Advanced Light Source BL6

Ultrafast X-ray Spectroscopy

U.S. DEPARTMENT OF ENERGY — Office of Science

BERKELEY LAB — Lawrence Berkeley National Laboratory

Structural Dynamics in Condensed Matter

Scientific Motivation:

An significant scientific challenge is to understanding the dynamic interplay between atomic and electronic structure – particularly in complex materials that are not well described by single-electron band models, or simple adiabatic potential energy surfaces. Ultrafast x-ray measurements on the fundamental time scales of the underlying correlations can offer new physical insights by separating correlated effects in the time domain while providing direct information about atomic and electronic structure.

Atomic/Electronic Structural Dynamics

fundamental time scales:
atomic motion - vibrational period: T_{vib} ~ 100 fs
electron-phonon interaction times ~ 1 ps

- ultrafast chemical reactions
- ultrafast phase transitions
- surface dynamics
- ultrafast biological processes

Femtosecond X-ray Science

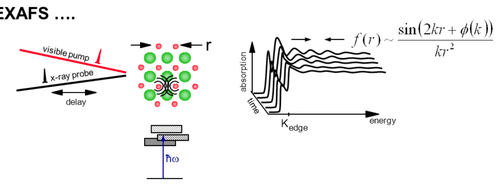
time-resolved x-ray spectroscopy

EXAFS – local atomic structure and coordination
(extended x-ray absorption fine structure)

XANES – local electronic structure, bonding geometry, magnetization/dichroism
(near-edge x-ray absorption fine structure)

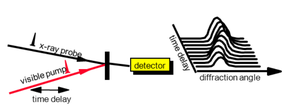
element specific
molecular systems and reactions
complex/disordered materials

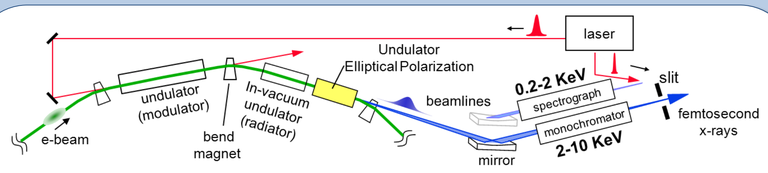
surfaceEXAFS, μEXAFS ….

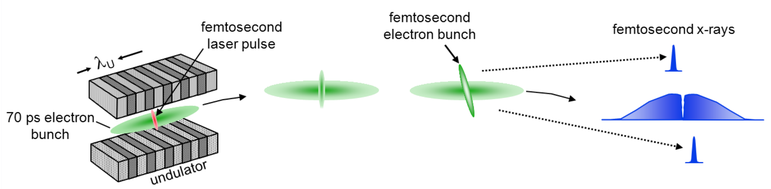


time-resolved x-ray diffraction

atomic structure in systems with long-range order/periodicity
phase transitions, coherent phonons





