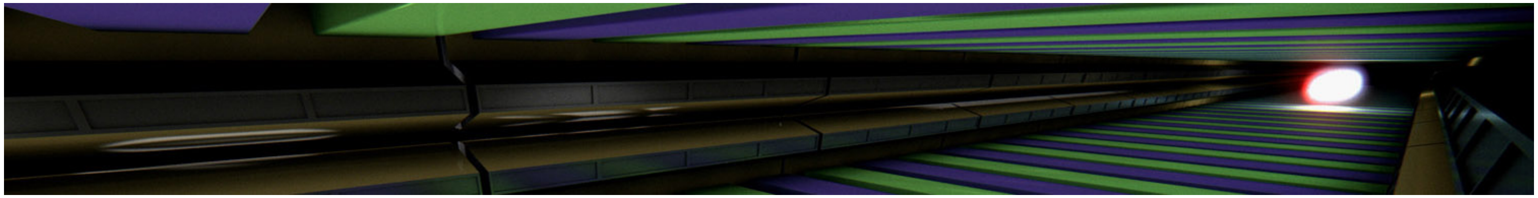


Tracking chemical reactions with ultrafast X-ray spectroscopies and scattering

Wojciech Gawelda

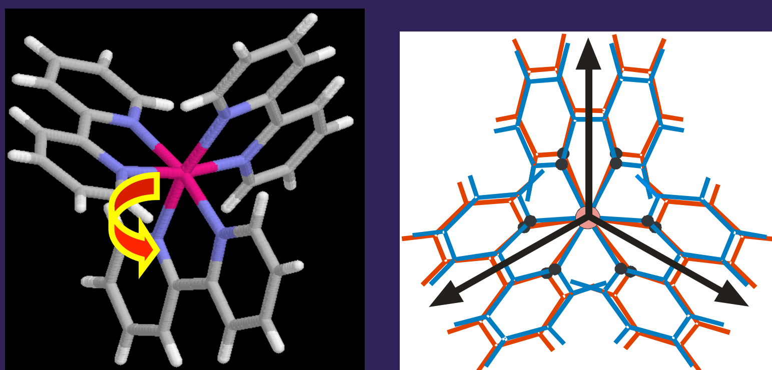
wojciech.gawelda@xfel.eu

FXE Instrument, European XFEL,

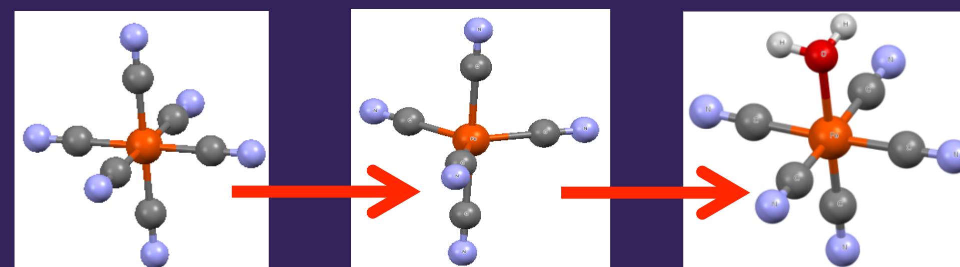
Hamburg, Germany

Mission: Nuclear, Charge and Spin Dynamics during an ongoing reaction „Elementary Steps in Photochemistry“

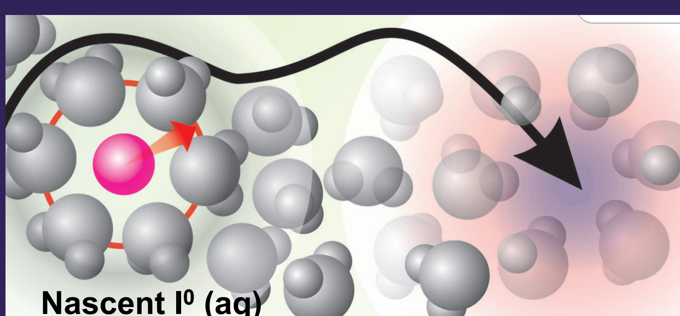
Intramolecular Charge Transfer



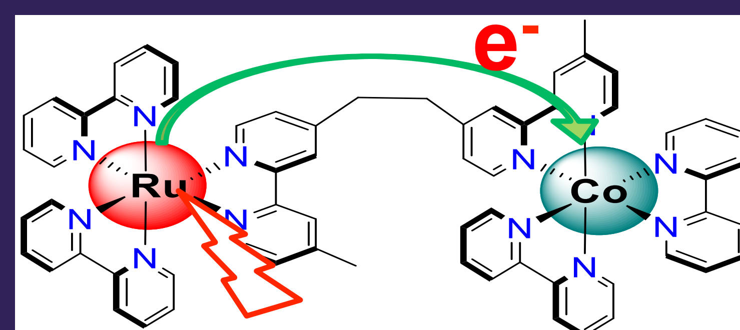
Ligand Detachment/Association



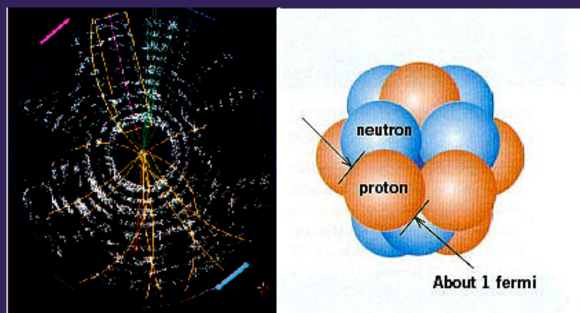
Solvation Dynamics



Elementary Steps in Charge Transport

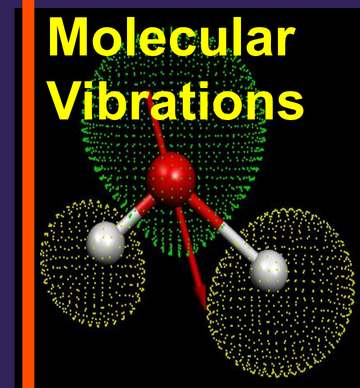


What are the fundamental timescales?

