PAUL SCHERRER INSTITUT

PSI

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Chemical Dynamics in Solution (2)

Ultrafast X-Ray Summer School (UXSS) – June 16th, 2023

UXSS 2023

Outline

1. Motivation
2. Potential Energy Surface Picture
3. Pump-probe schemes
4. Time resolved X-ray methods
   - X-Ray Absorption Spectroscopy
   - X-ray Emission Spectroscopy
   - X-ray Solution Scattering

5. Ultrafast X-rays sources – Virtual Experiment
6. Heme Protein Dynamics
7. C-H Activation
8. Perspectives for the future

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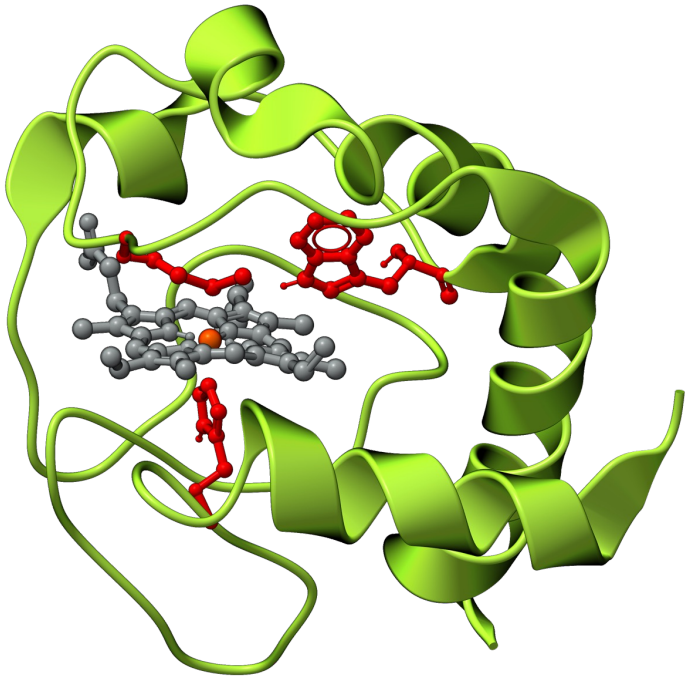
Virtual Experiment



Virtual Experiment – What to measure?

What do you want to learn about your sample?

“Electronic” Information
Excited state energy levels? Valence orbital dynamics?
Spin states?

- XANES
- XES (Core-to-core, VtC)

“Structural” information
Large-scale molecular motion?
Photofragmentation?
Solute-solvent interactions?

- XDS
- EXAFS

Virtual Experiment – Where to measure?

What X-ray source do you need?

How fast is the process I want to probe?

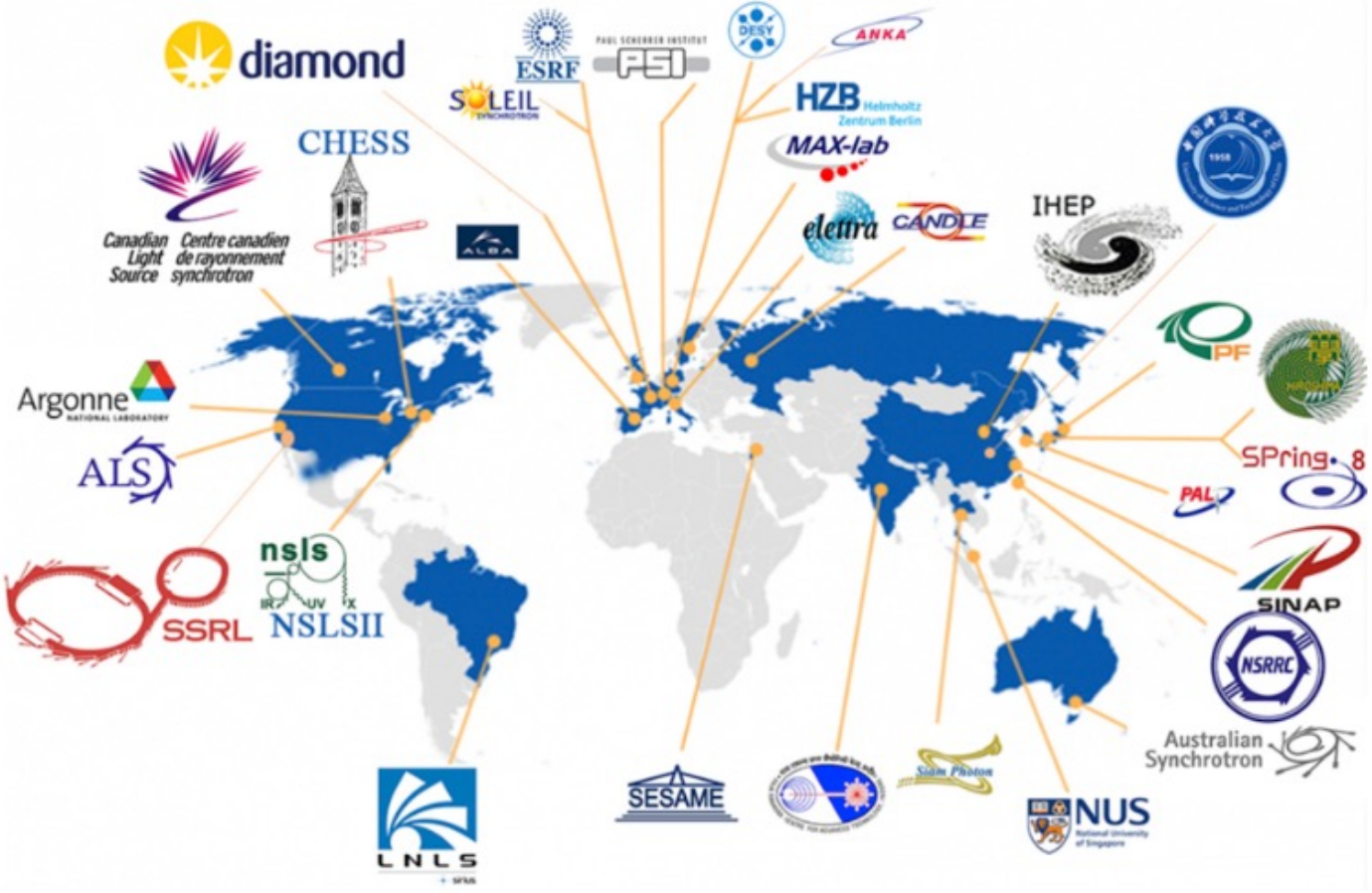
Ultrafast (<100 ps)

A bit slower (> 100 ps)