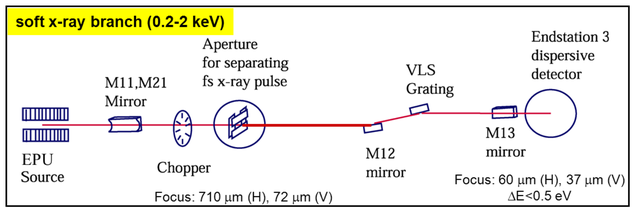


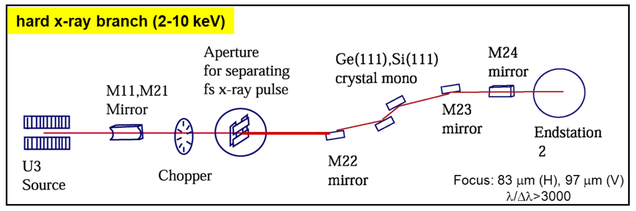
1 laser modulation of e-beam energy

2 spatial separation dispersive bend

3 undulator beamlines

A. Zholents and M. Zolotorev, *Phys. Rev. Lett.*, **76**, 916 (1996)
Schoenlein et al., *Science*, **287**, 2237 (2000)

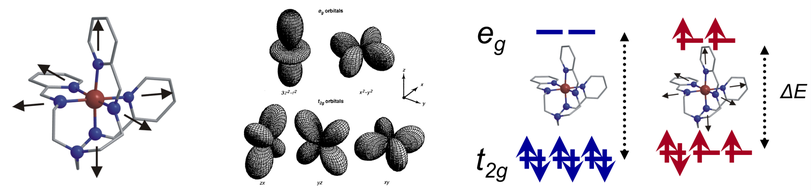


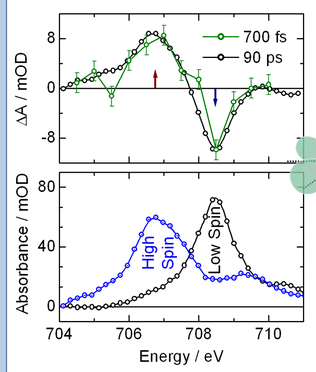


Beamline flux at the sample position is ~2×10^8 photons/s in picosecond mode and ~2×10^4 photons/s in femtosecond mode (@ 4 KHz).

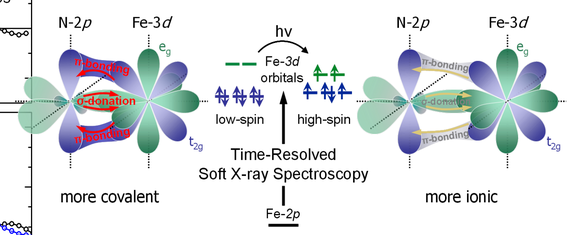
Ligand-Metal Interactions

Octahedral Fe^{II} complex | **HOMOs & LUMOs** | **Low-Spin** | **High-Spin**

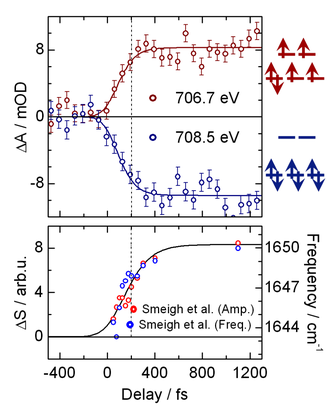




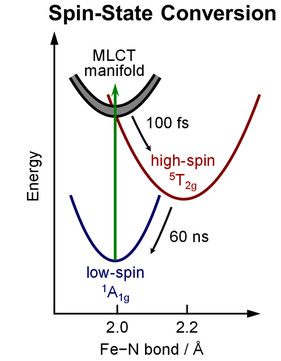
Detail changes orbital interactions



Khalil et al. *JPCA* **110**, 38 (2006)
Huse et al. *JACS* **132**, 6809 (2010)



Model for Ultrafast Spin-State Conversion



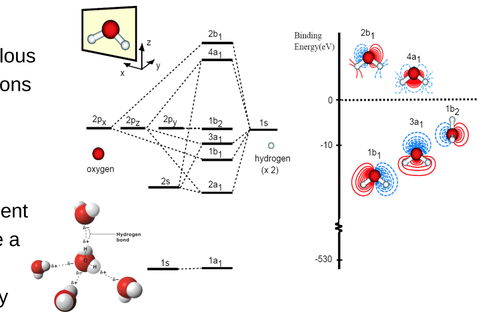
- **Changes in charge distribution and covalent interactions accessible**
- **Information on symmetry-specific orbital interactions**
- **Electronic & structural information complement to understand chemical pathways**
- **Advanced multiplet theory and ab-initio electron structure calculations - future**

Hydrogen-Bond Dynamics in Water

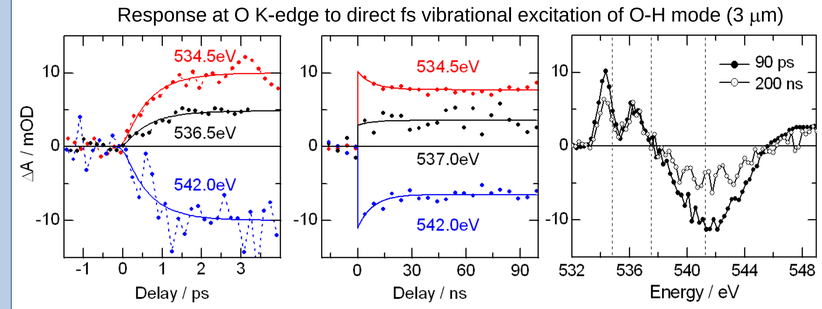
Structural Dynamics

- Anomalies render water an ideal medium for life. Linking its anomalous properties to microscopic interactions is one of the main goals in water research
- Weak but distinct electronic interactions and structural rearrangement on a multitude of time scales pose a great challenge to understanding structural dynamics experimentally and theoretically