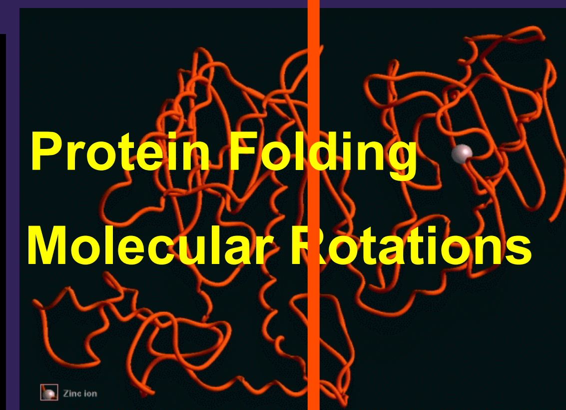


Femtochemistry, Photosynthesis and Catalysis

Vision



Molecular Vibrations



Protein Folding

Molecular Rotations

Strings, Cosmology

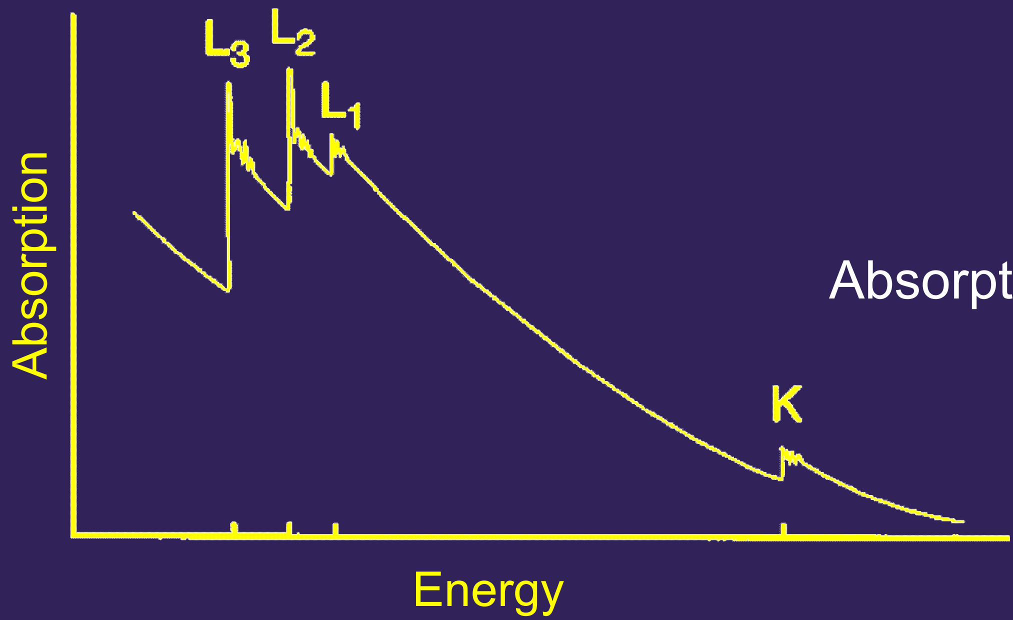
Particle Collisions

Electron dynamics

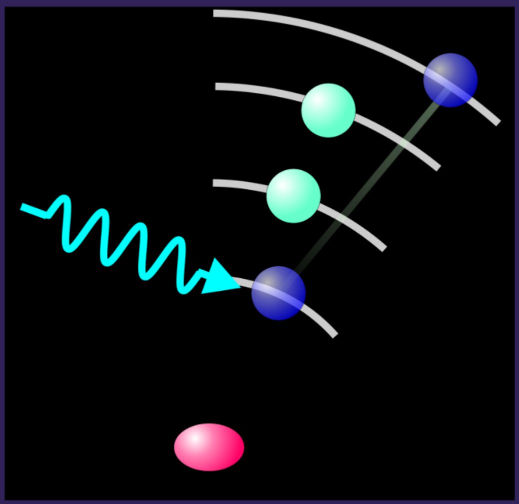
harpo	yacto	zepto	atto	femto	pico	nano	micro	milli
10^{-27}	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}