X-ray FEL

Synchrotron

Virtual Experiment – X-ray Sources



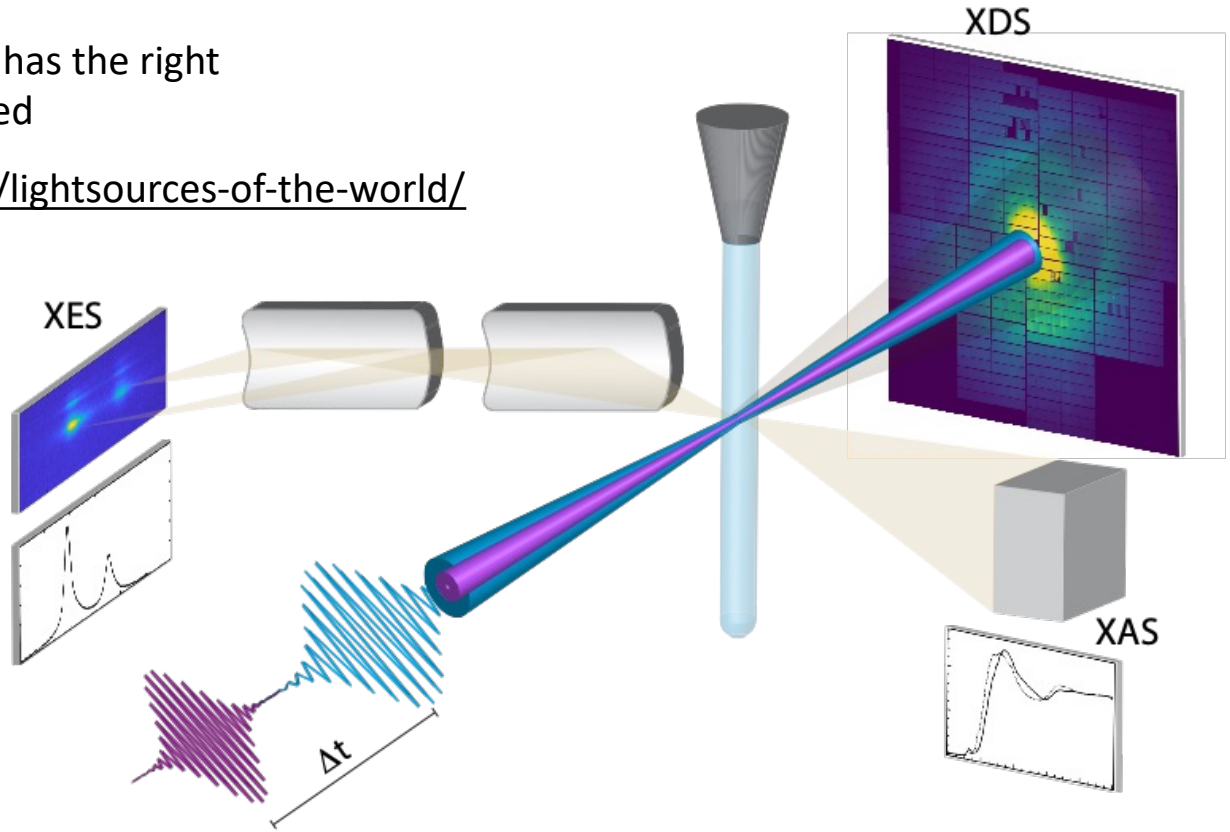
Virtual Experiment – X-ray Sources

Virtual Experiment - Instrumentation

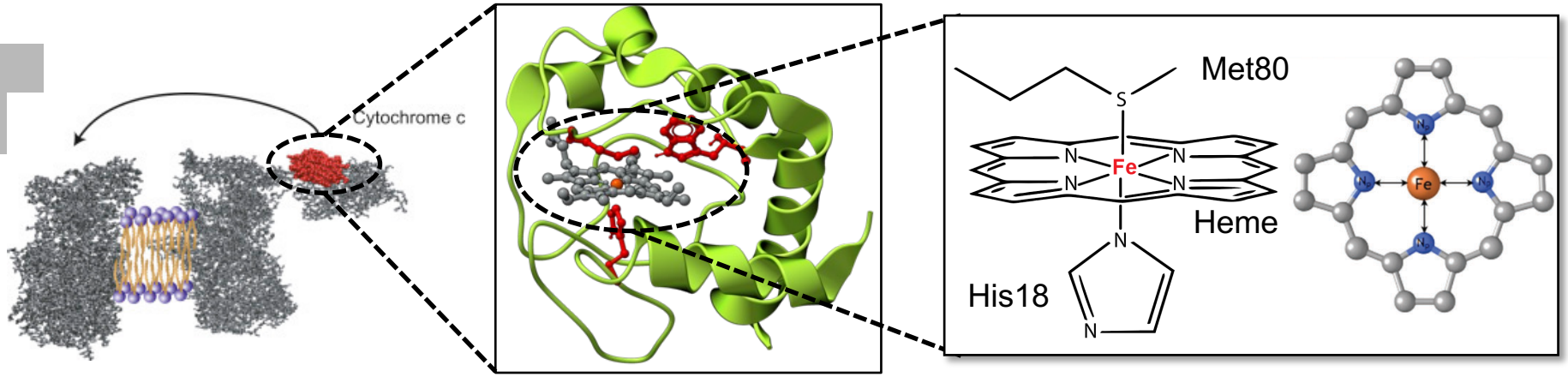
Choose a beamline that has the right instrumentation you need

https://lightsources.org/lightsources-of-the-world/

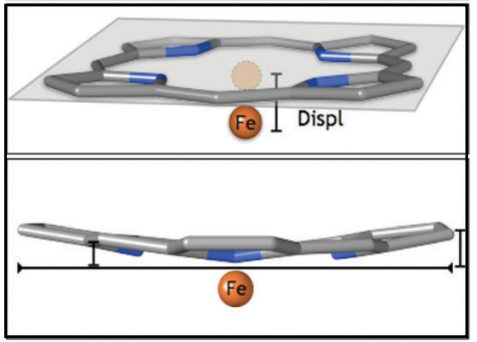
- Sample delivery
- Sample environment
- Detectors
- Spectrometers
- Pump Laser
- X-ray properties
- Time Resolution
- …



Scientific Case #1: Cytochrome C



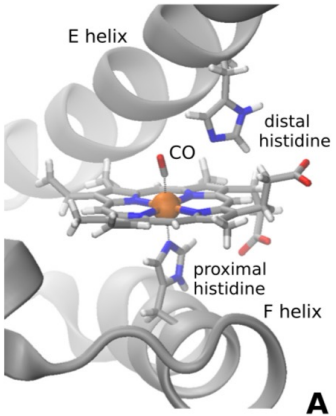
- Cytochrome C: responsible for electron transfer in the transport chain in the mitochondria, which is the pathway for the synthesis of ATP
- Heme structure: Porphyrin ring with center Fe ion
- Heme group binds to histidine (His18) and methionine (Met80) residues
- Fe can be ferrous (Fe^{2+}) or ferric (Fe^{3+}) oxidation state
- **Iron can be in or out of the heme plane** depending on coordination and spin state

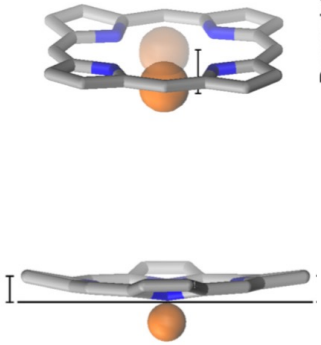


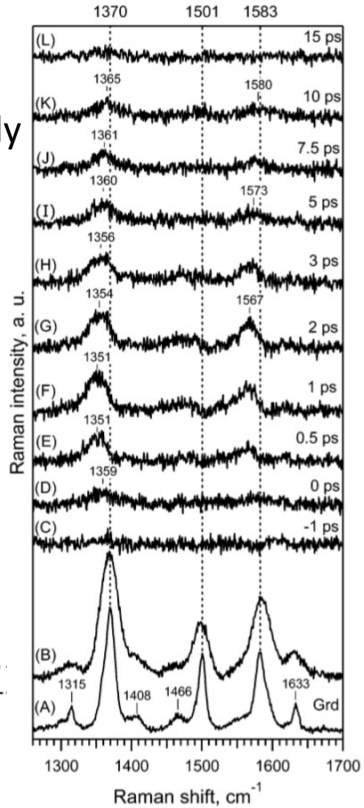
Oxidation State Matters!

Fe(II) systems

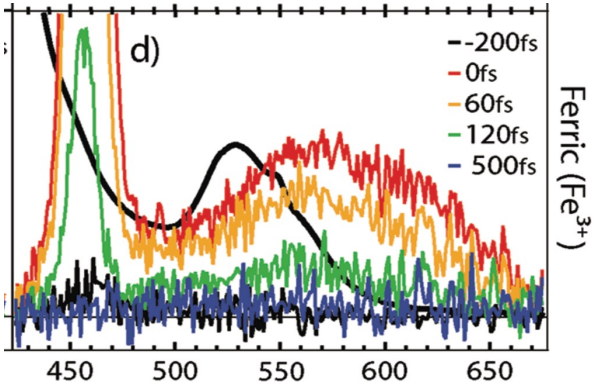
- Ligand dissociation and doming possibly followed by recombination
- Observed across different systems (MbCO, MbNO, Cyt C, etc)







Cyt C - Fe(III)



- No dissociation in Fe(III) systems
- Relaxation suggested to be mostly thermal
- Some evidence that the relaxation involves a cascade through transient electronic states

Negrerie *et al., J. Phys. Chem. B*, 110, (2006)

Mara *et al*, *Science* 356 (2017)