Relevant orbitals

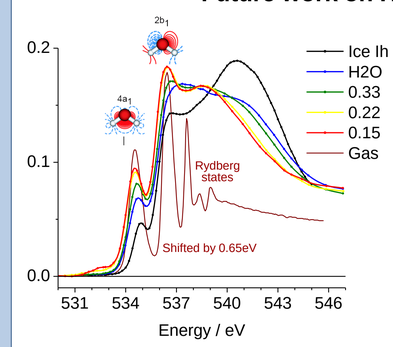


Response at O K-edge to direct fs vibrational excitation of O-H mode (3 μm)

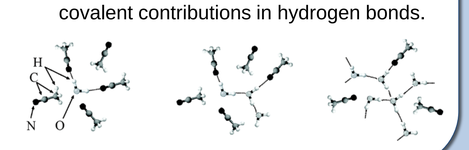


Huse et al. *PCCP* **11**, 3951 (2009) Wen et al. *JCP* **131**, 234505 (2009)

Future work on Hydrogen-bonded systems



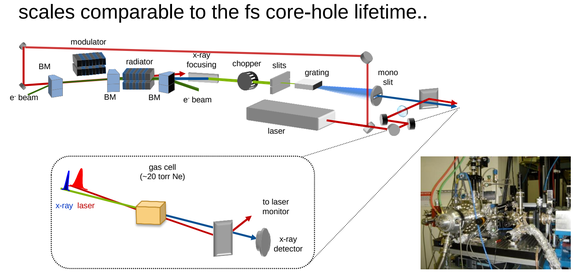
- X-ray spectroscopy is sensitive to hydrogen bonding by probing the valence charge distribution of oxygen
- Model systems such as binary mixtures of acetonitrile and water allow for simpler hydrogen bond geometries, revealing the meaning of x-ray spectroscopic signatures and conversely providing information on covalent contributions in hydrogen bonds.



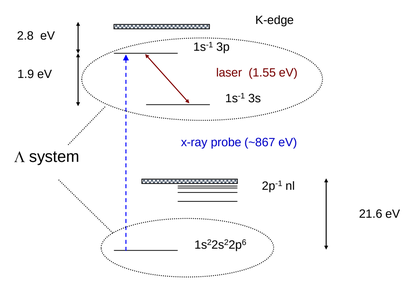
Controlling X-rays with Light: X-ray Transparency

L. Young (ANL), A. Belkacem (LBNL)

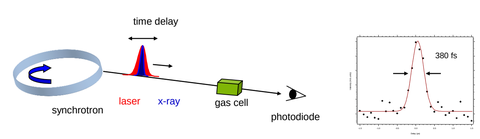
Can light be used to control X-ray interactions with matter, analogous to Electromagnetically Induced Transparency? Control concepts rely on imposed coherence among eigenstates. Rapid core-hole filling makes this a challenge, and requires driving a coherent electronic response on time scales comparable to the fs core-hole lifetime..



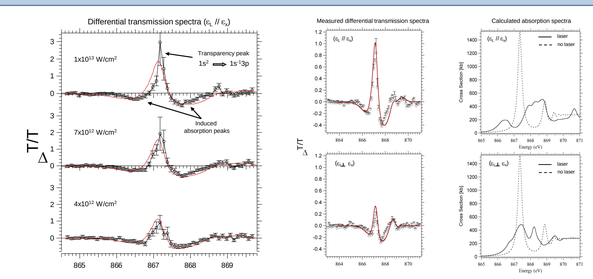
An intense fs optical 'dressing' pulse co-propagates with a fs X-ray pulse through a Ne gas cell and X-ray transmission is measured as a function of optical intensity.



Relevant energy levels in Ne. X-rays probe core-excited Rydberg states coupled by an intense optical field.



225 fs x-ray pulse-duration measurement



Left: Change in x-ray transmission vs. optical intensity. Right: dependence on laser polarization (ε_L).

- **X-ray transparency has been demonstrated, indicating that light can be used to control x-ray/matter interactions.**
- **A fs transparency window created by an ultrashort laser pulse was used to demonstrate an all-photonic cross correlation measurement of an ultrashort x-ray pulse**

T.E. Glover, M.P. Hertlein, S. H. Southworth, T.K. Allison, J. van Tilborg, E.P. Kanter, B. Krassig, H.R. Varma, B. Rude, R. Santra, A. Belkacem, L. Young, *Nature Phys.* **6**, 69 (2010).