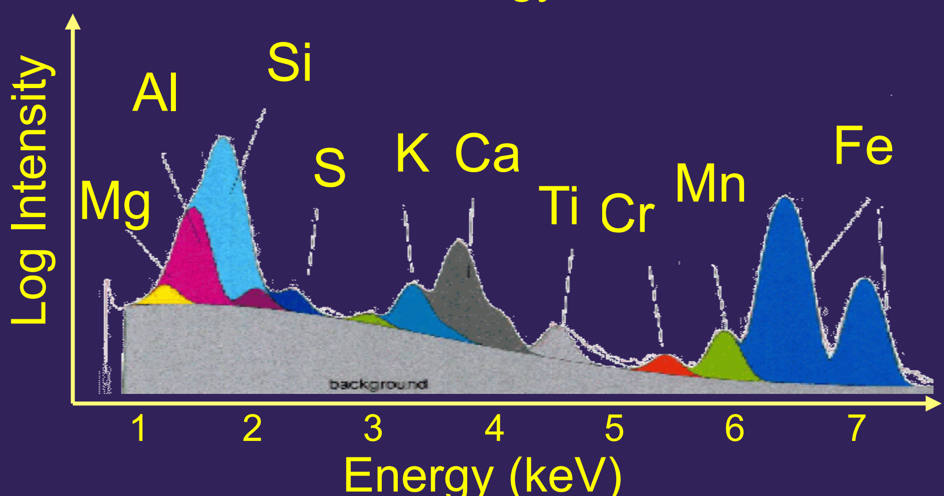
Time /seconds

X-ray Spectroscopy

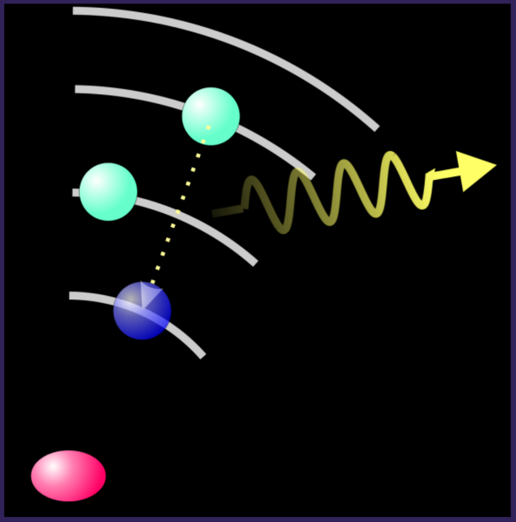


Absorption: **XAS**

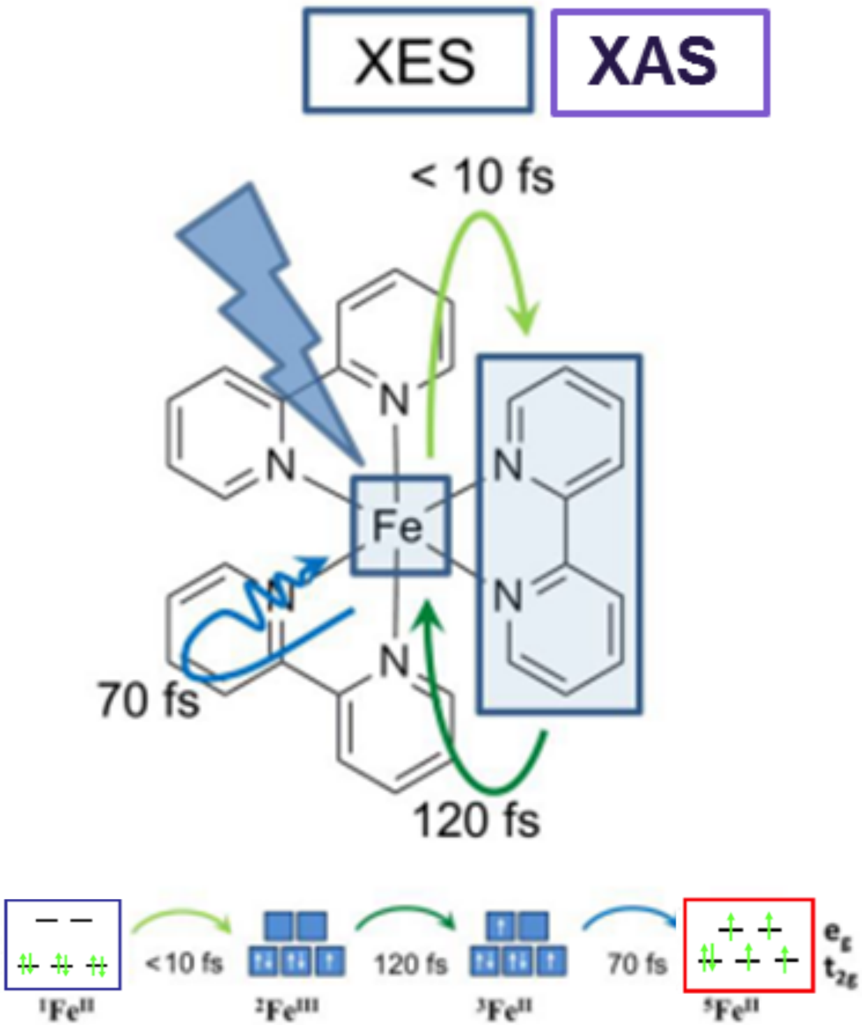


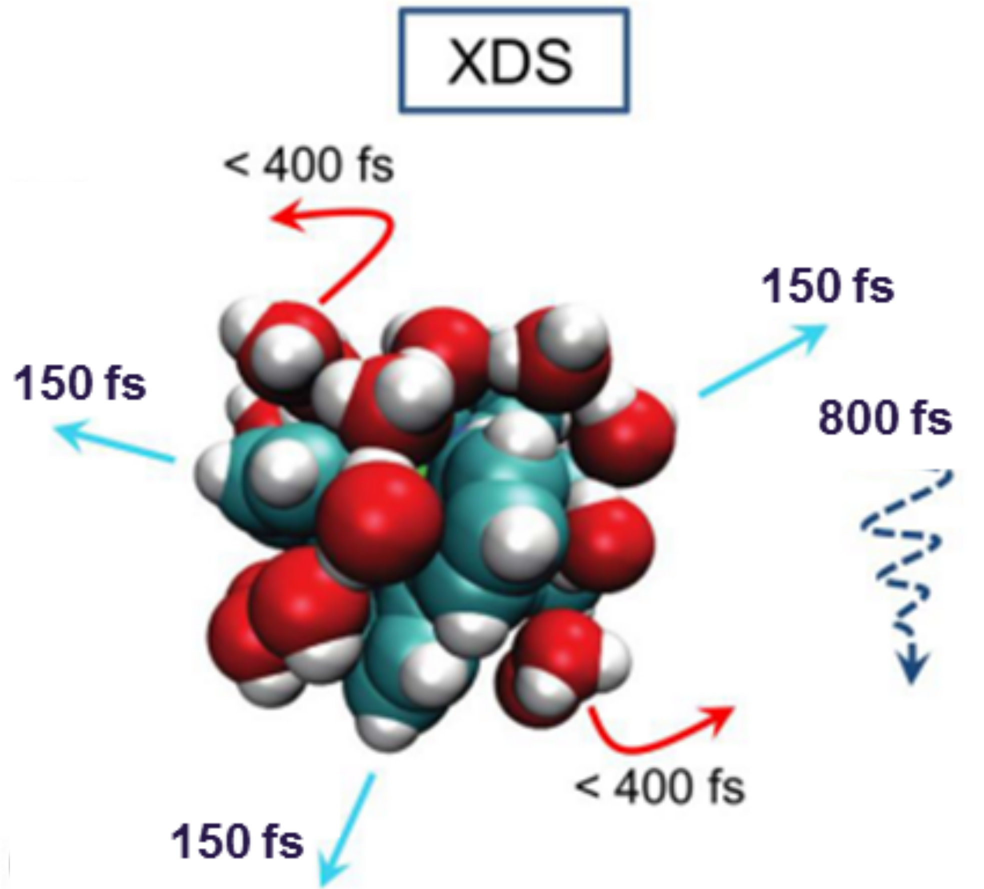


Emission: **XES**



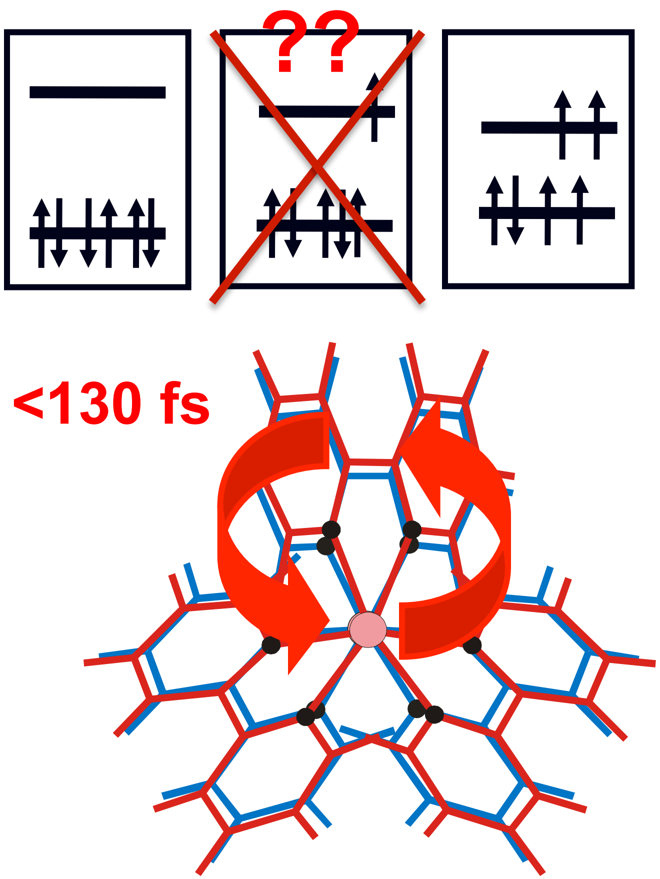
Electronic and Structural Dynamics in $[Fe(bpy)_3]^{2+}$