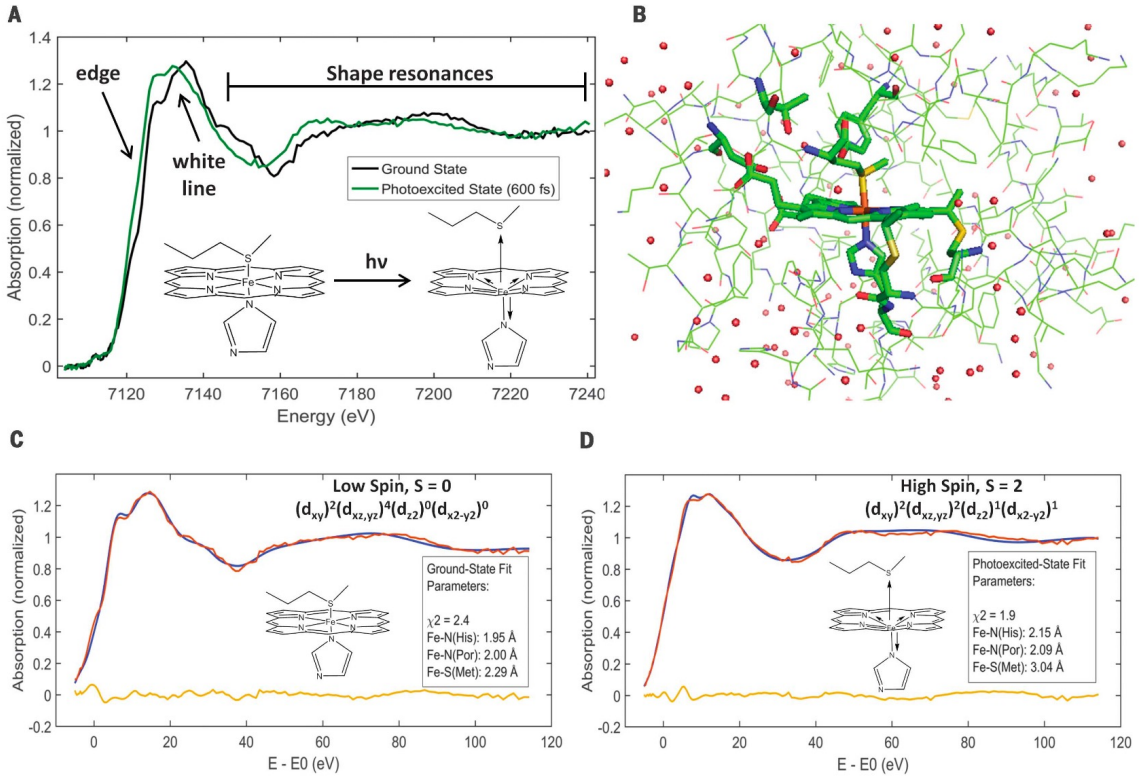
Levantino et al., Structural Dynamics, 2, (2015)

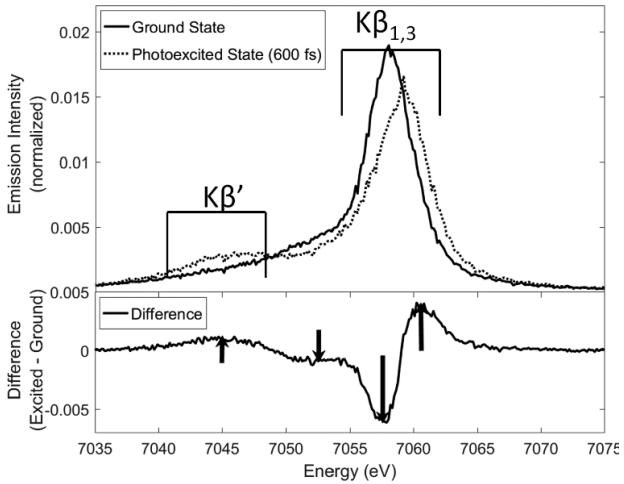
Silatani *et al, PNAS*, 112, 42 (2015)

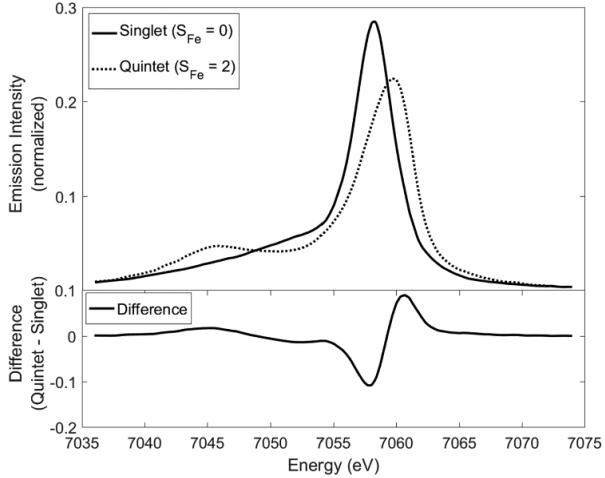
O. Bräm *et al. J. Phys. Chem. B,* 115, (2011)

