Ultrafast chemical dynamics with optical and X-ray pulses

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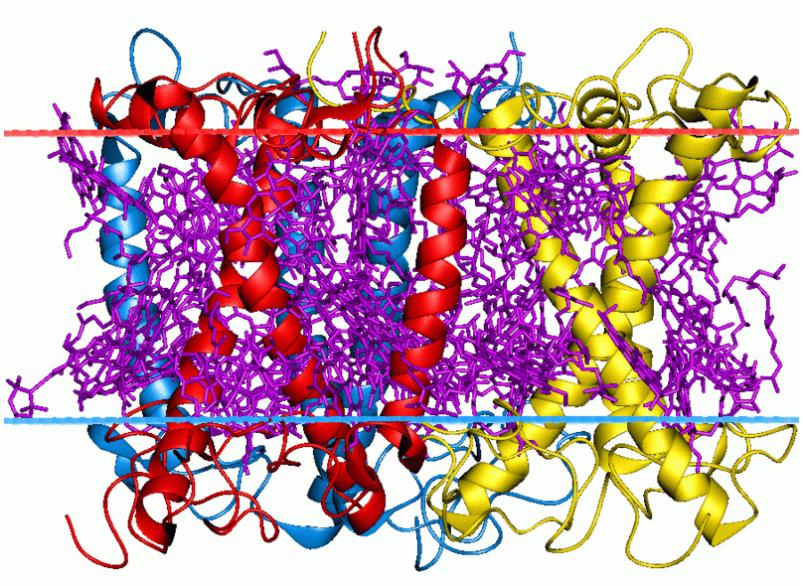
LAUSANNE CENTRE FOR ULTRAFAST SCIENCE LACUS

SwissFEL kick-off users meeting (Villigen, Dec. 2016)

"If you want to understand function, study structure" (Francis Crick)

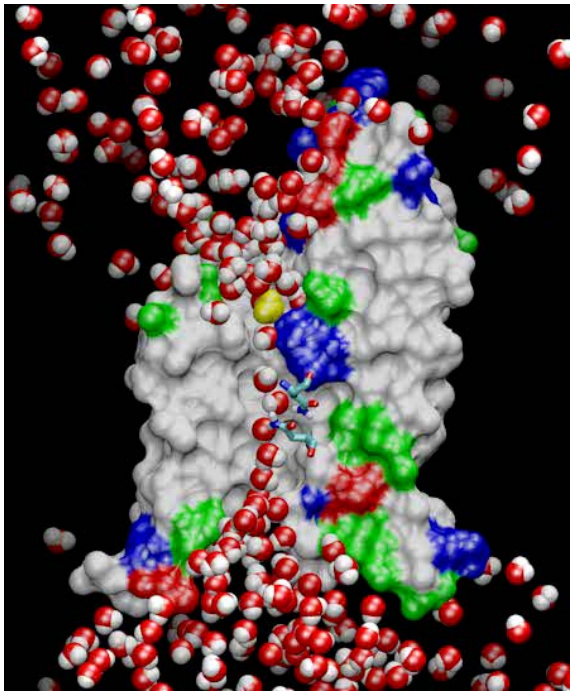
Structure

- X-ray crystallography
- electron microscopy
- NMR
- atomic force microscopy
- electron diffraction
- X-ray absorption spectroscopy



Side view of the light-harvesting complex II in chlorophyll (PDB)

Dynamics



Water transport through an aquaporin channel in a cell membrane
http://www.ks.uiuc.edu/Research/aquaporins/
Tajkhorshid et al. Science 296 (2002) 525-530

"Only when one may trace the path of atoms in the course of catastrophic vibrations that sever chemical bonds can the true mechanism of change be properly characterized"