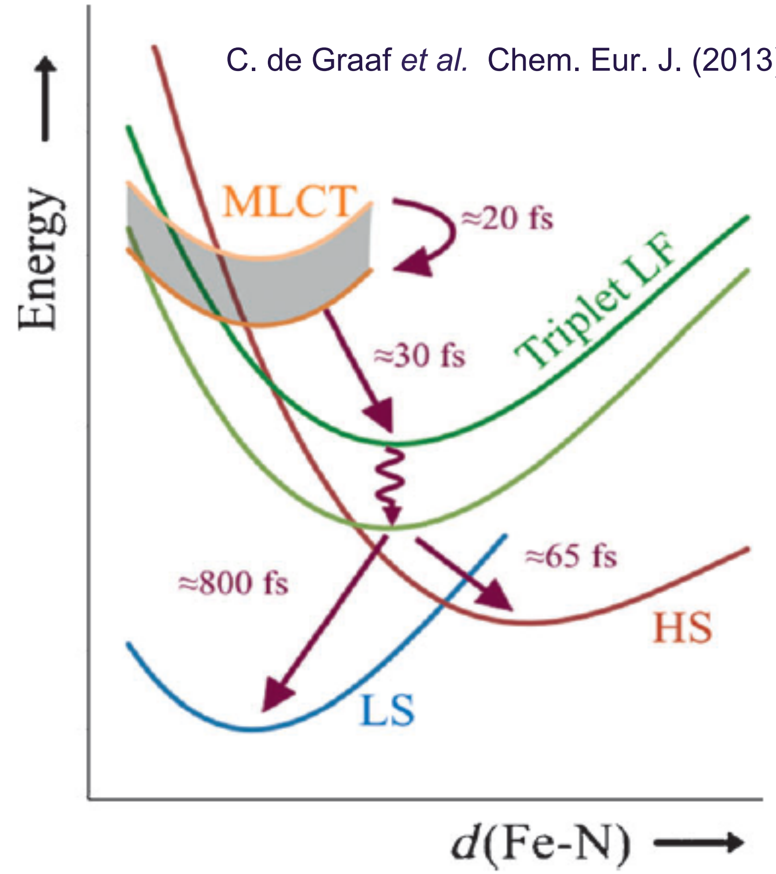




$\Delta R_{Fe\text{-}N} = 0.2$ Å $\Delta n(H_2O) = -2$ $\Delta T = 2.3$ K

Combined optical and x-ray results





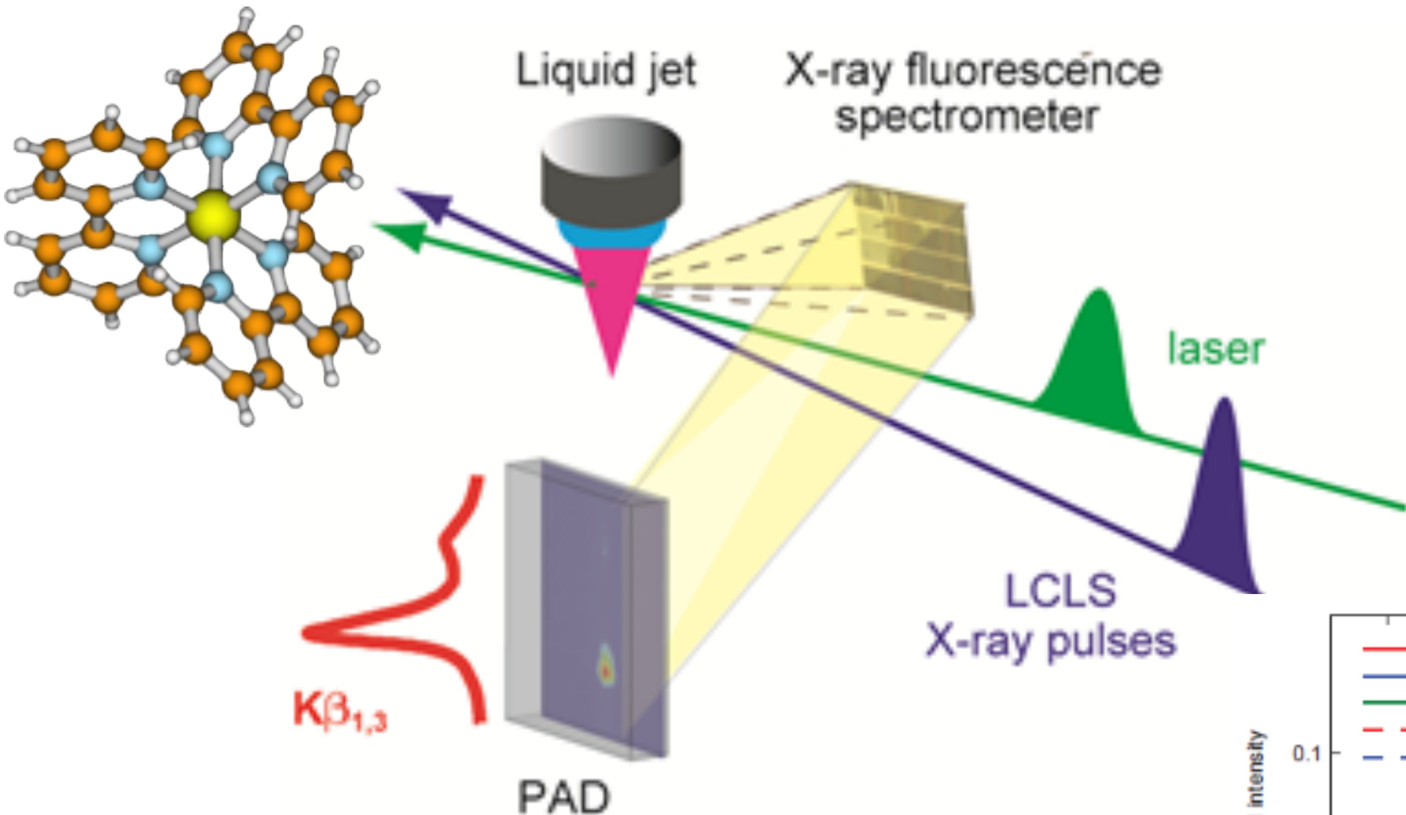
Ultrafast spin conversion: within electron back-transfer time from bpy to metal?

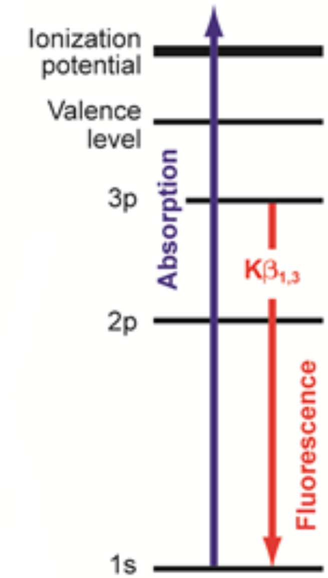
No intermediate states detected…

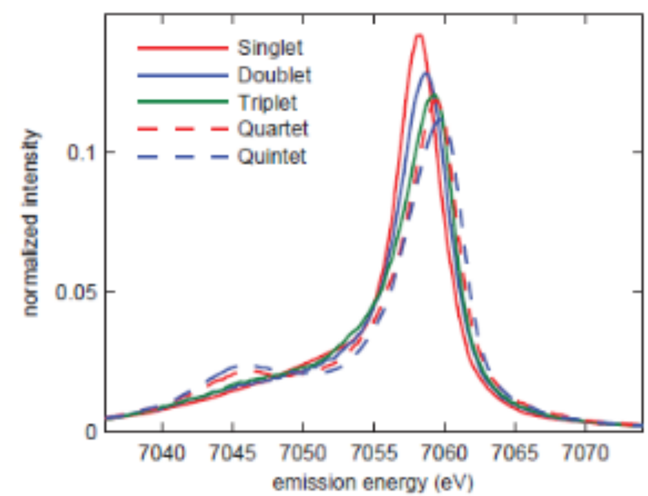
No MLCT signature detected…

→ Need now a ultrafast *Spin*-Sensitive Tool!!