C. Consani *et al. Chemical Physics* 396 (2012)

Ferrous Cytochrome C



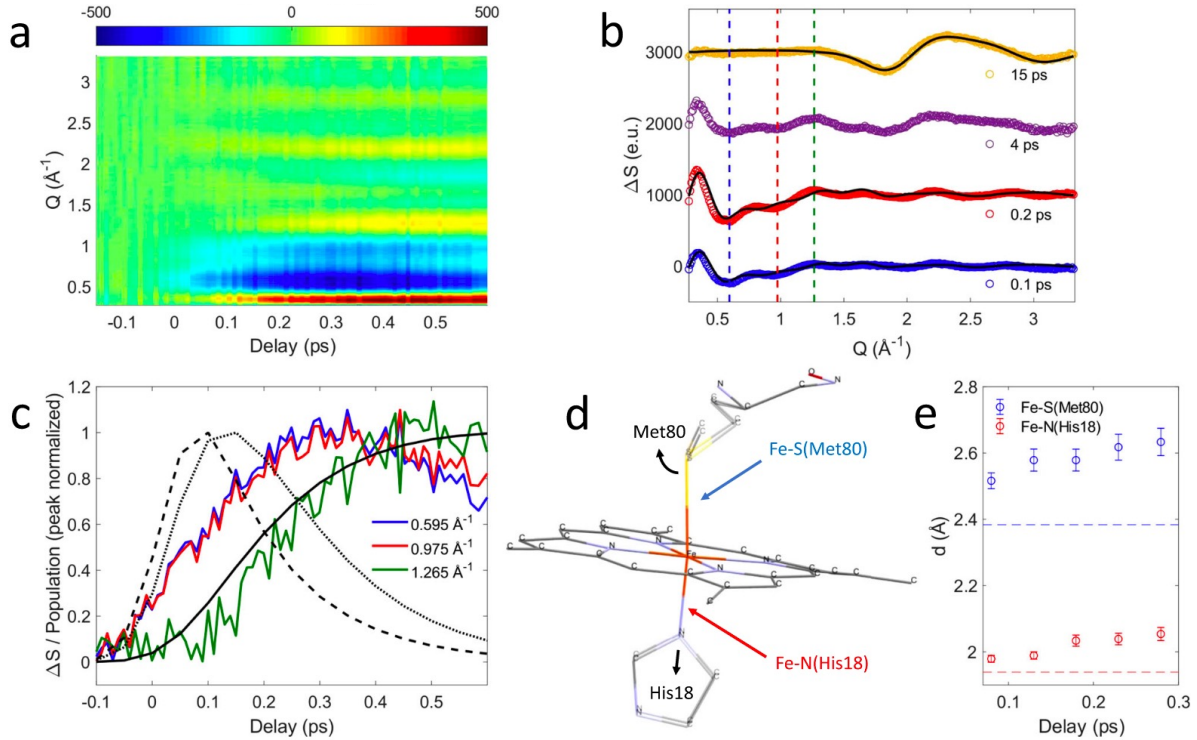




Mara et al., *Science* **356**, 1276–1280 (2017) 2

Ferrous Cytochrome C

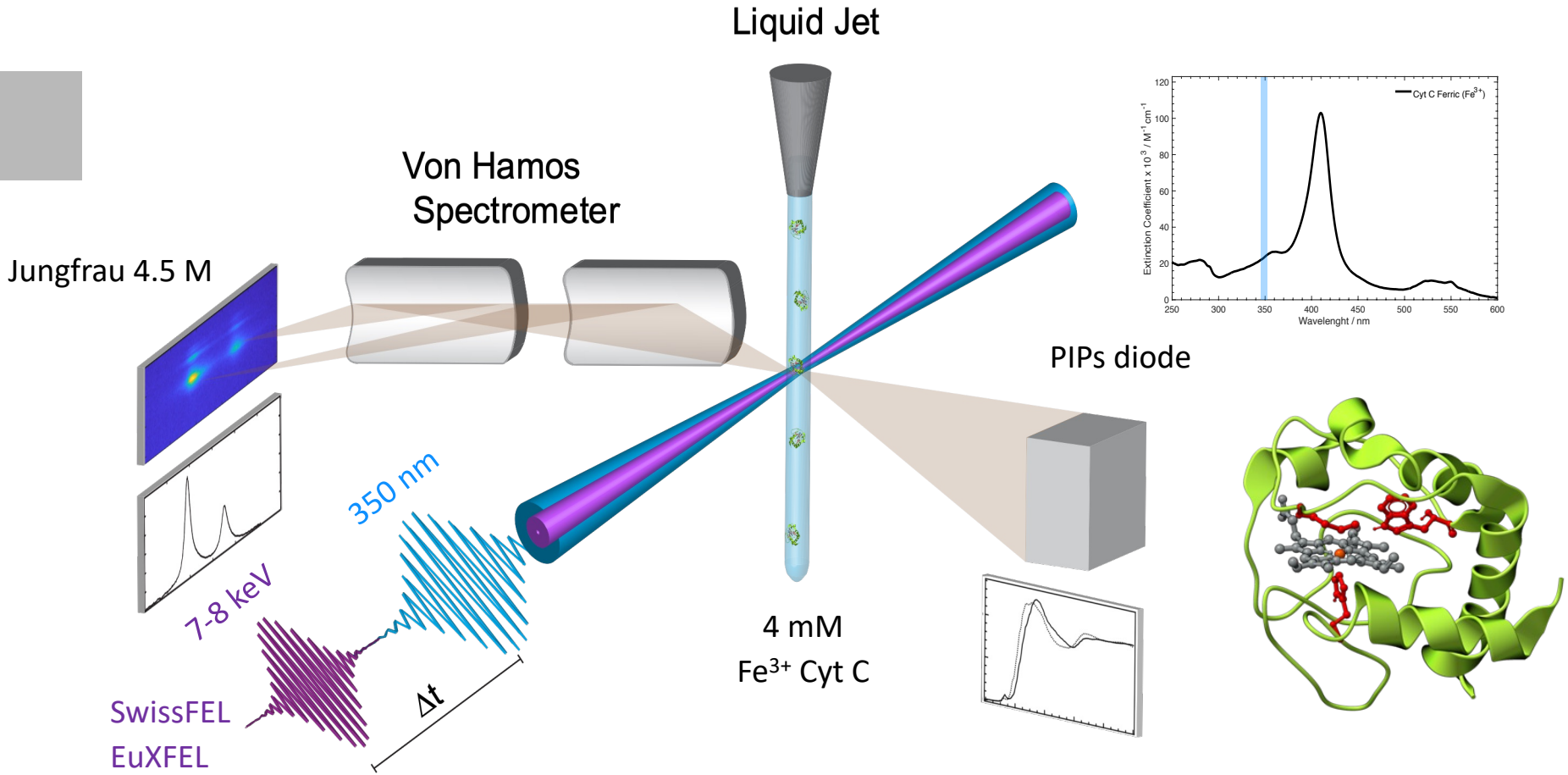
Reinhard et al, *Nat Comm,* **12**, 1086 (2021)



What is the relaxation mechanism in ferric systems?

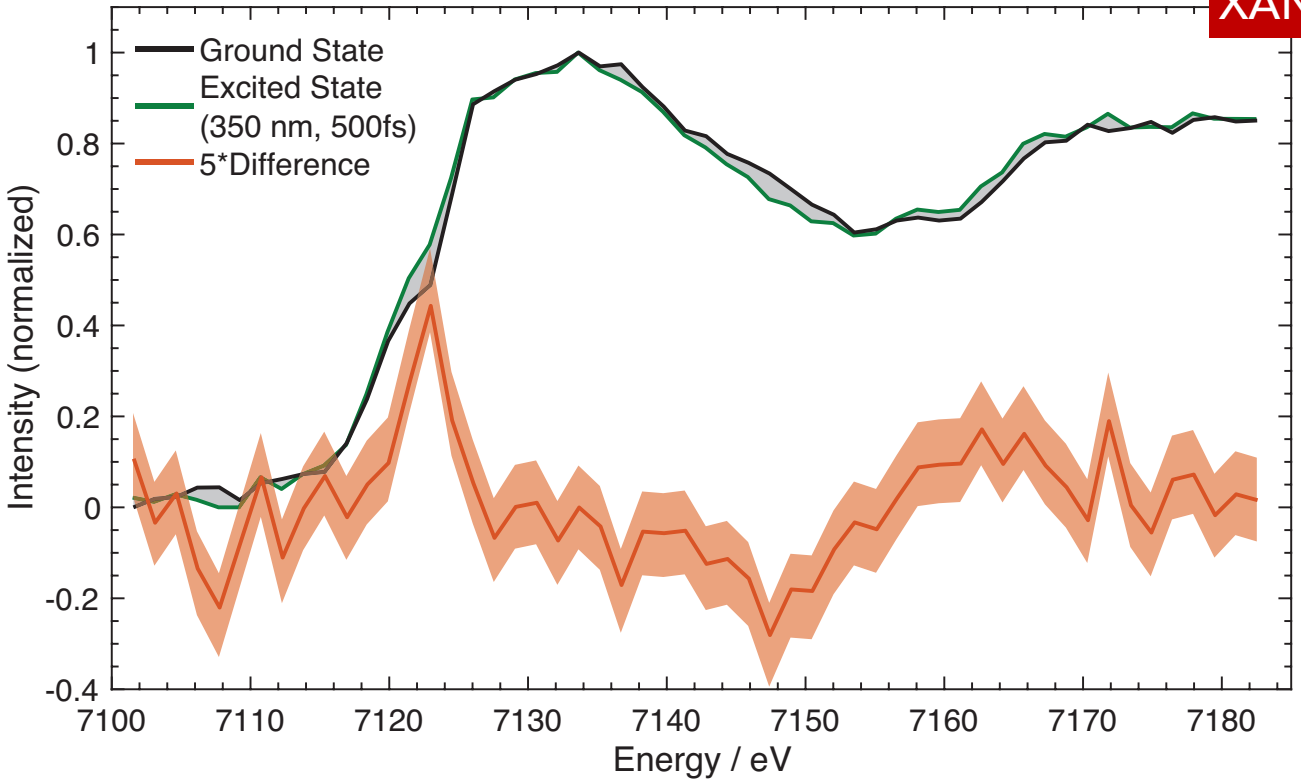
Does it relate at all to its biological function?