J. M. Thomas, Nature (1991)

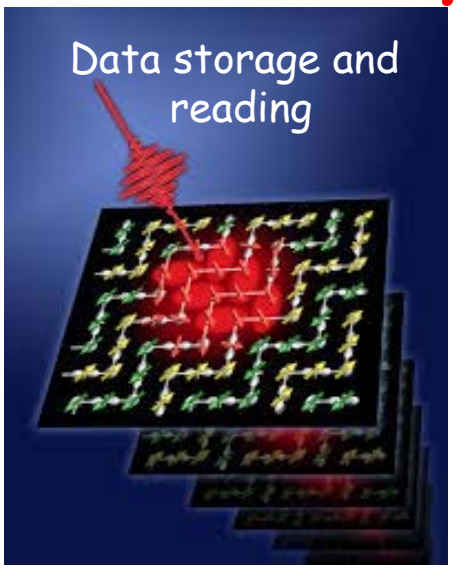
Structural methods

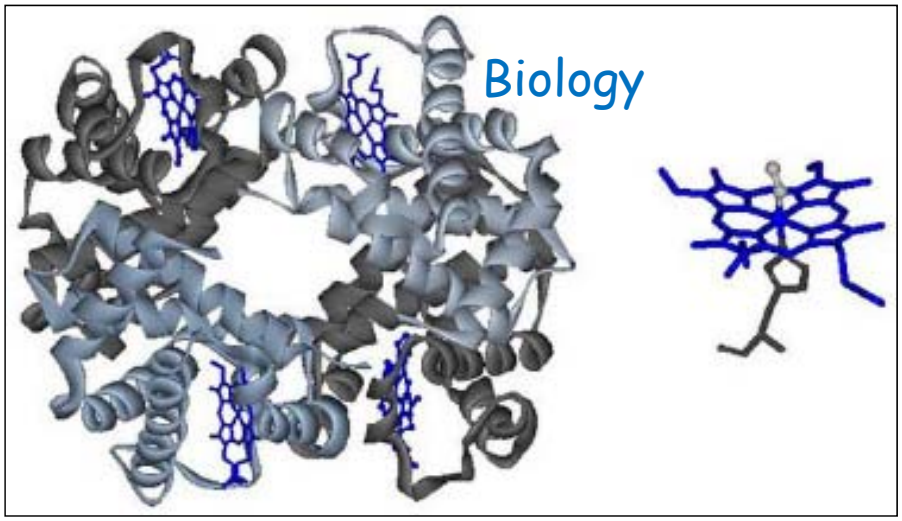
Electron diffraction and microscopy

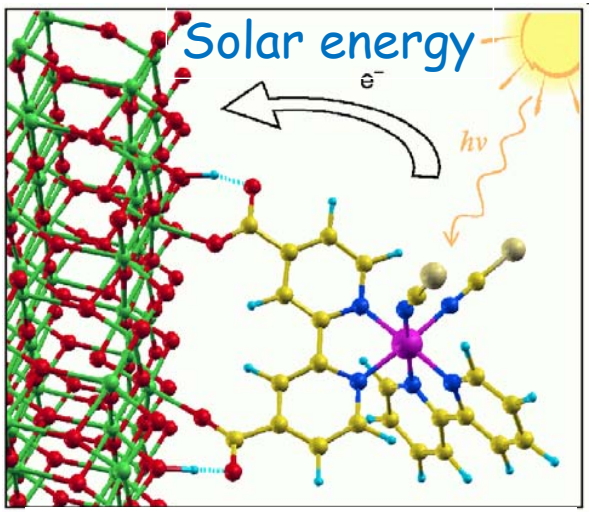
X-ray diffraction and scattering

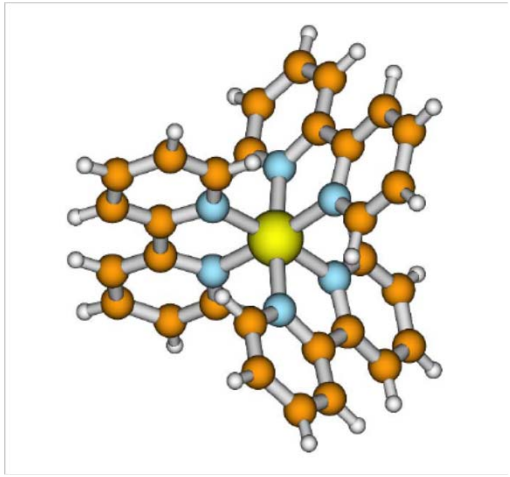
X-ray spectroscopies

Spin dynamics in metal-complexes

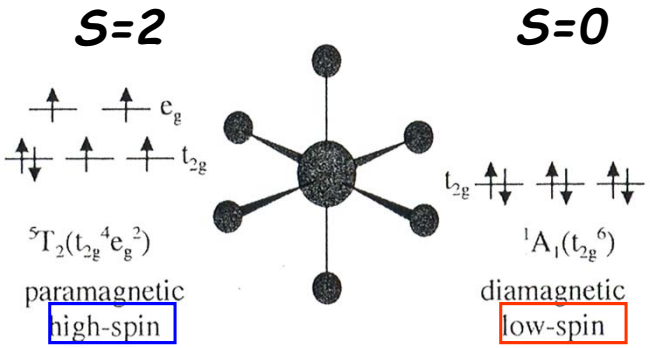


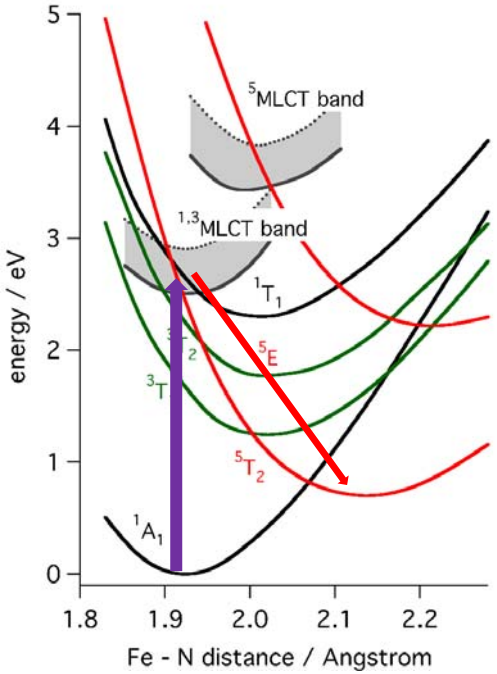






$[Fe(bpy)_3]^{2+}$





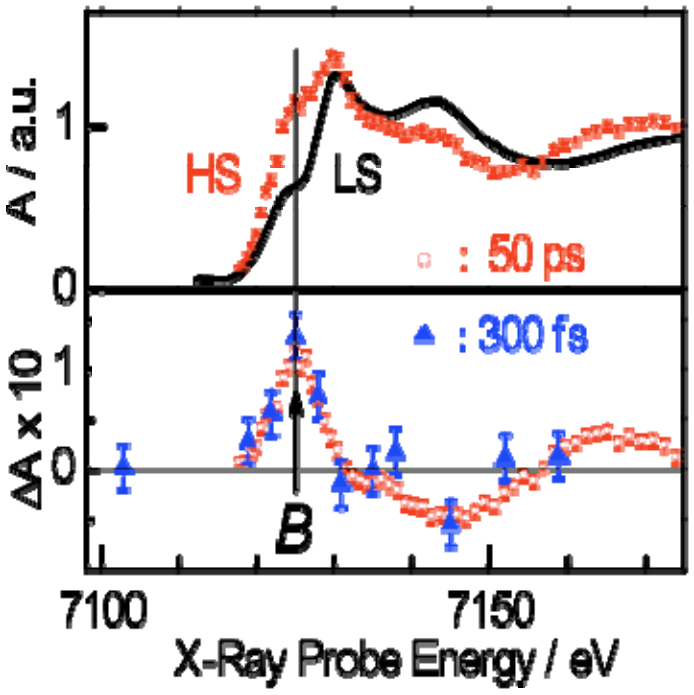
What is the structure change upon Spin Cross-Over (SCO)?

How fast is light-induced SCO?

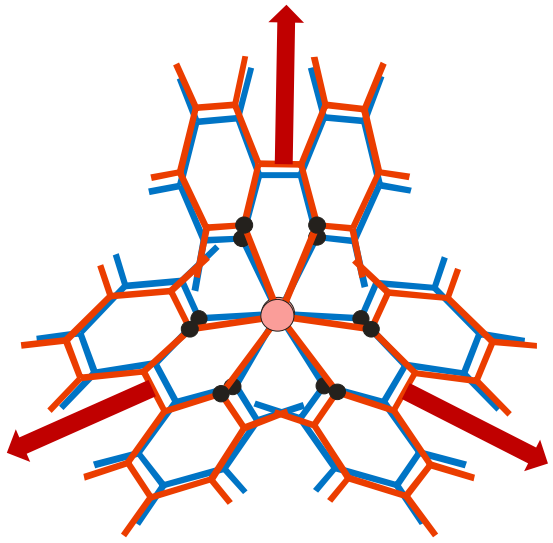
What is the mechanism for light-induced SCO?

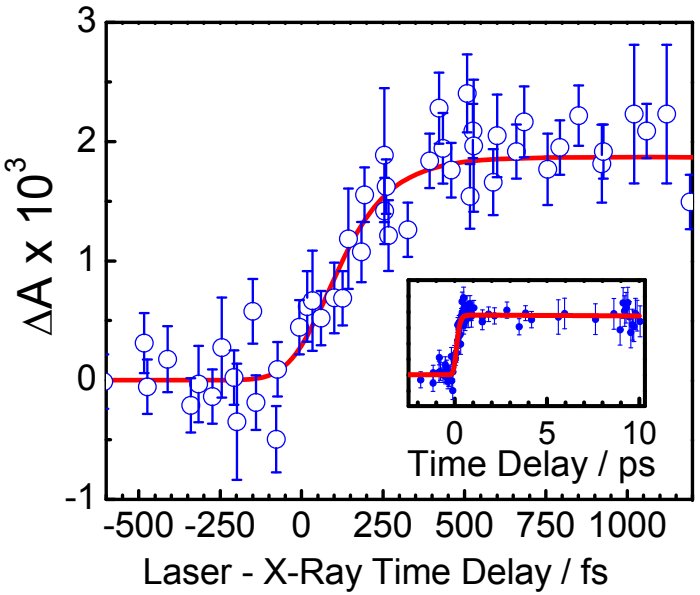
Spin cross-over: Ps/Fs Optical (visible, UV) and X-ray studies

Ps and fs Fe K-edge probe



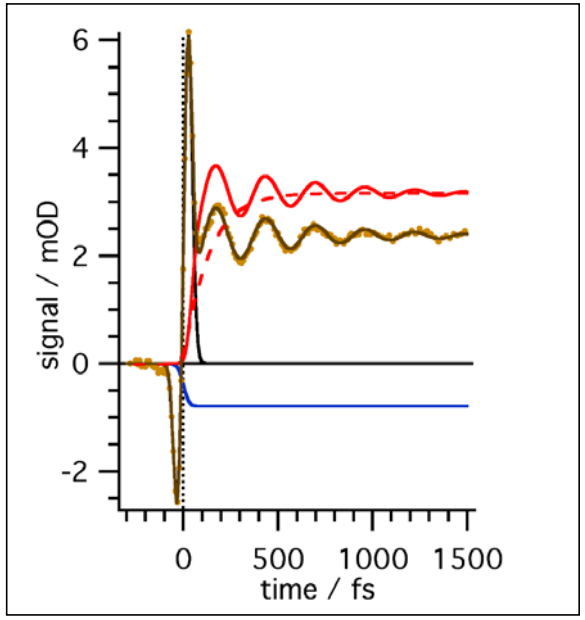
W. Gawelda et al. *JACS* (2007); *Phys. Rev. Lett.*, (2007)





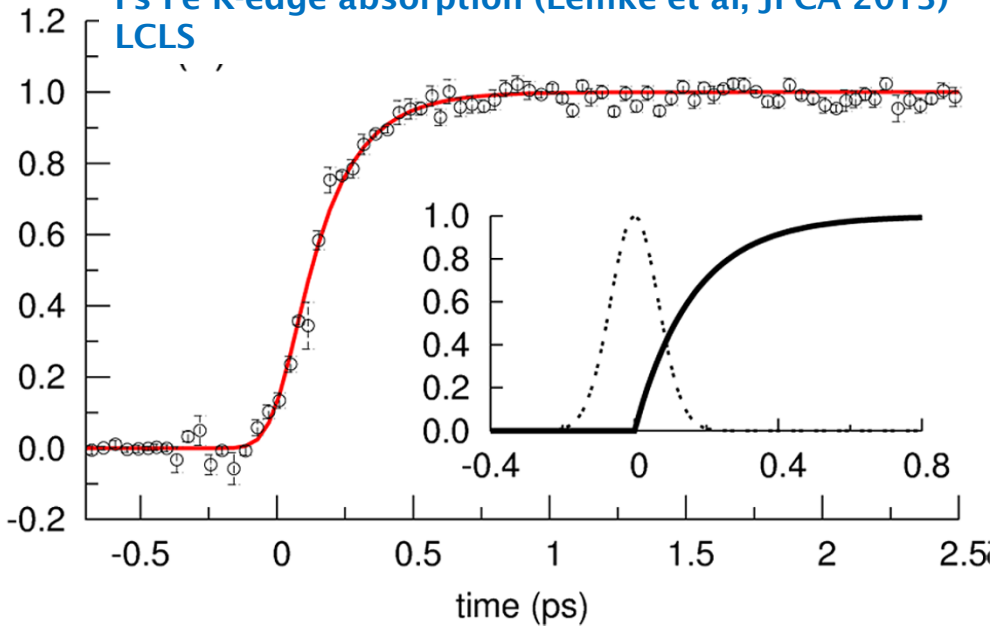
Ch. Bressler et al. *Science* (2009)
Slicing