Spin dynamics in Fe(II) complexes

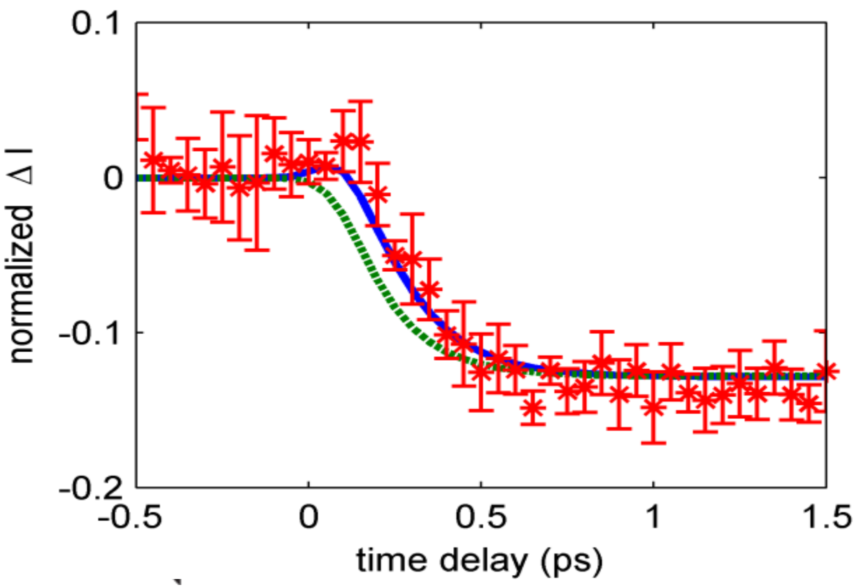


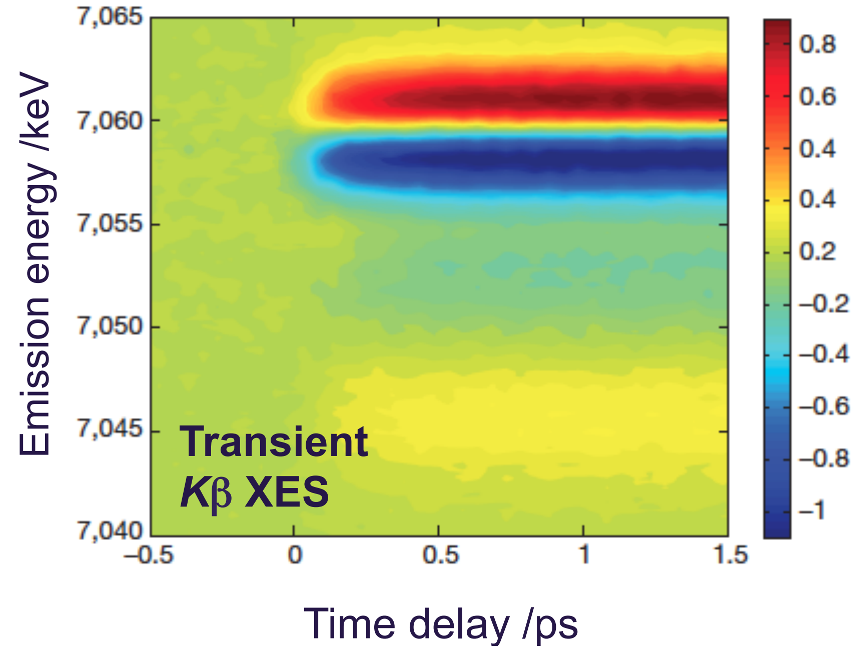




W. Zhang, *et al.*, Nature 509, 345 (2014)

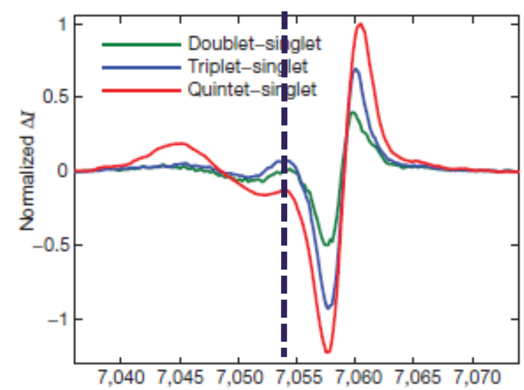
Tracking the intermediate states via fs transient XES





MLCT→$^{5}T_{2}$ state = 150 ± 50 fs

^{3}T→$^{5}T_{2}$ state = 70 ± 30 fs

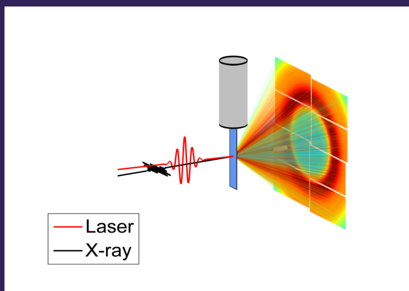


The spectral signature of the intermediate $^{3}T_{1,2}$ state(s) should be clearly distinguishable from MLCT and $^{5}T_{2}$ spectra

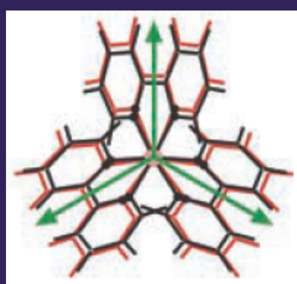
W. Zhang, *et al.*, Nature 509, 345 (2014)

X-ray Scattering in Molecular Liquids

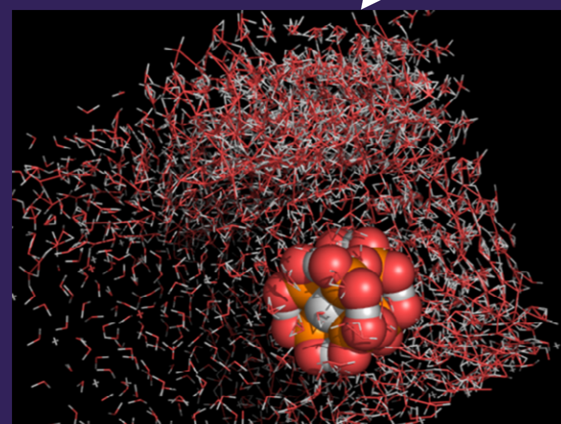
The transient XDS signal arise from the structural changes in:



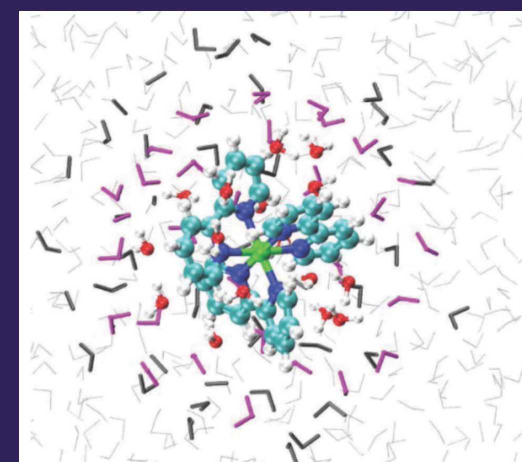
$$\Delta S(Q, \Delta t) = \Delta S_{solute} + \Delta S_{solvent} + \Delta S_{cage}$$



Solute Structure



Bulk Solvent



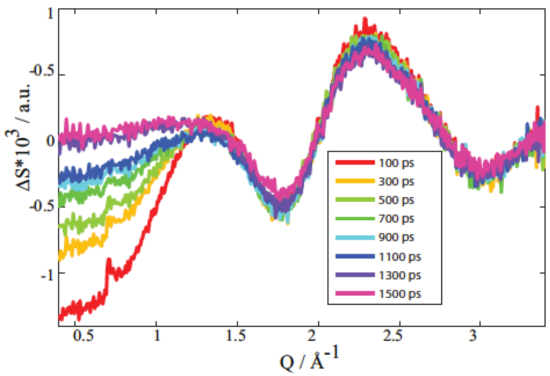
Szymczak et al., 2013

Solute-solvent interaction
(”solvation shell”/cage)

