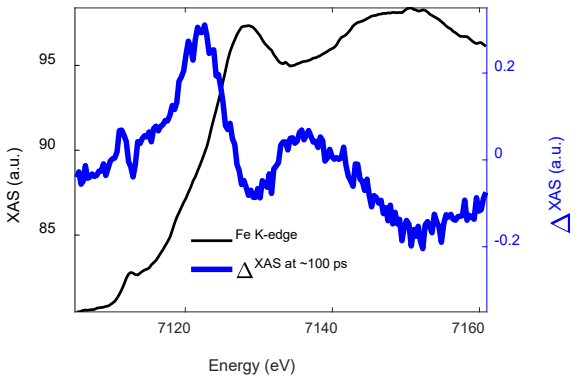


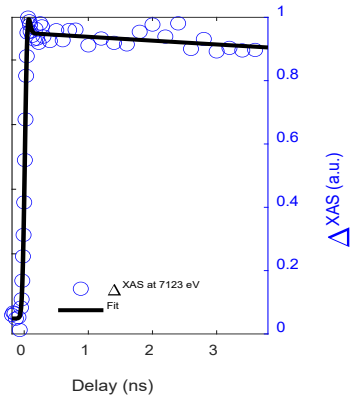




$Fe_2(CO)_4(CN)_2(\mu\text{-pdt})$



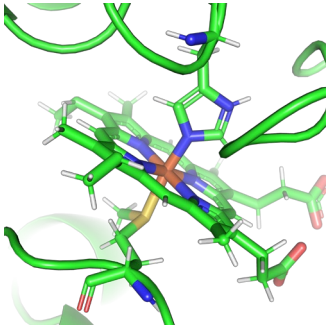




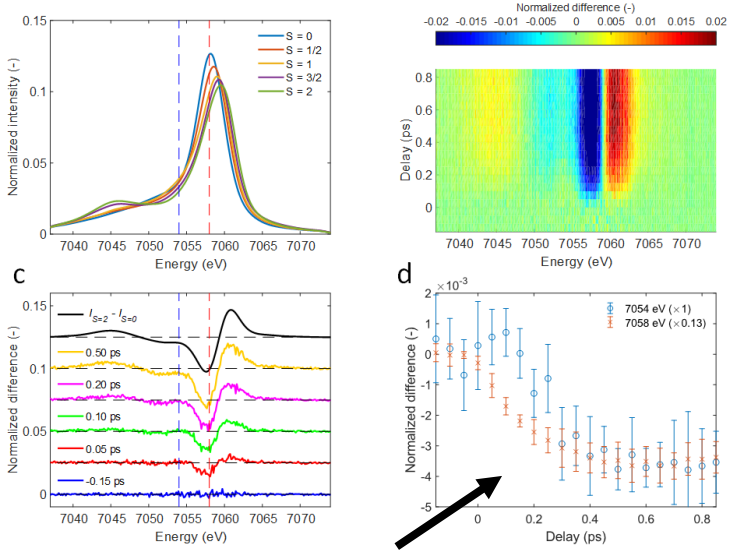
Ligand dissociation of biomimetic molecules show sub-ps dynamics

Unpublished research

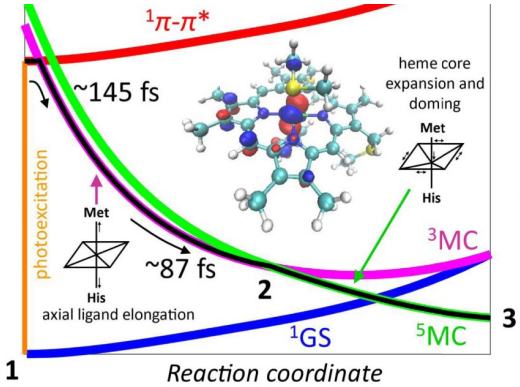
LCLS: Understanding ultrafast axial ligand dissociation pathways in heme proteins



Reinhard *et al.*,
Nature Communications **12**,
1086 (2021)



Short-lived
intermediate



SLAC is a unique position to enable the study of ultrafast sub-ps dynamics with LCLS

Current status and Future prospects

- Time domain-based science is a SLAC core competency
- Beam Line 15-2 has been commissioned and has met the targeted performance metrics; in particular have successfully demonstrated the capabilities to perform time-resolved studies for XAS, XES and RIXS.
- The recent availability of the time-resolved mode during normal SPEAR3 operations allows us to build a regular access-based science program. Importantly, more time-resolved capabilities are under preparation (Beamline 17)
- **LCLS** and **SSRL** have been working collaboratively on complementary developments to enable a premier and unique time-resolved science program
- The high rep-rate and energy range of LCLS-II benefits tremendously from the collaborative developments with SSRL on tender x-ray regime and the existing high-rep rate time-resolved mode.

Contributions and Developments

- D. Skoien, M. Reinhard, T. Kroll

- D. Harrington, T. Rabedeau, N. Boiadjeva, A. Maciel, A. Prado, T. Huynh, D. Zhang, D. Day, L. Campos, C. Ramirez, M. Latimer, J. Corbett, J. Safranek, K. Tian, M. Padilla

- A. Garcia-Esparza, J. Spies, M. Qureshi, T. Hersbach, O. Paredes, X. Li, B. Matson,

Stanford Synchrotron Radiation Lightsource is a National User Facility operated by Stanford University on behalf of the U.S. Department of Energy