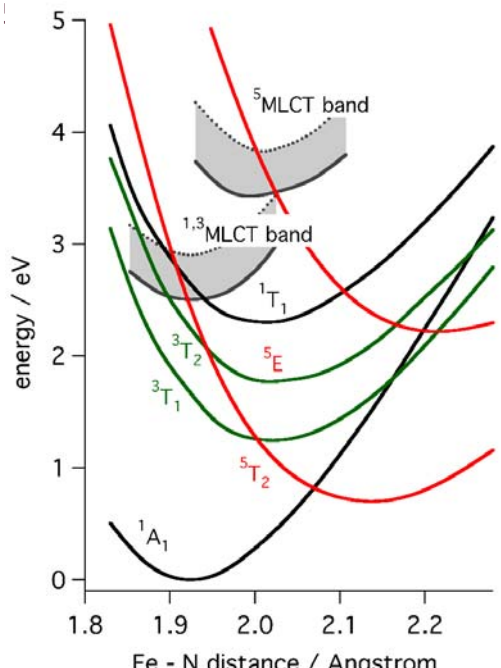
UV and visible probes



C. Consani et al. *Angew. Chem. Int. Ed.* (2009)
G. Auböck and M. Chergui, *Nat. Chem.*

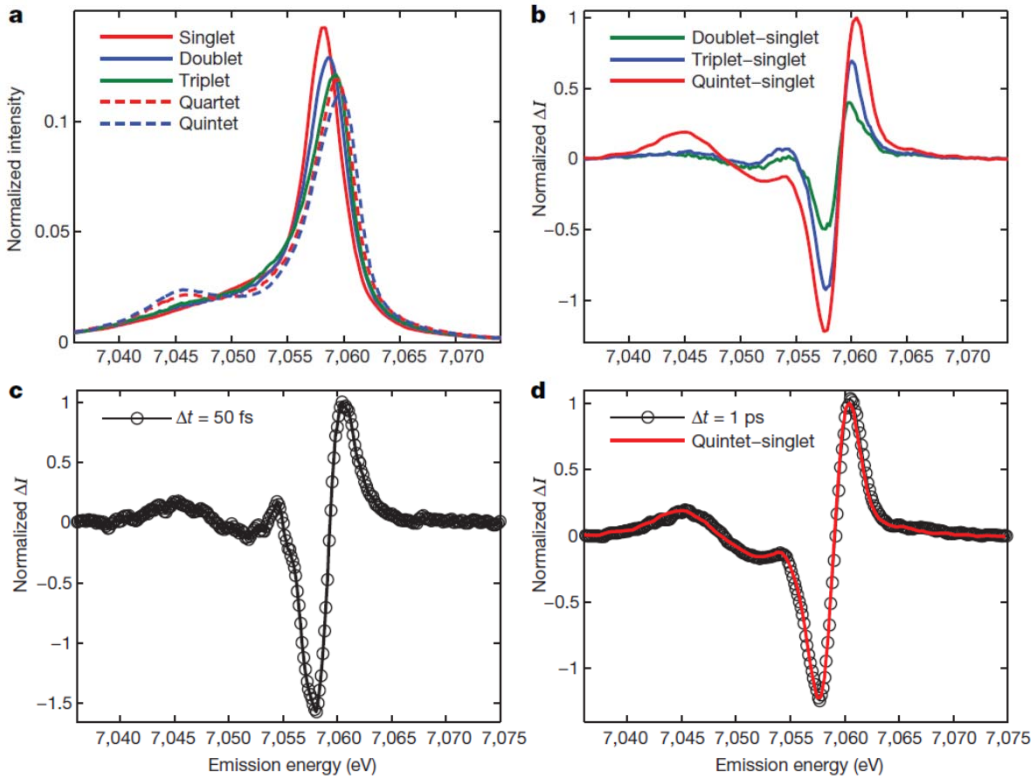
Fs Fe K-edge absorption (Lemke et al, JPCA 2013)
LCLS

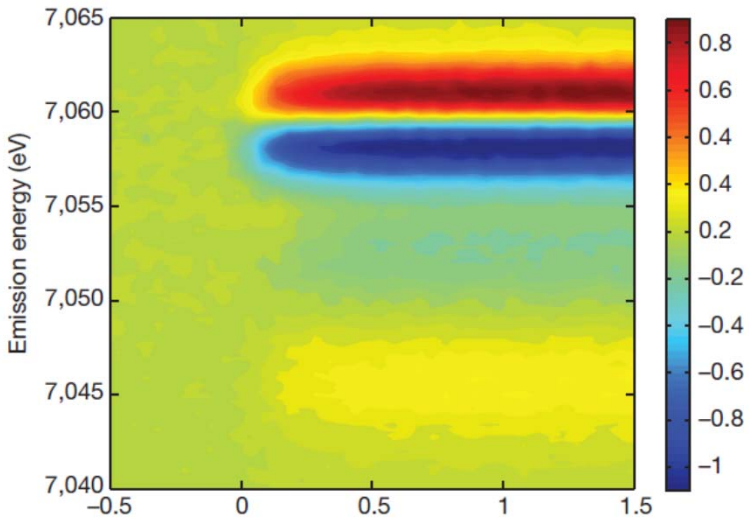


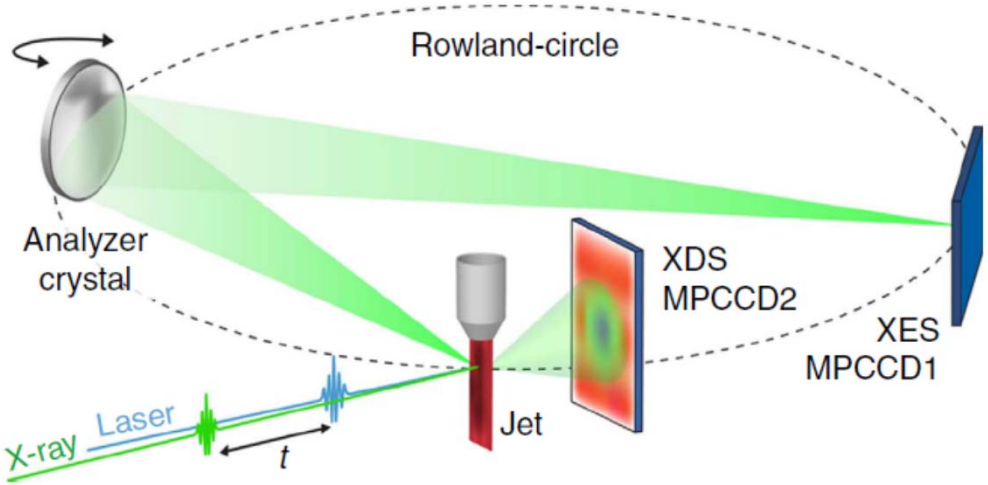


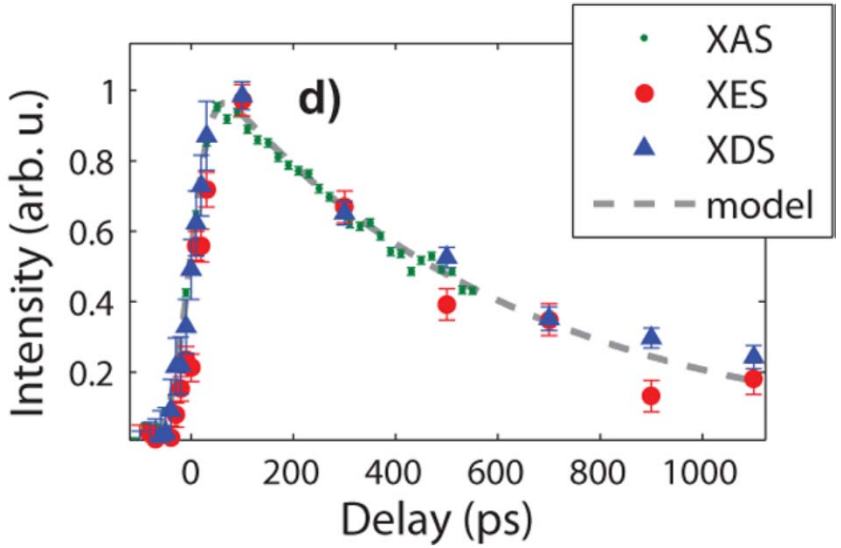
Femtosecond optical pump/X-ray emission probe at an XFEL

Zhang et al. *Nature* (2014)
LCLS





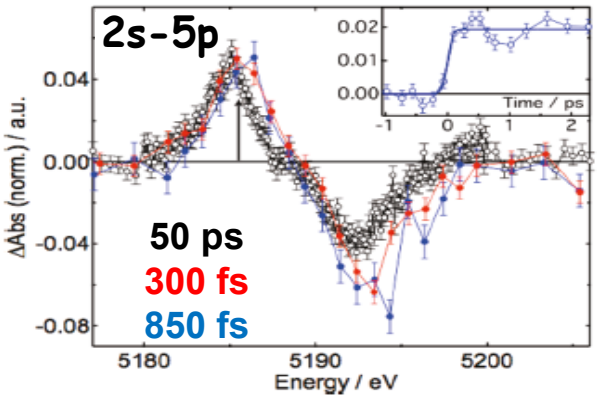




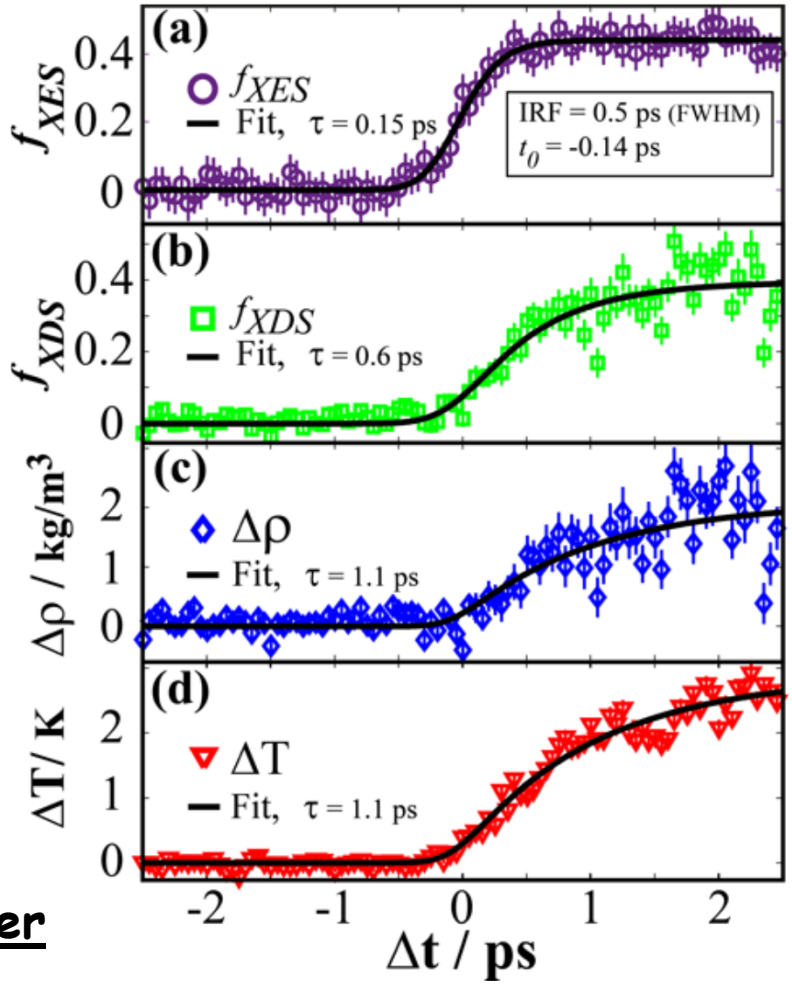
Haldrup et al, JPCA 2012 and Bressler et al, Farad. Disc. 2014

Solvation Dynamics

Iodine L_1-edge (2s)