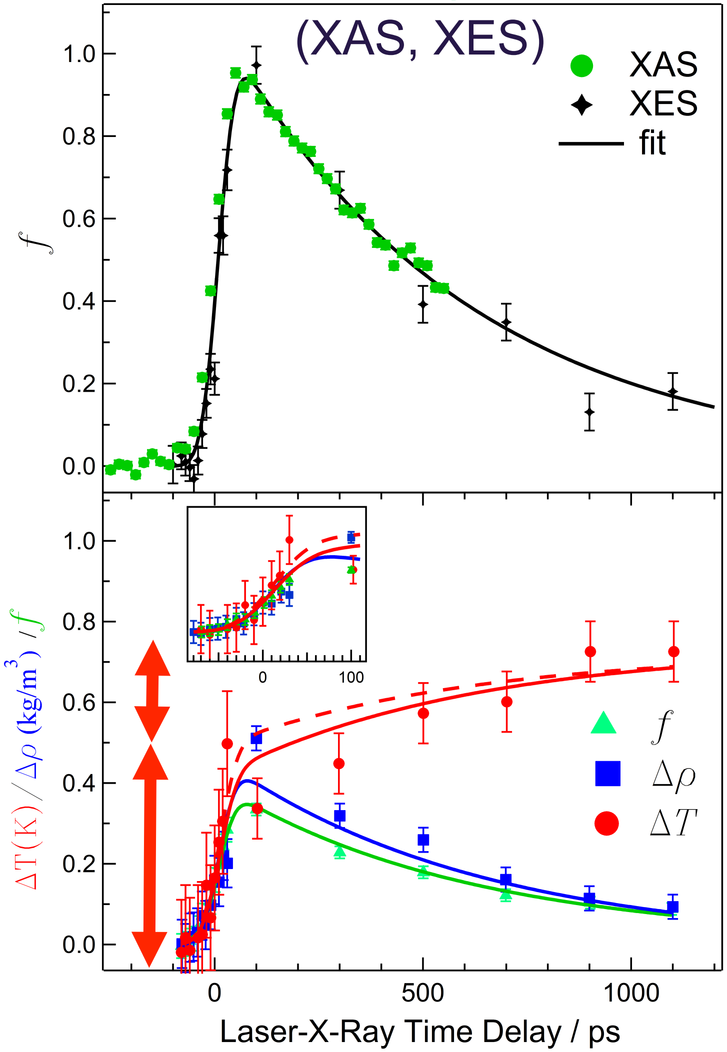
$$\Delta S_{Calc} = \alpha \Delta S_{Solute} + \Delta T \left.\frac{\partial \Delta S}{\partial T}\right|_{\rho} + \Delta \rho \left.\frac{\partial \Delta S}{\partial \rho}\right|_{T}$$

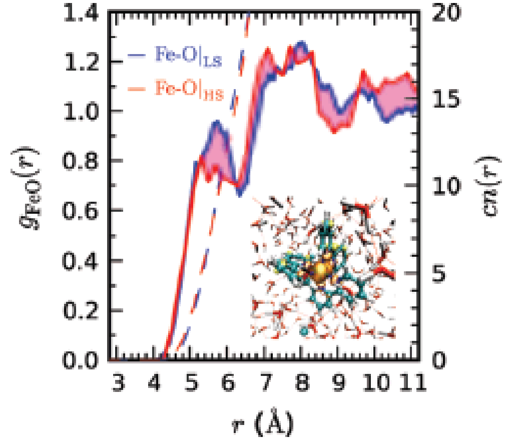
Courtesy: K. Haldrup

Combining XAS/XES with simultaneous XDS (100 ps)