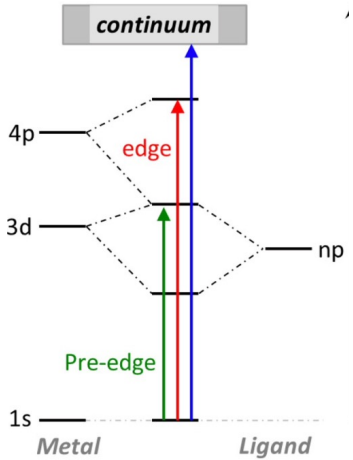
Experimental Setup



Doming in Ferric Cytochrome C

XANES





C. Bacellar *et al*, *PNAS* 117(36), (2020)

Doming in Ferric Cytochrome C

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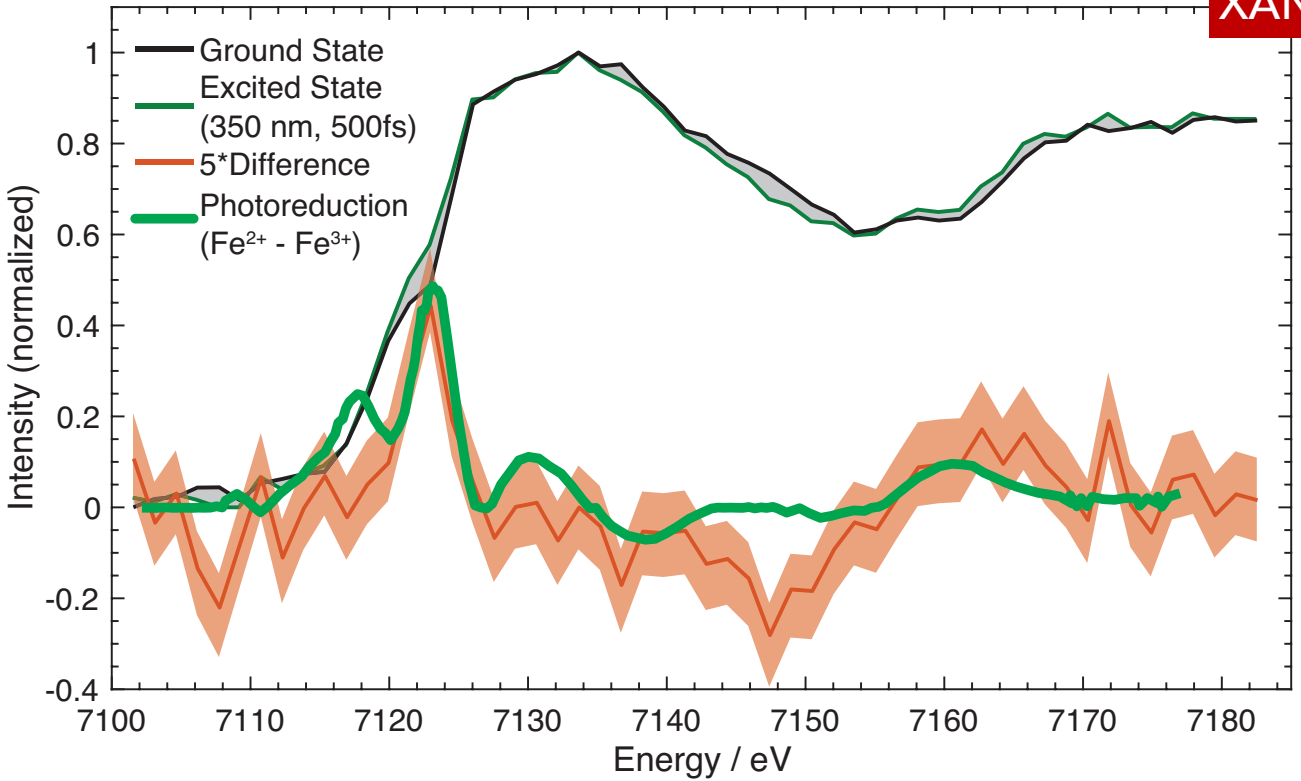

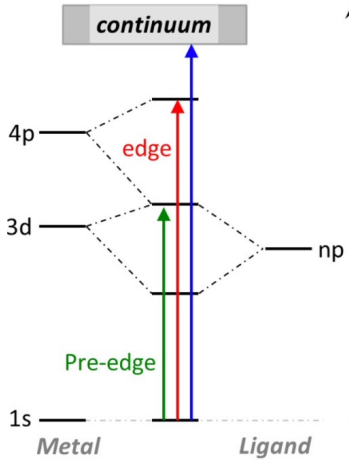

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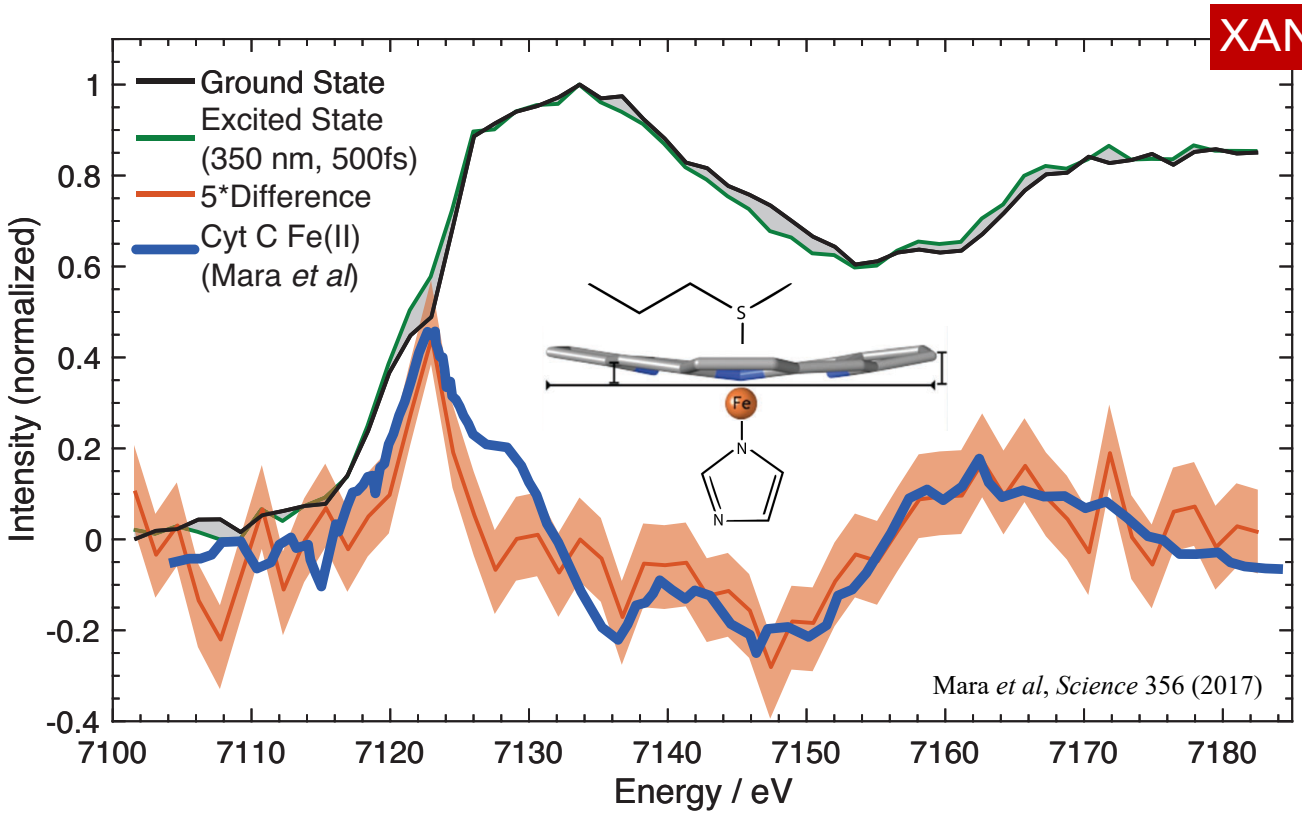
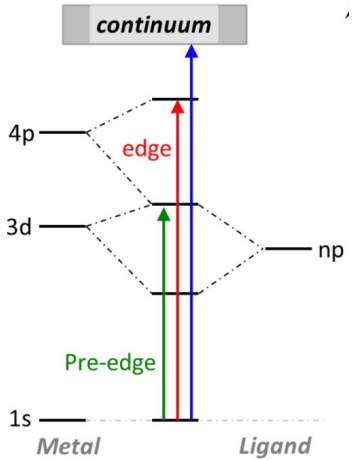
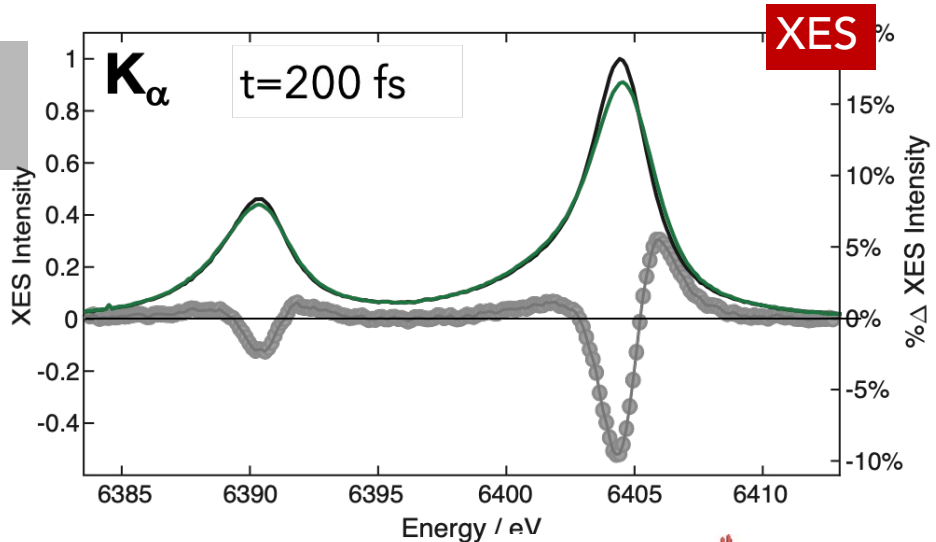
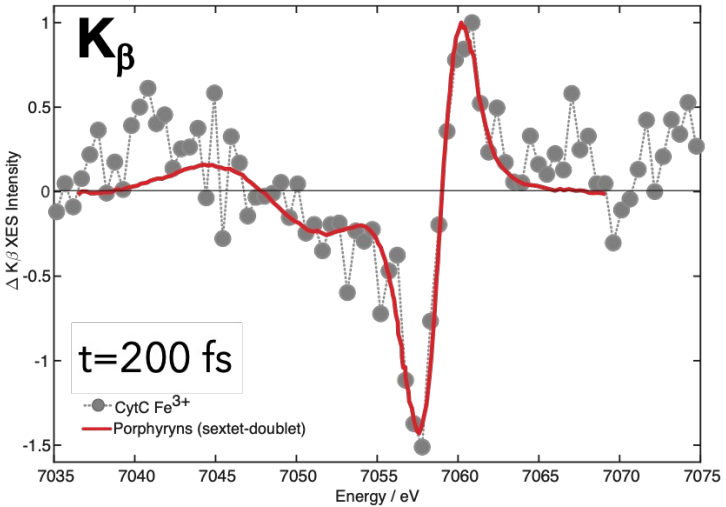