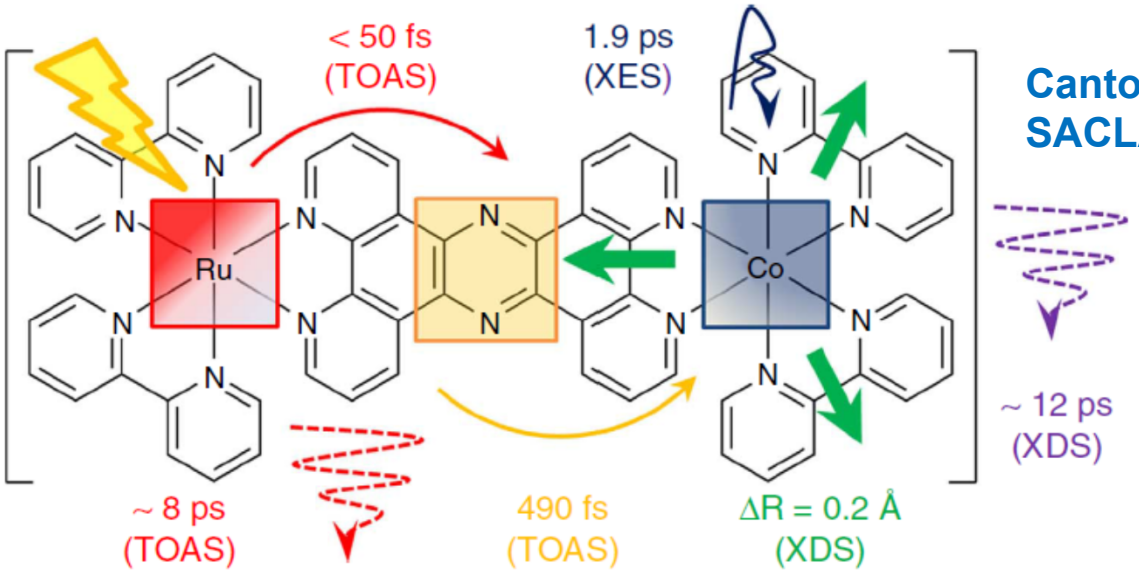


Pham et al, JACS (2011)
Slicing



Haldrup et al, JPCB 2016
LCLS

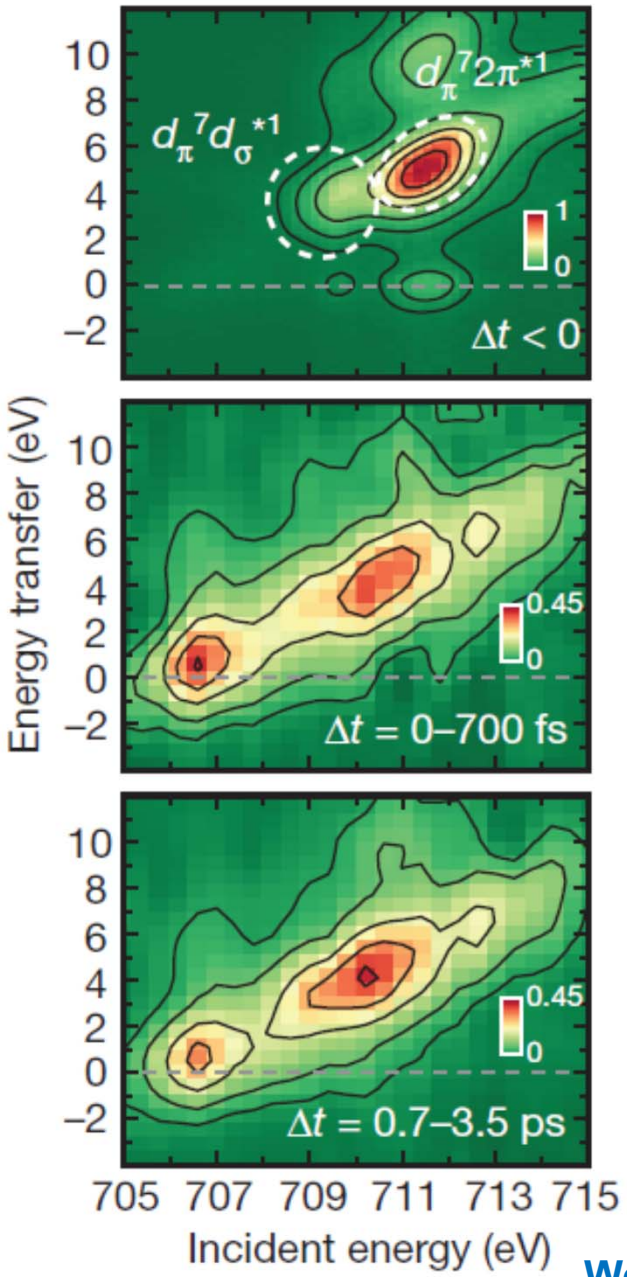
Intermolecular charge transfer

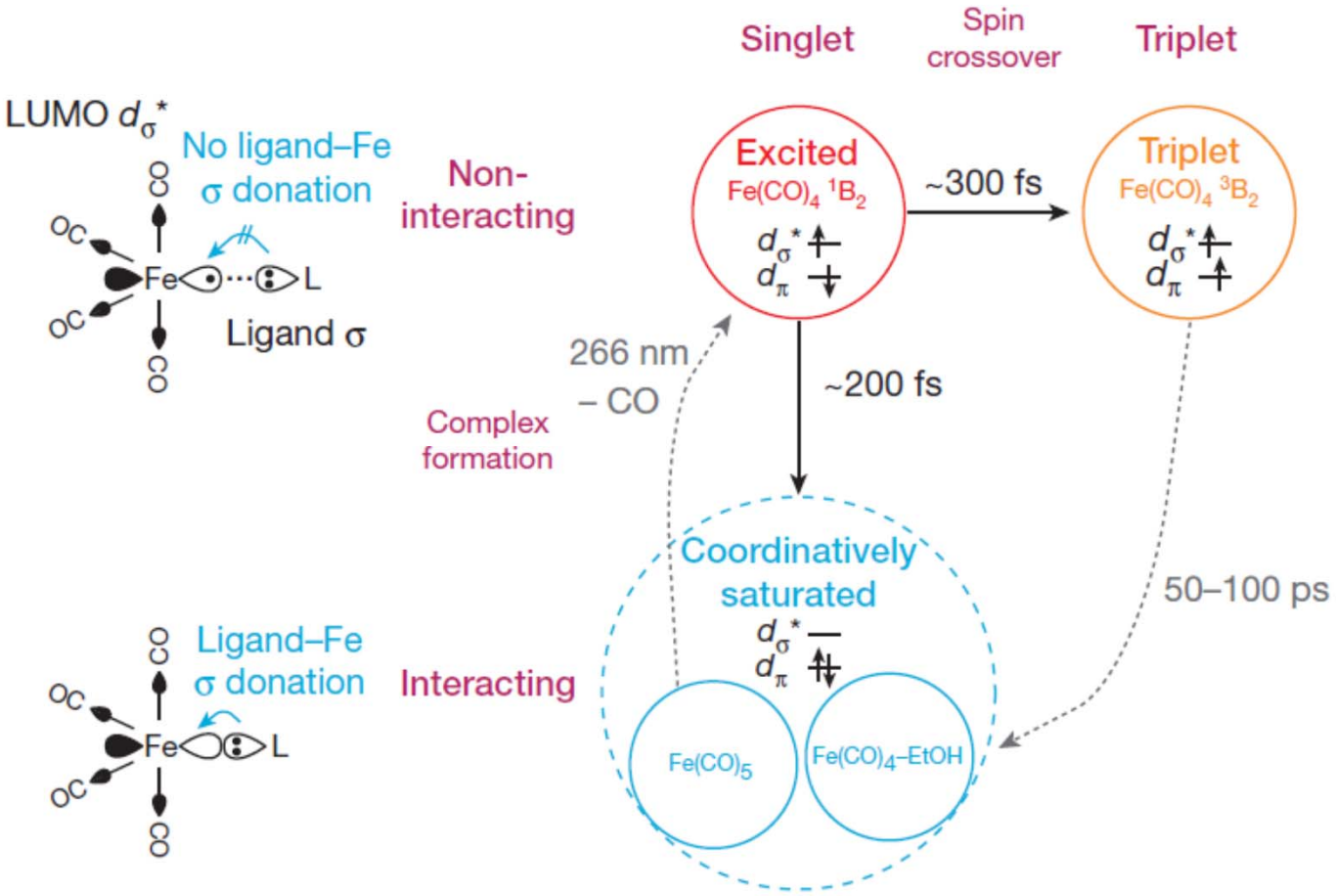


Canton et al, Nat. Comm. 2015
SACLA

Femtosecond optical pump/soft X-ray RIXS probe at an XFEL

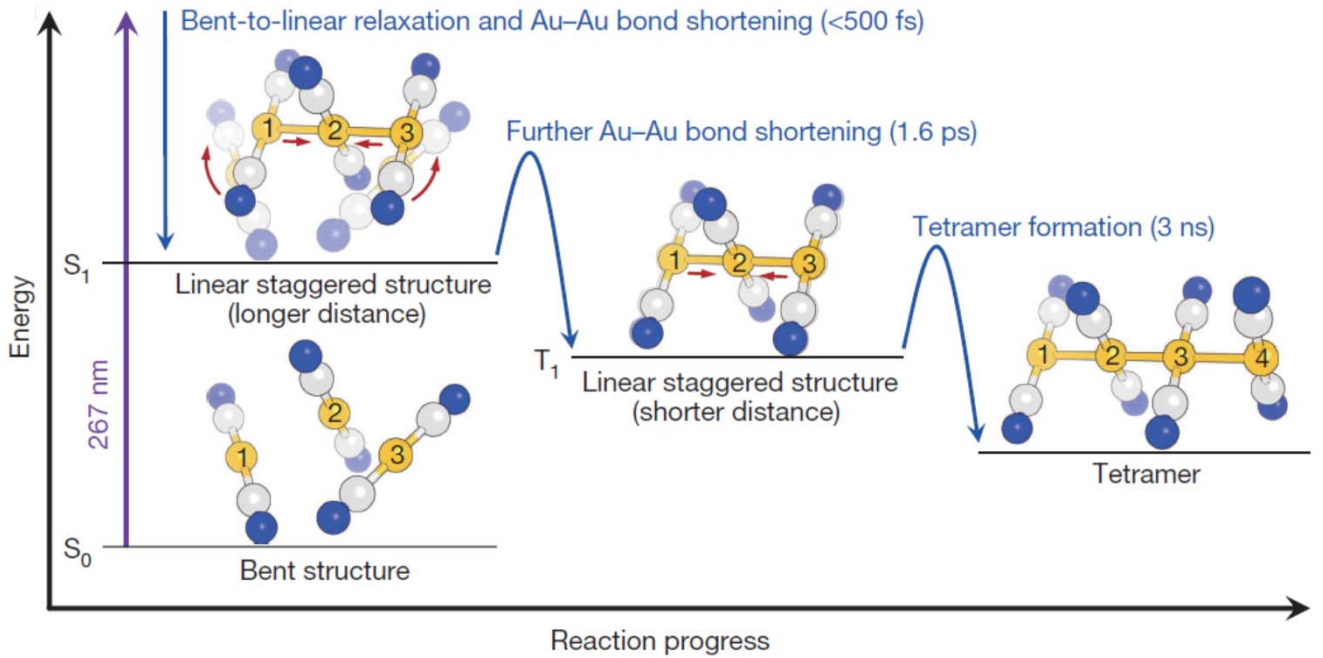
Dissociation and binding of a solvent molecule: $Fe(CO)_5$