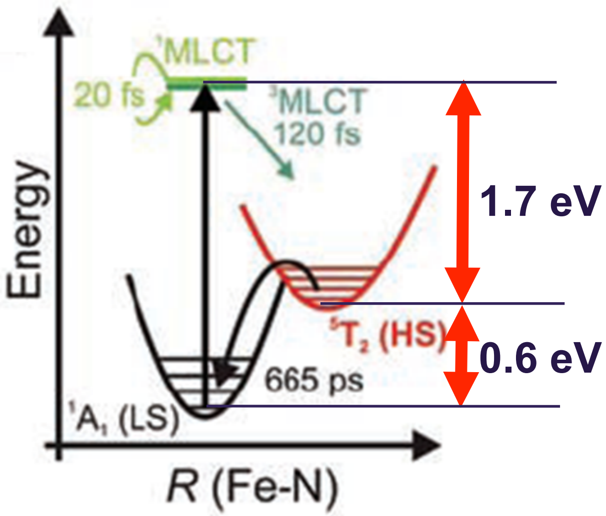


Fractional Population

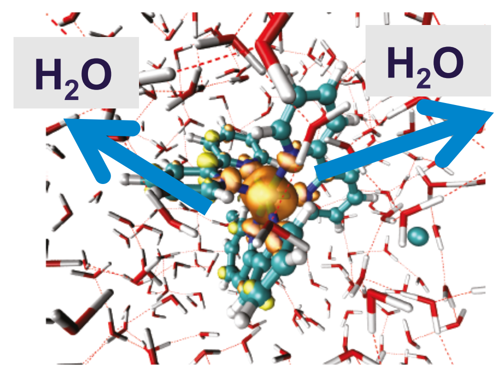




Heat



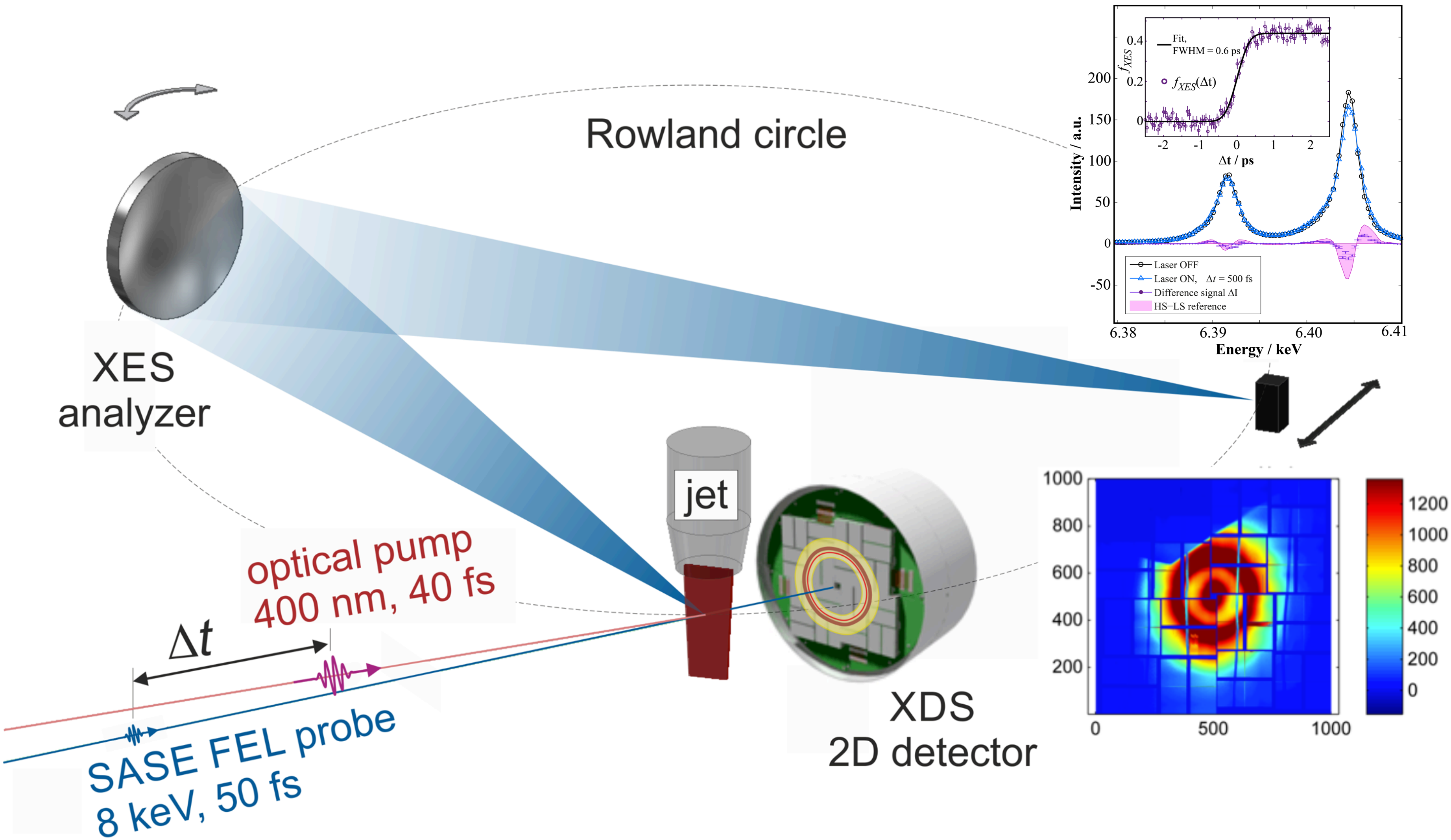
Density



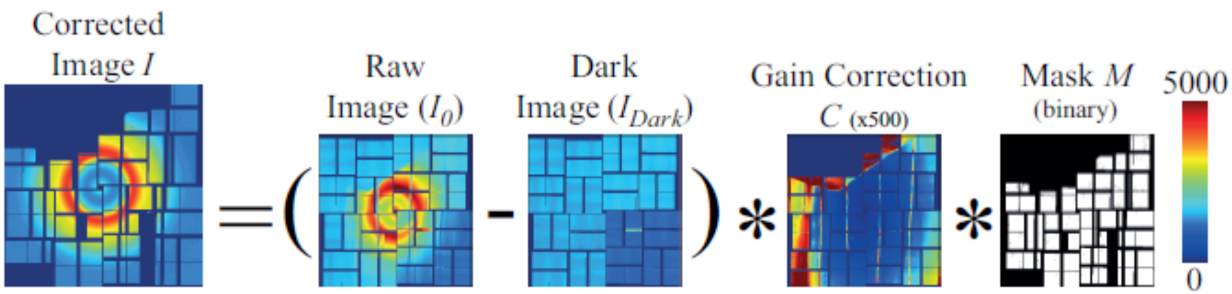
Daku and Hauser (2010)

C. Bressler *et al*, Faraday Discussions (2014)

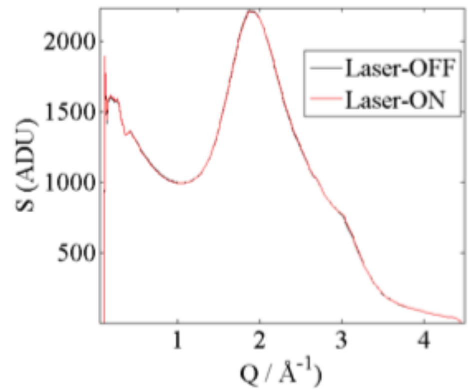
Combining X-ray spectroscopies with scattering at XFEL



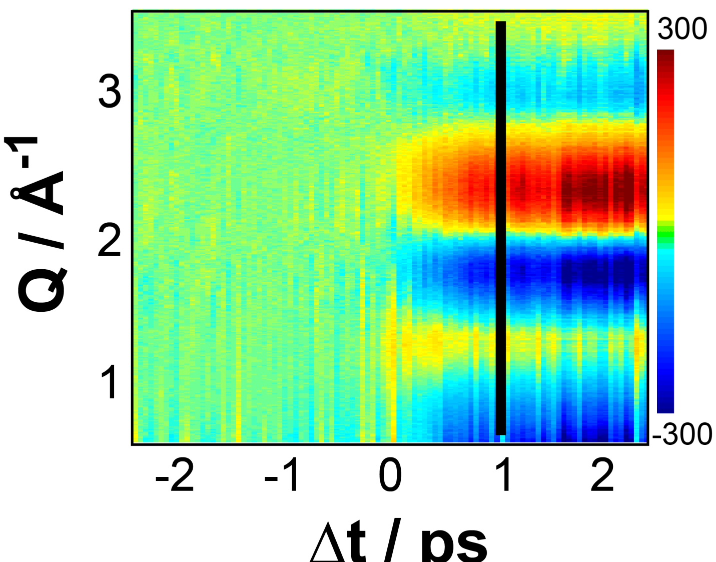
Femtosecond X-ray Diffuse Scattering (XDS)