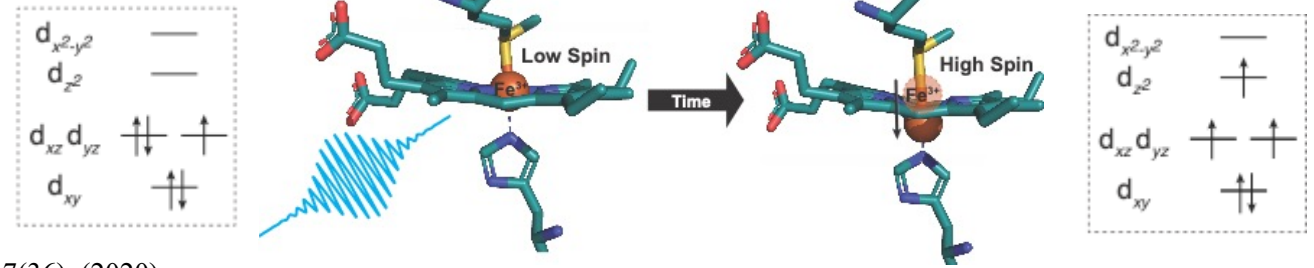


C. Bacellar *et al*, *PNAS* 117(36), (2020)

Spin Cascade in Ferric Cytochrome C







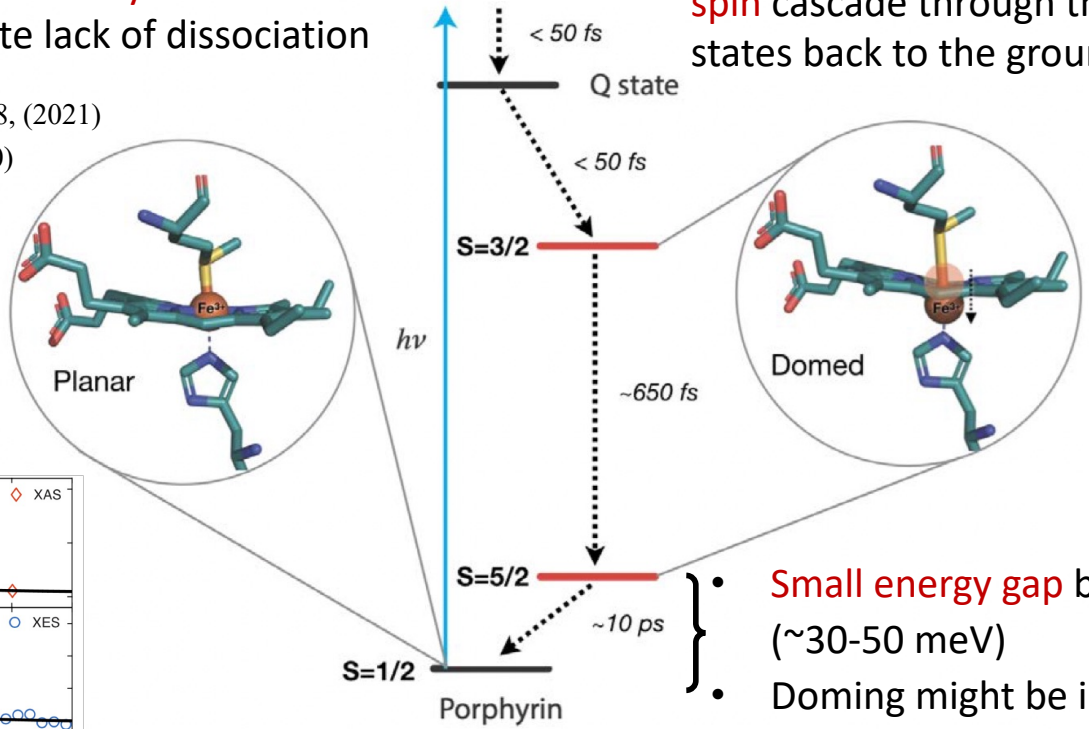
C. Bacellar *et al*, *PNAS* 117(36), (2020)

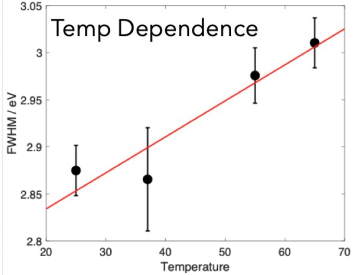
Ferric Cytochrome C - Photocycle

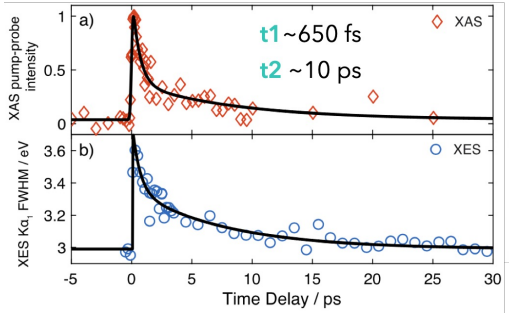
- Photoexcited ferric Cyt C exhibits doming despite lack of dissociation

Bacellar *et al, Faraday Discuss,* 228, (2021)
Bacellar *et al*, *PNAS* 117(36), (2020)

- Relaxation goes through a high spin→ low spin cascade through the metal centered states back to the ground state