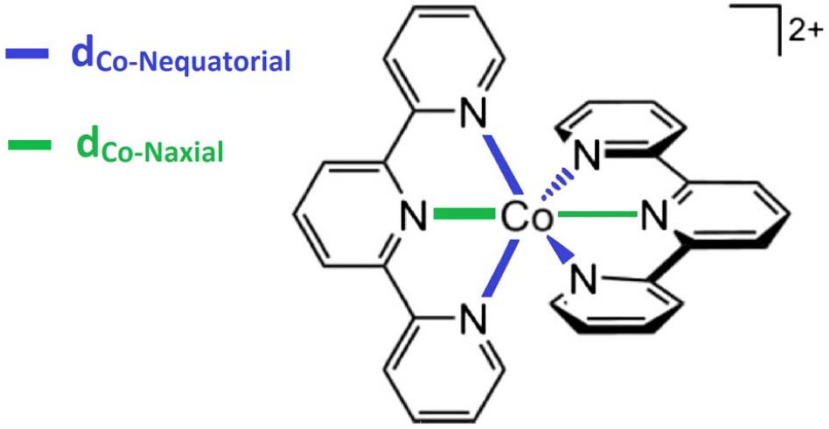


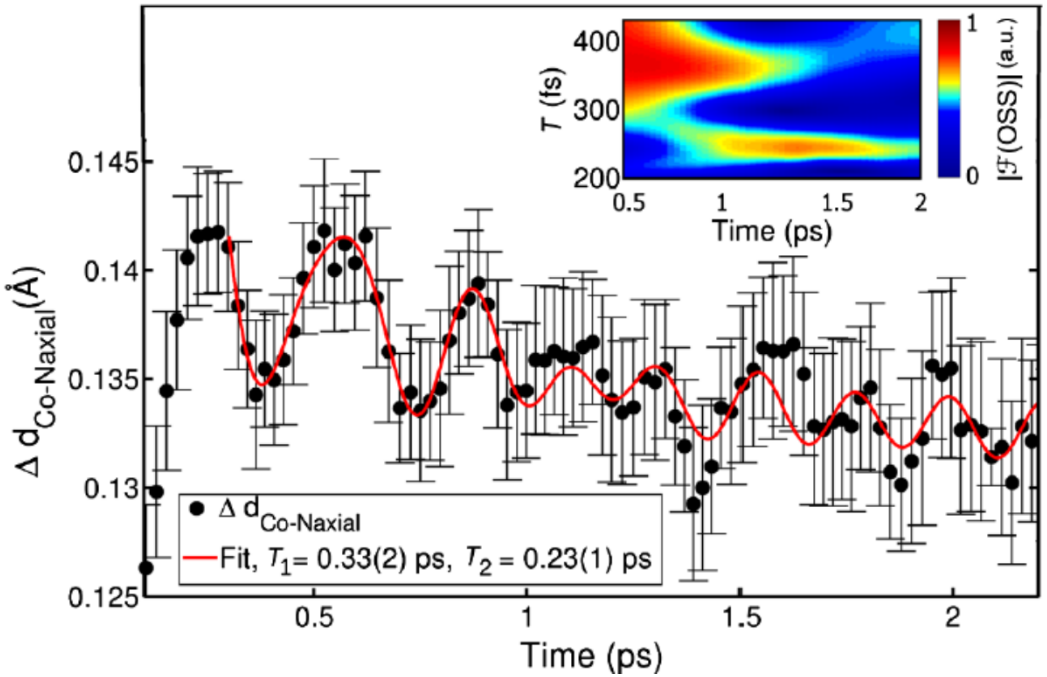
Wernet et al, Nature 2015 and Kunnus et al, Struct. Dyn. 2016
LCLS

Femtosecond optical pump/X-ray scattering probe in solutions



Kim et al, Nature 2015 and Struct. Dyn. 2016
SACLA



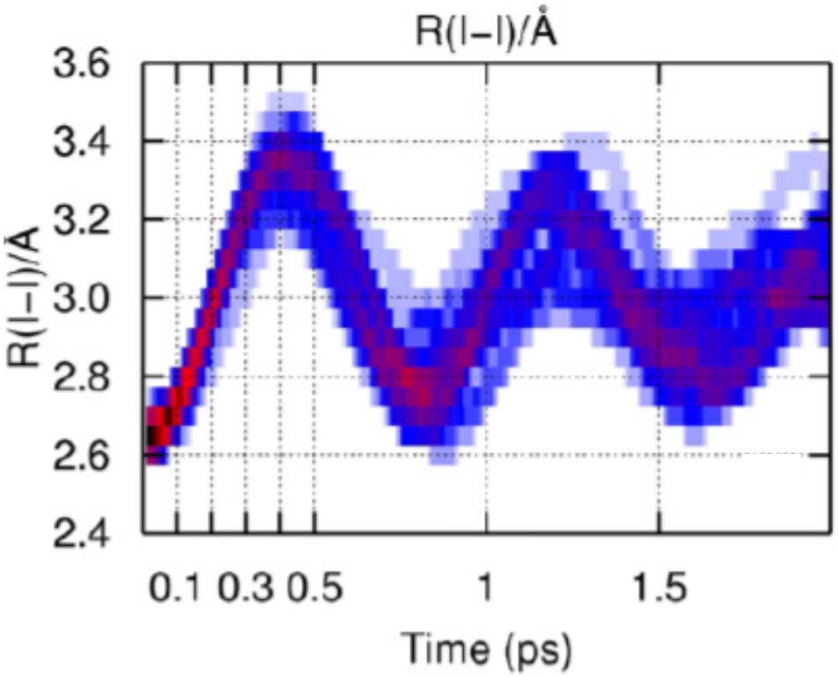


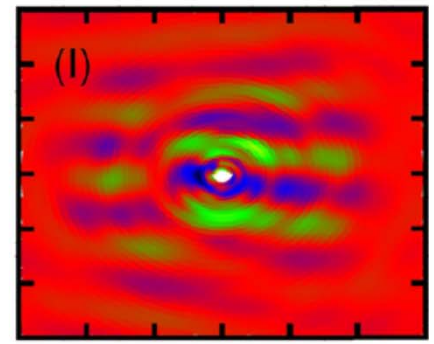
Biasin et al, Phys. Rev. Letters 2016
LCLS

Wave packet dynamics and Solvation Dynamics

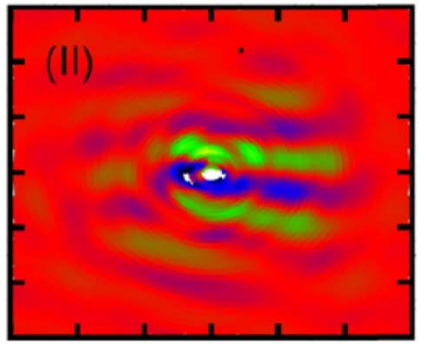
Penfold et al, New J. Phys. 2012

Di-Iodine in n-hexane, photoselection

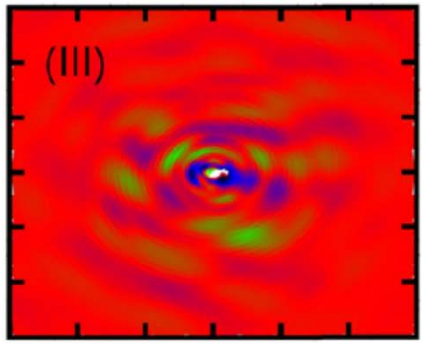




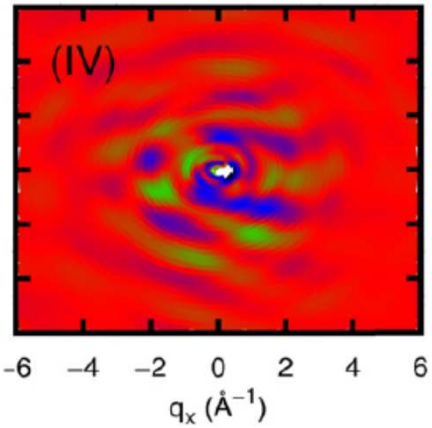
100 fs



200 fs



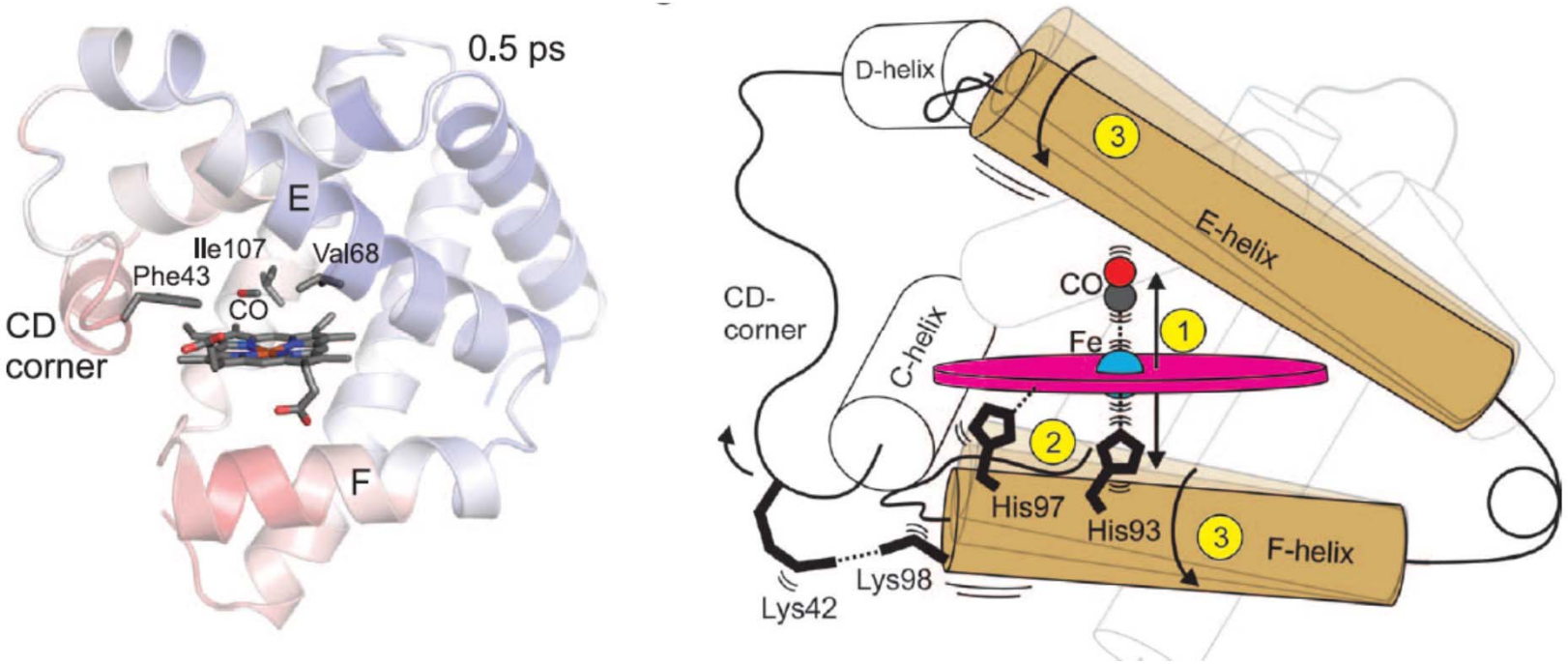
300 fs



400 fs

Protein dynamics: Myoglobin-CO

Levantino et al, Nat. Comm. 2015: solution small-angle scattering (SAXS)



Baerends et al, Science 2015: SFX studies

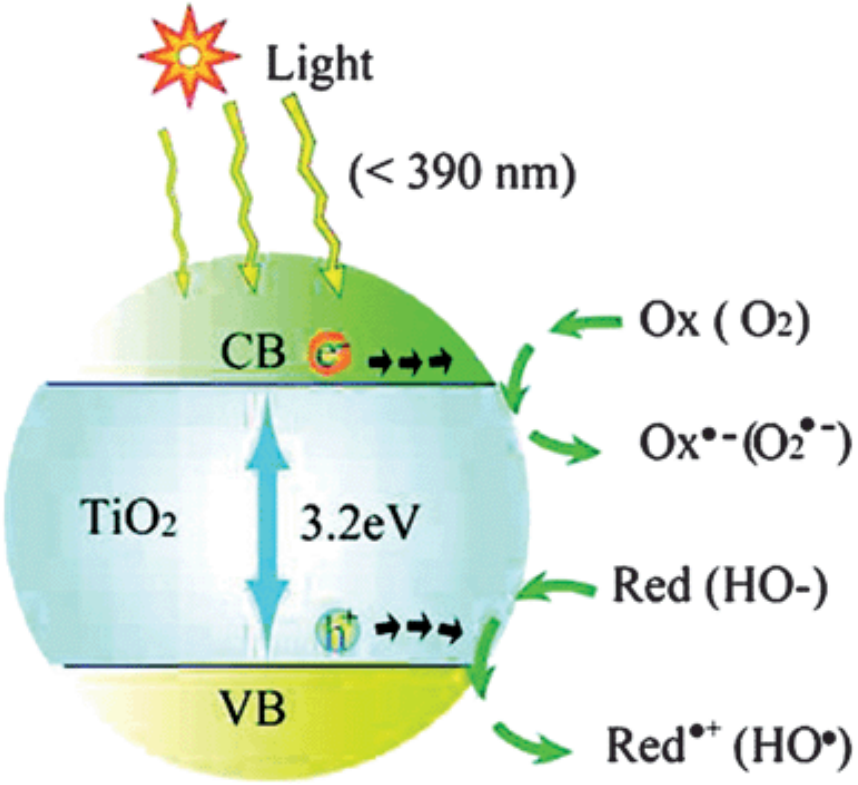
Levantino et al, Struct. Dyn. 2015: fixed energy fs XAS

Sension et al, in progress: polarized fs-XANES on Vitamin B12

Solar Materials: Transition metal oxides

Photocatalysis

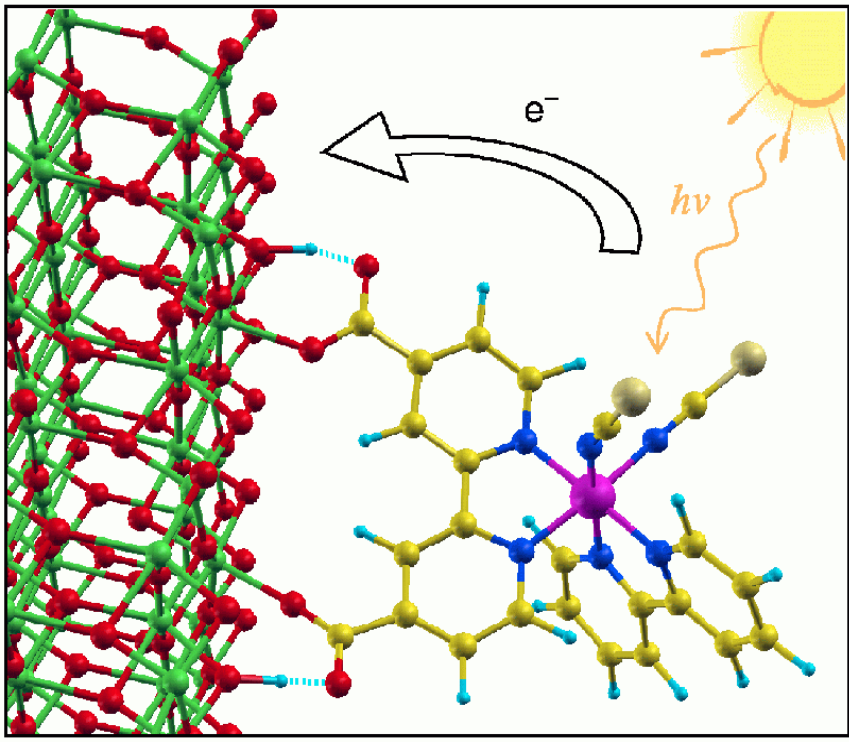
Fujishima, Honda (1972)



- Charges at surfaces
- Long time trapping

Solar energy

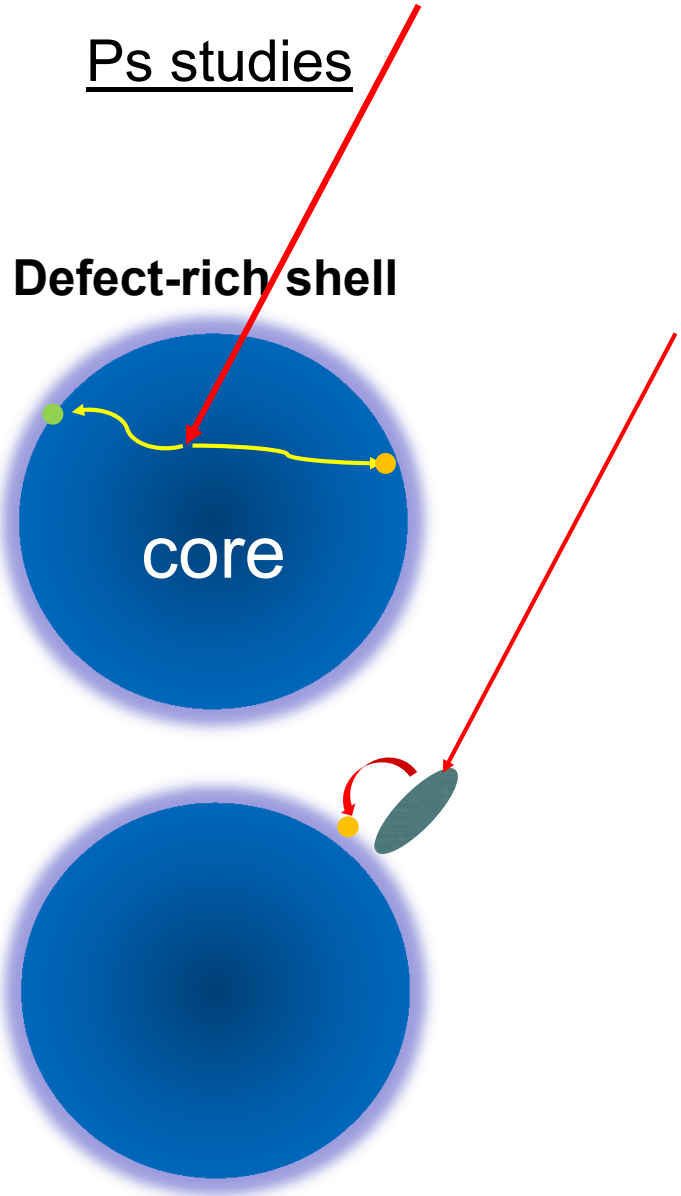
Grätzel, O'Regan (1991)