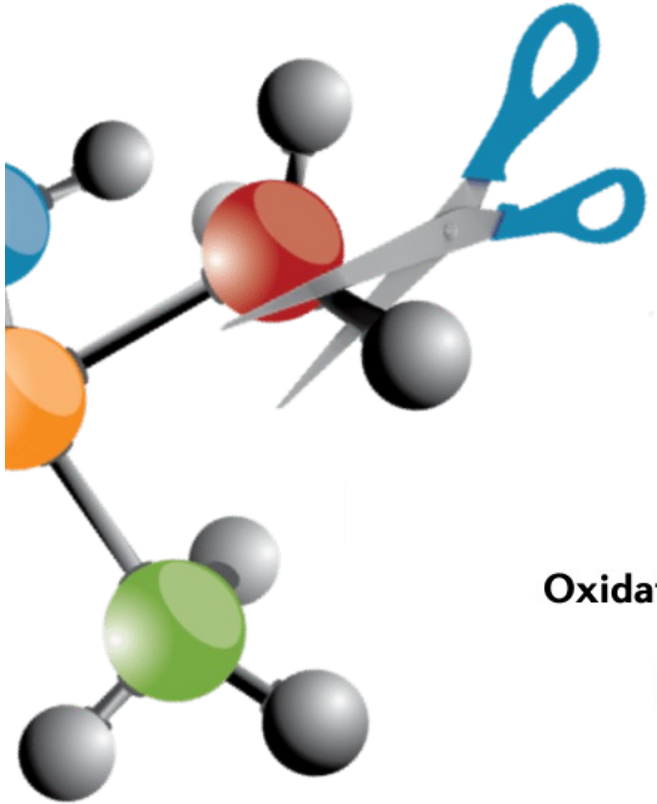




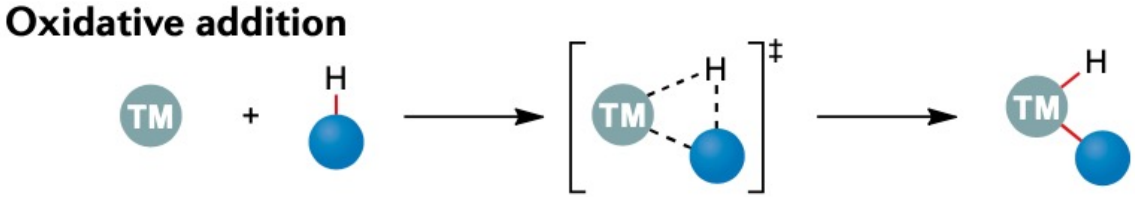


- Small energy gap between HS and LS (~30-50 meV)
- Doming might be involved in the biological redox processes

Scientific Case #2: C-H Activation

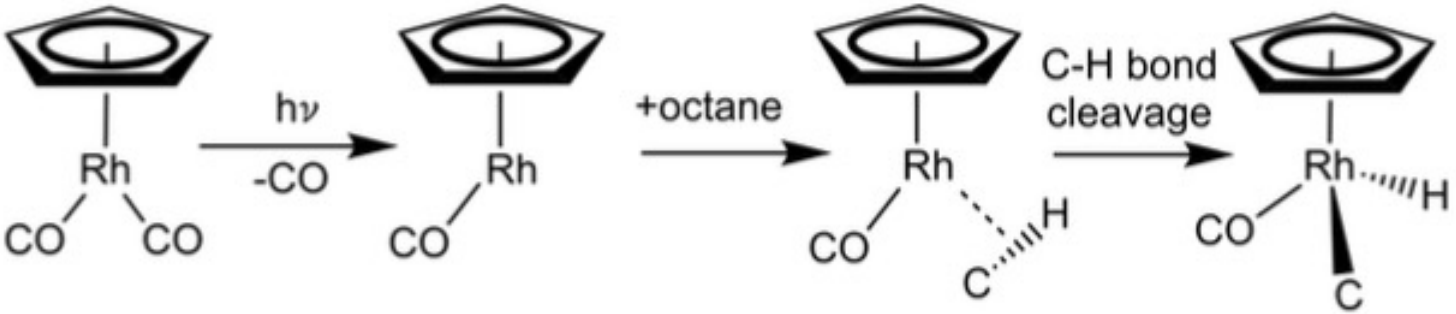


- Breaking C-H bonds is hard (bond dissociation energies ~100 kcal/mol), but extremely important to synthetic chemistry
- Ability to turn alkenes (including CH_4) into functionalized groups
- Oxidative addition is one of the mechanisms that leads to CH activation

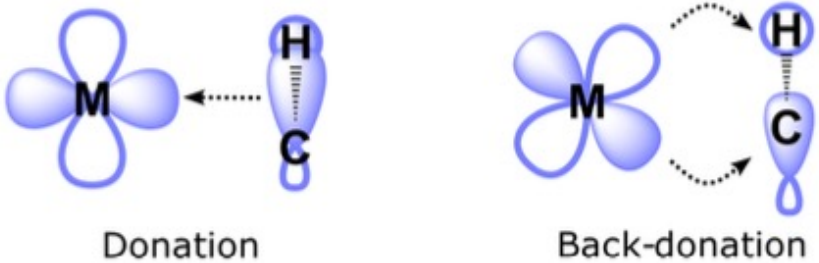


C-H Activation

Cyclopentadienyl Rhodium Carbonyl Complex



Metal-alkane bonding

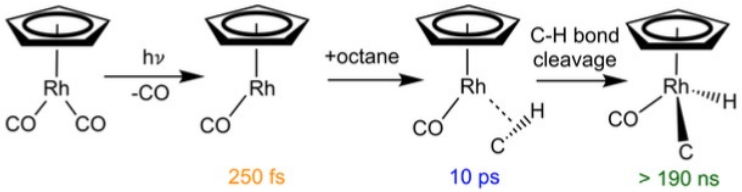


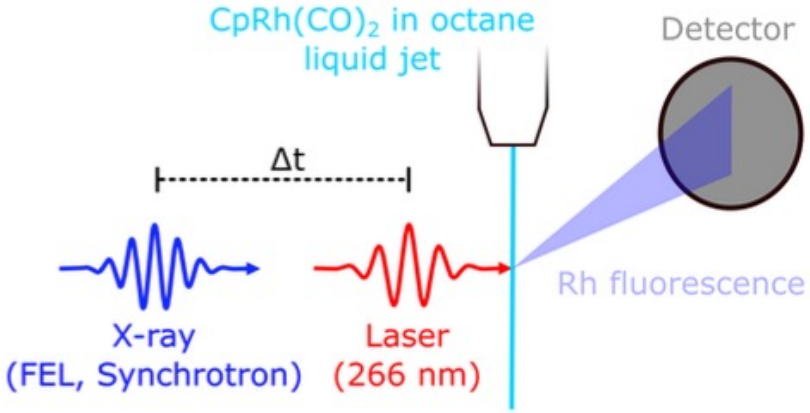
Raphael Jay

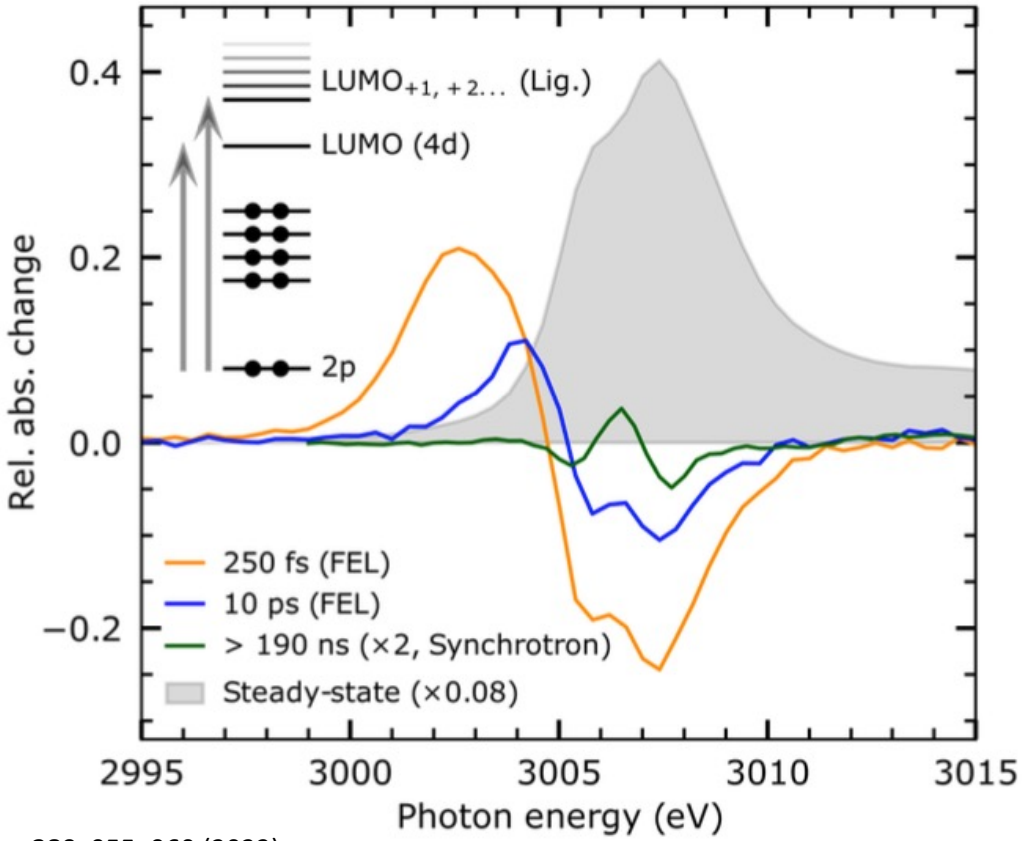
Philippe Wernet

Jay et al., *Science,* **380**, 955–960 (2023)

C-H Activation

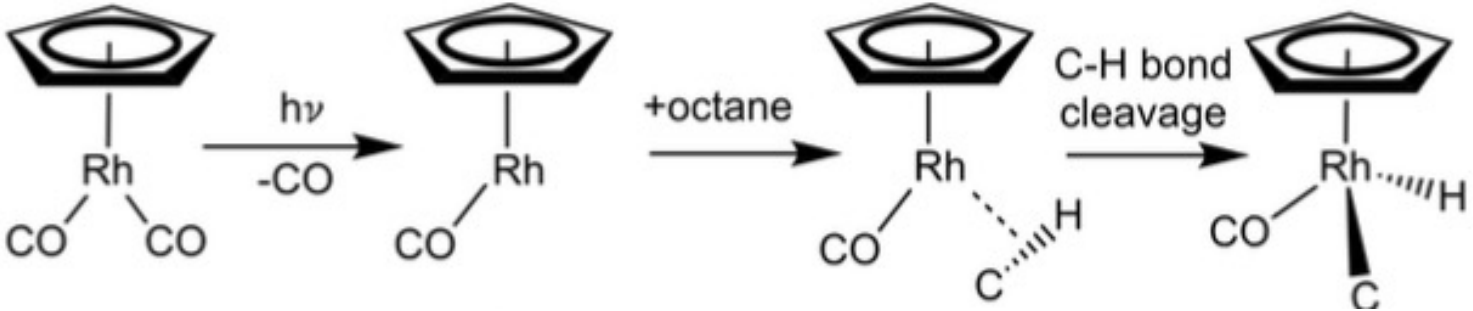




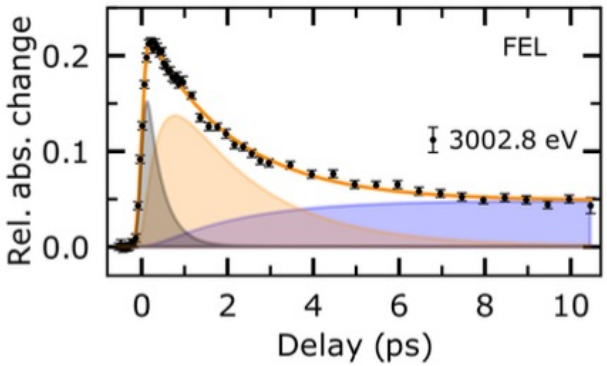


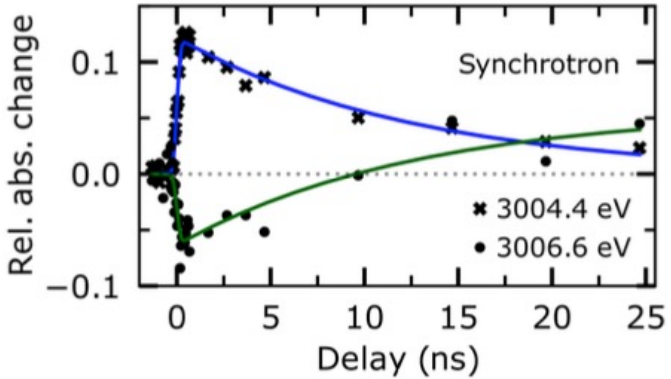
Jay et al., *Science,* **380**, 955–960 (2023)

C-H Activation



~350 fs **~2 ps** **~14 ns**





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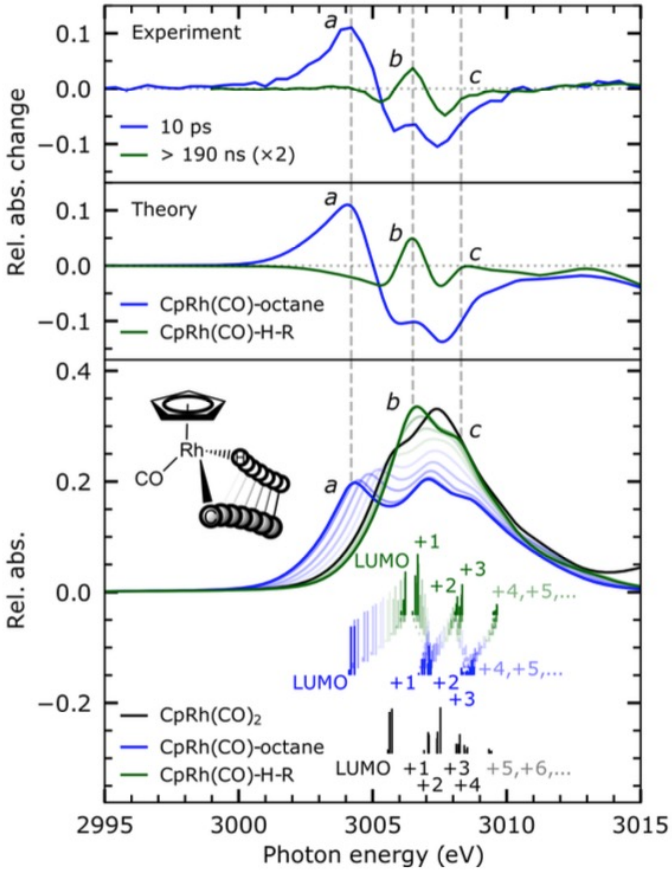
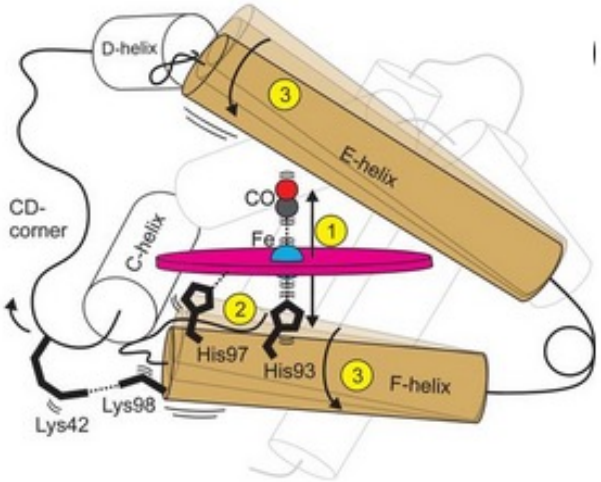


Jay et al., *Science,* **380**, 955–960 (2023)

Future Perspectives

Pushing to Faster and Faster Time Scales…

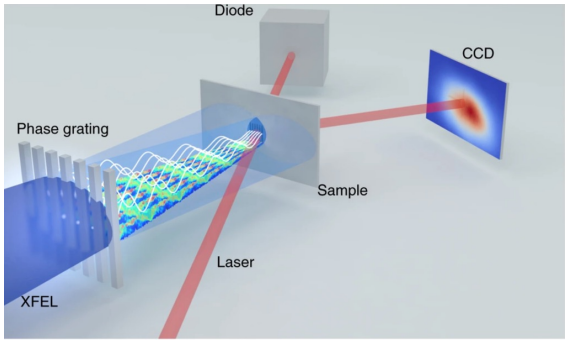


T. Barends et al, *Science* **350**, 445 (2015)

- Access to fast wavepacket dynamics, transitions through conical intersections and initial relaxation processes in chemical and biological systems

…And to More Challenging Experiments

- Photon-hungry techniques such as RIXS, VtC, X-Ray Raman as well as non-linear processes such as transient grating, four wave mixing.
- More complex samples (low concentration, low sample volumes, short-lived species)
- Special machine modes (attosecond, large bandwidth, two color X-ray experiment)



Rouxel et al, *Nat Photonics*, **15**, 499–503 (2021)

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Rebeca Castillo

Technician

Dardan Gashi

Laser

Philip Johnson

+ Many Thanks to

Christoph Bostedt

Machine

Support groups

User groups


References
Questions?