- Long range transport
- High mobility: no trapping

Bare and dye-sensitized Titanium Dioxide nanoparticles: Ti K-edge and Ru L-edges spectra

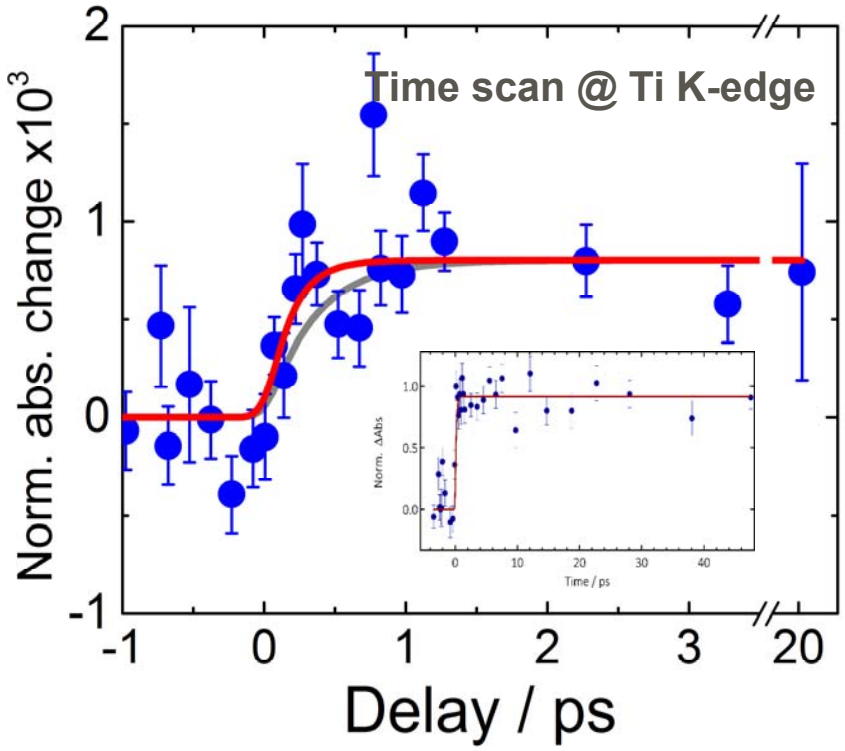
Ps studies



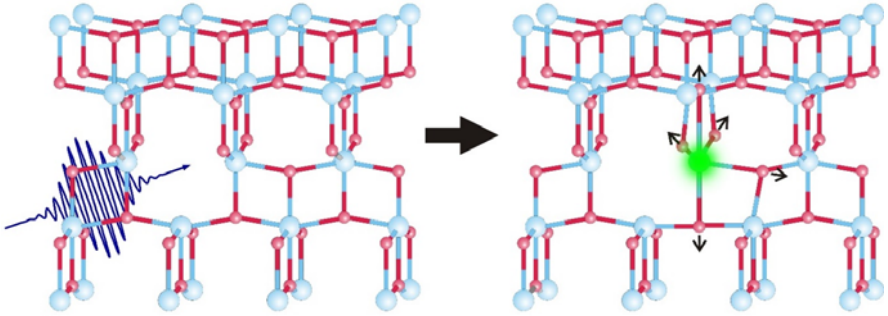
Electron trapping at pentacoordinated defects
Bulk case: trapping deep inside surface shell
Injection: trapping on the outer surface

Rittmann-Frank et al, Ang. Chem. Int. Ed (2014)

Fs studies on bare NPs

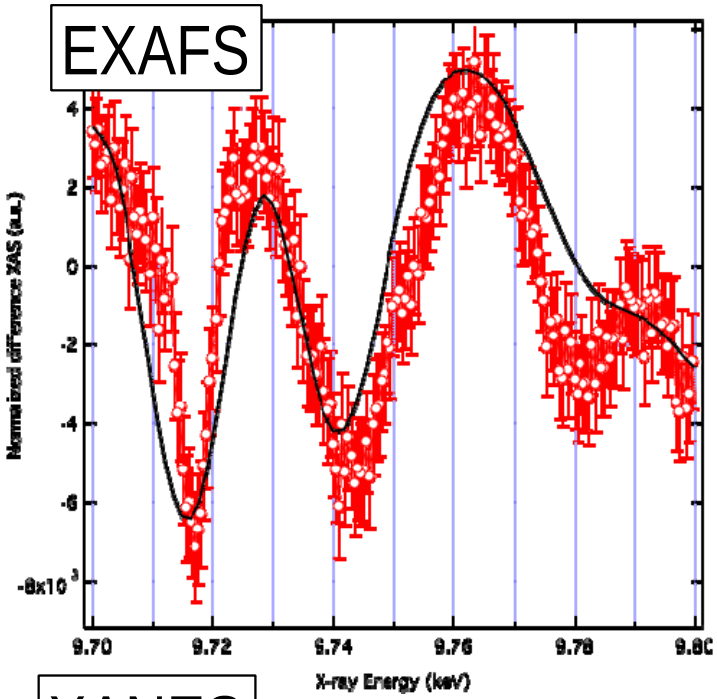


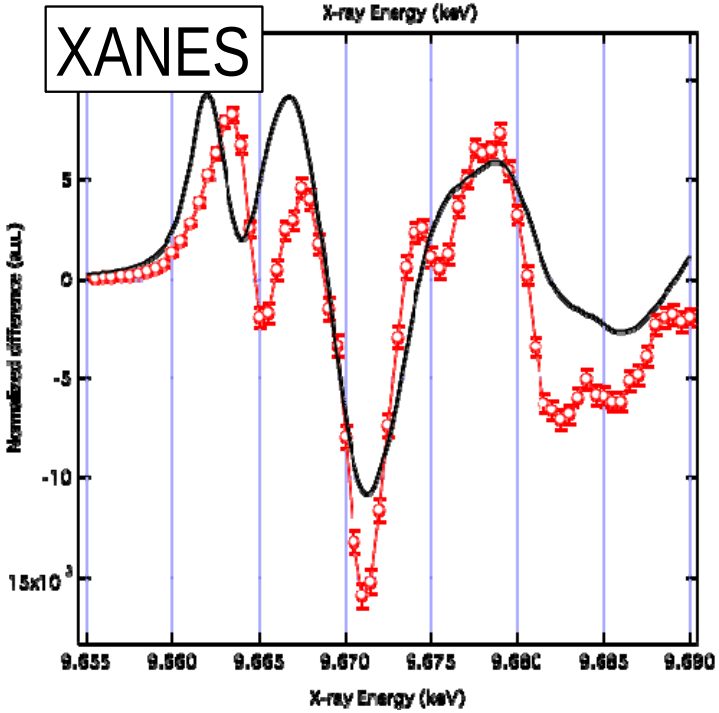
Electron trapping time <200 fs

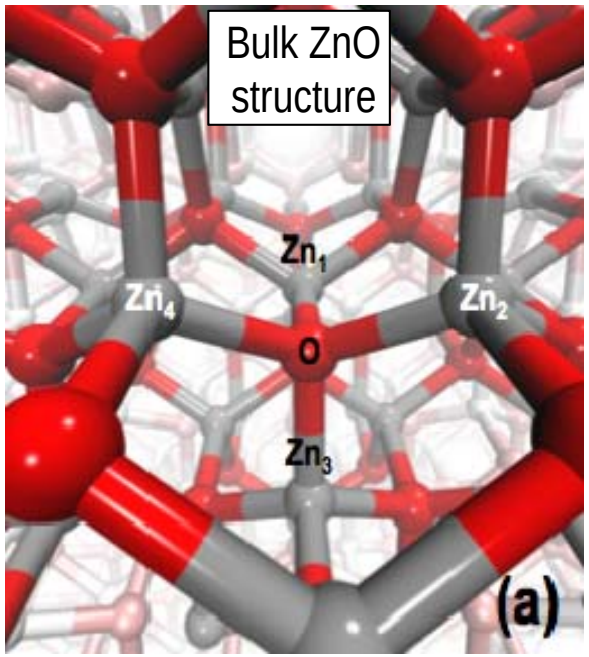


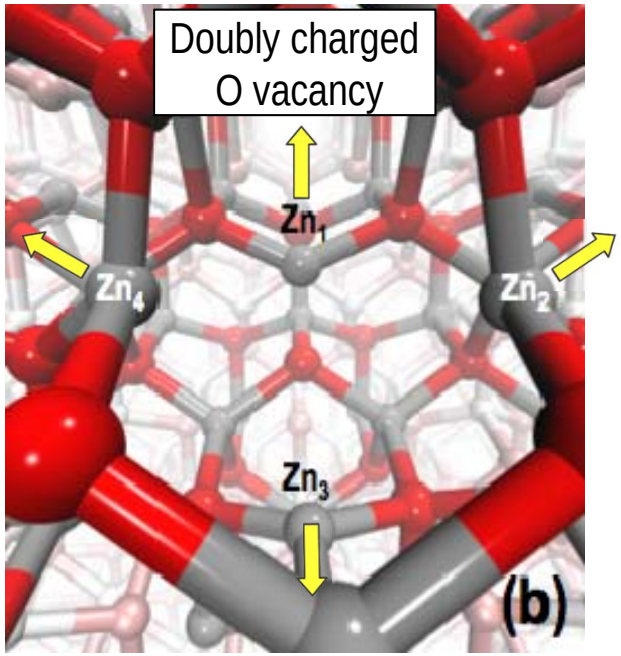
Santomauro et al, Scient. Rep. (2015)
Slicing

Ps and fs X-ray absorption and emission of ZnO: Hole polaron formation site at singly charged Oxygen vacancies









Coll. C. Milne, APS, SACLA

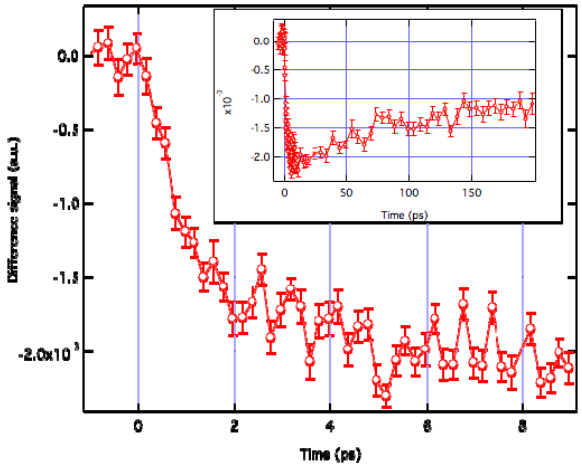
Hole trapping sites are native singly-charge oxygen defects

$$V_O^{+} + h^{+} \rightarrow V_O^{++}$$

Expansion of the 4 neighbouring Zn atoms by ~20%

Strong signature in transient X-ray spectra

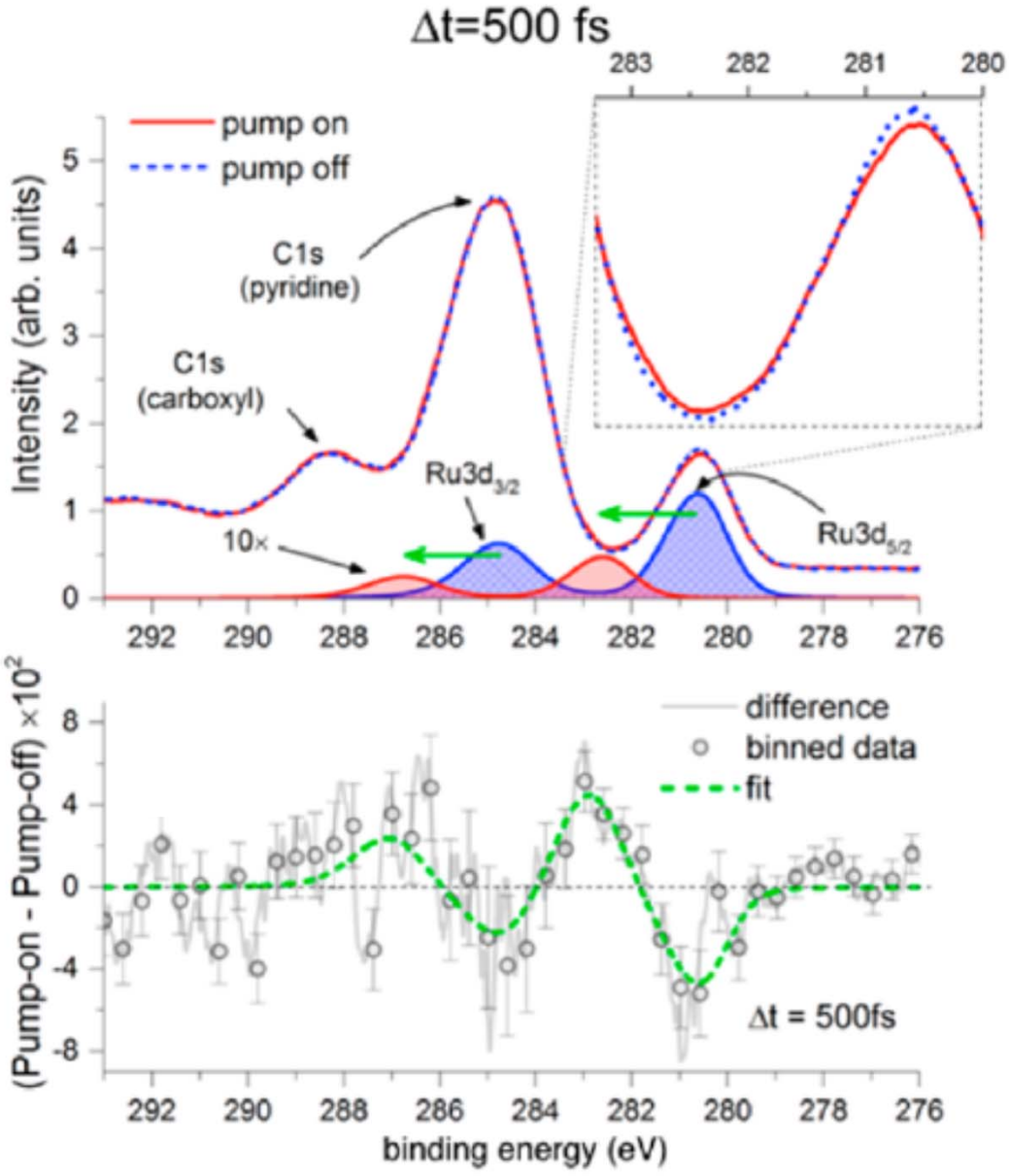
Hole trap is final state of green luminescence



Hole trapping occurs in approx. 1.2 ps

Ultrafast photon-in/electron-out experiments: XPS, ESCA, ARPES, Auger

Interfacial Charge Dynamics



Gessner et al, J. Electron Spectrosc. Relat. Phenom. 2015; Acc. Chem. Res. 2015

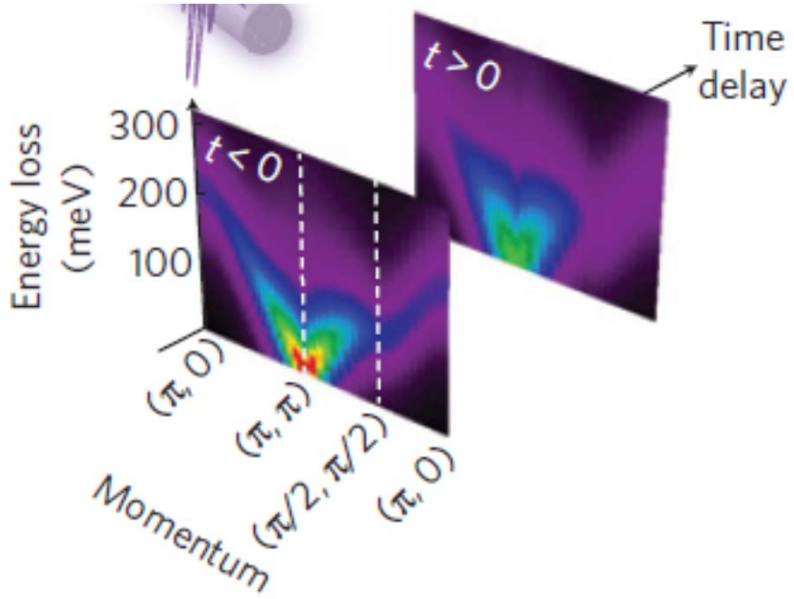
LCLS

New Perspectives with X-ray Free Electron Lasers

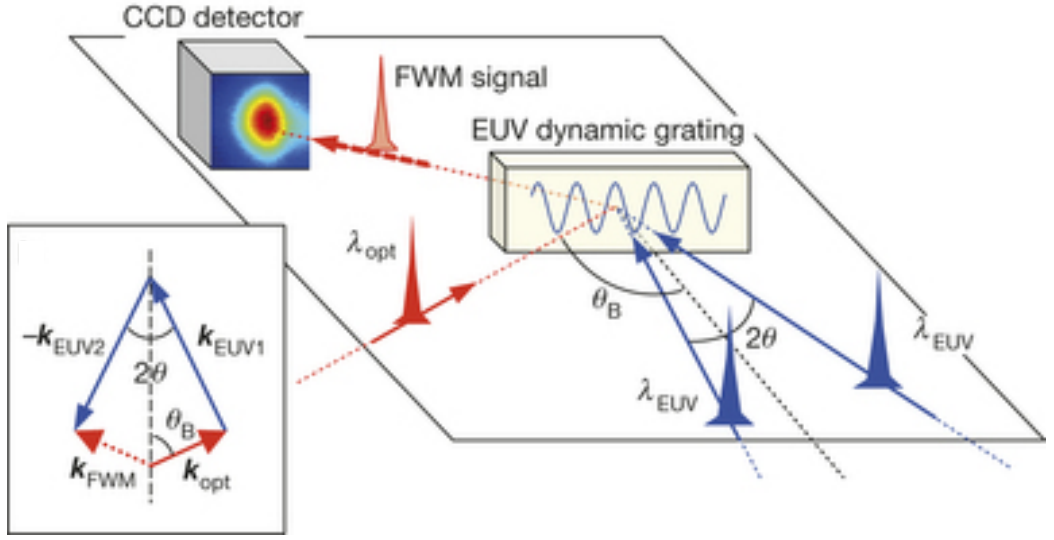
The one category of experiments only possible at XFELs

Ultrafast photon-in/photon-out experiments (RXES, RIXS)

Non-linear X-ray optics



Fs-RIXS of solids
Dean et al, Nat. Mat. (2016)
LCLS



Fs X-ray transient gratings,
Bencivenga et al, Nature (2015)
FERMI

The Future is bright!