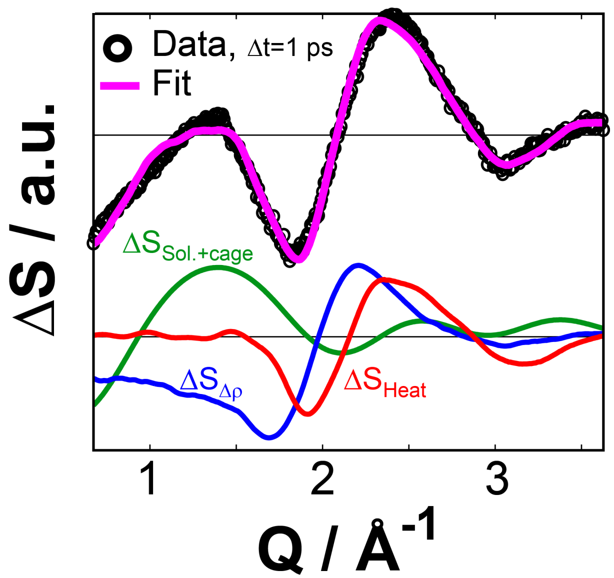


K. Haldrup, *Philos. Trans. R. Soc. Lond. B, Biol. Sci.* (2014)



Radially-integrated data





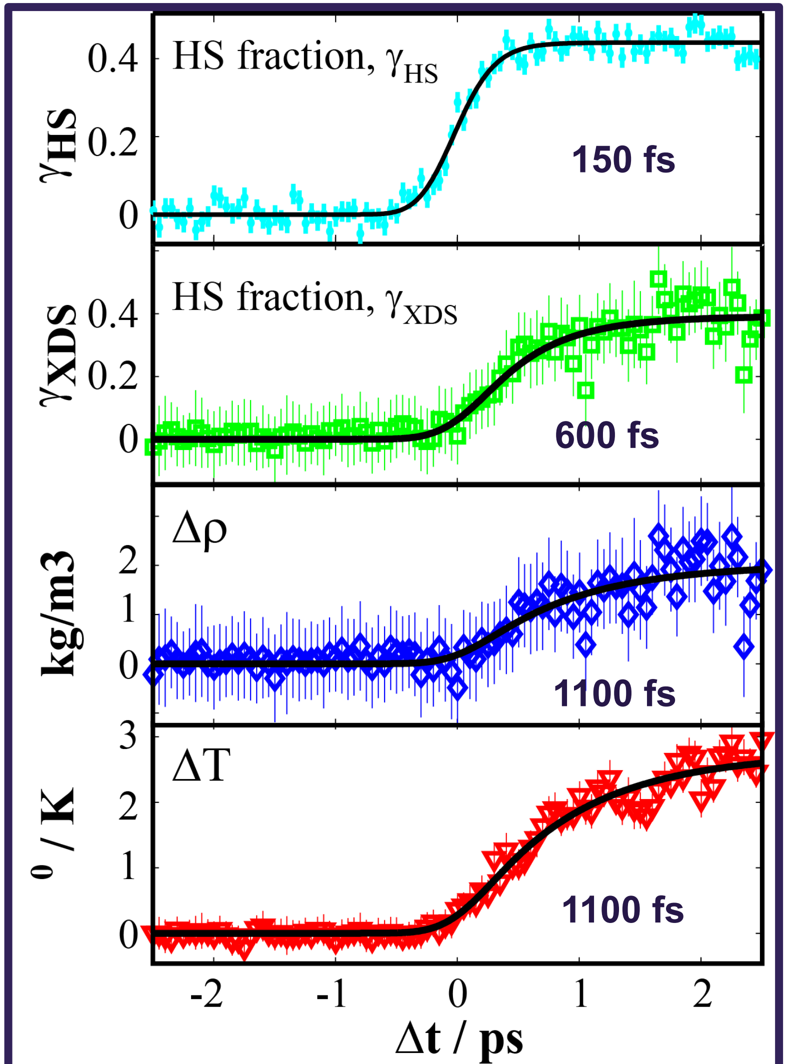
Local Structure

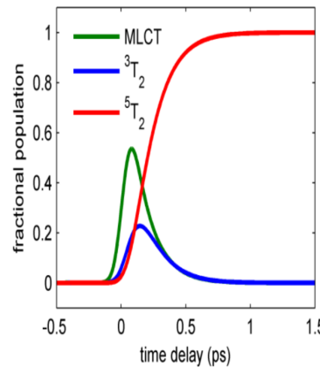
Bulk Heat

Bulk Density

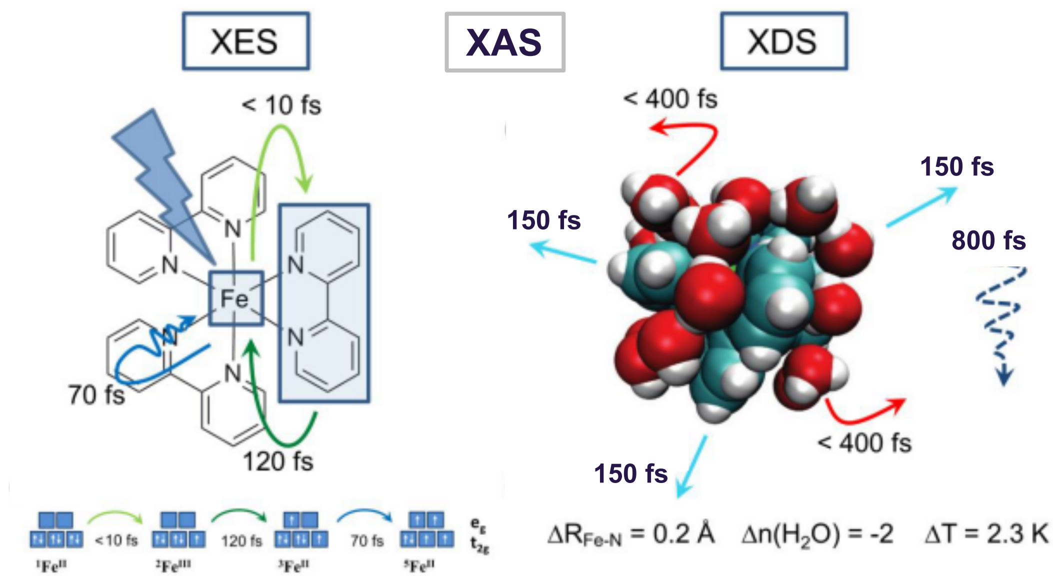
K. Haldrup *et al.*, submitted (2014)

Starting to look into solute-solvent interactions…

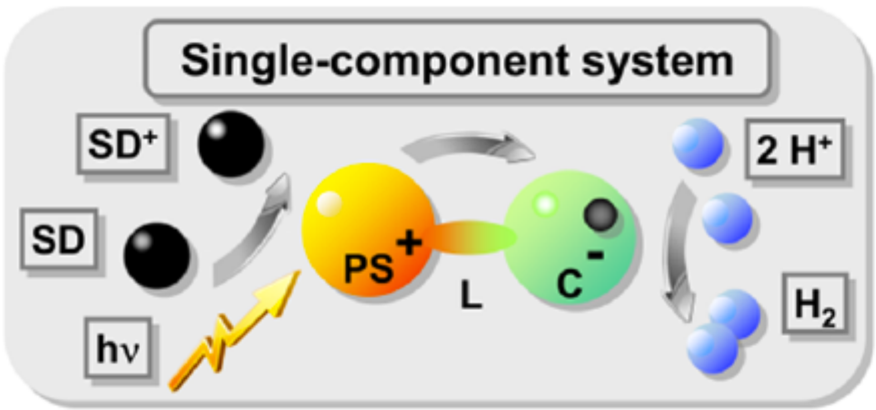




W. Zhang *et al.*, Nature **509**, 345 (2014)



Towards more complex systems



- Light absorption → PS
- Electron transfer via PS* from SD
- First redox on R (reduction)
- Further redox from R to C
- C transfers 2 electron to react further with H^+
- Hydrogen is formed!
- Solvent can be used as an electron donor

PS → photosensitizer

SD → sacrificial donor (electron source)

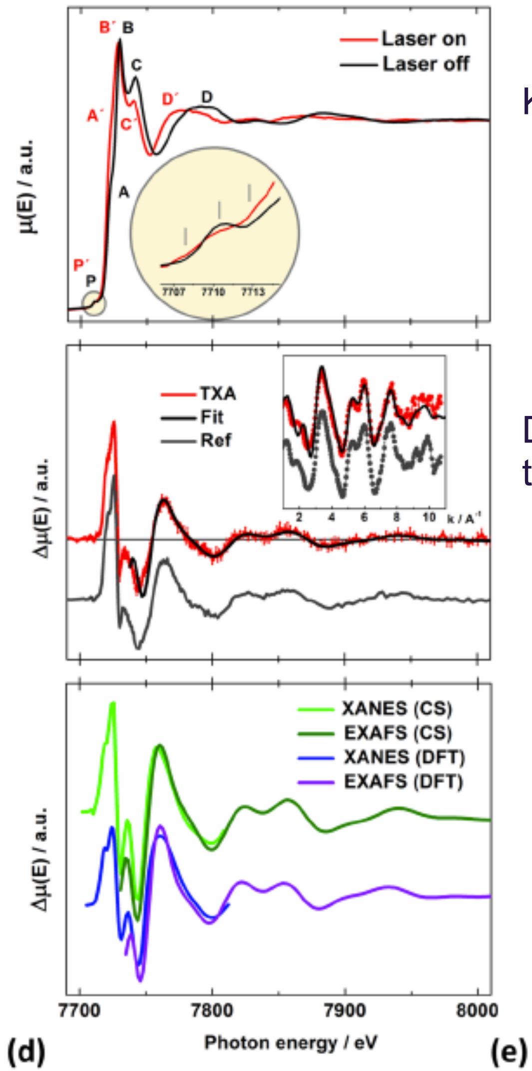
R → Relay (electron transporter)

C → Catalytic center

- The goal is to use first-row TMs as PS
- Decrease degradation, increase turnover rate
- Use rigid linkers instead of diffusion processes
- Act as an electron relay and reservoir

Detailed understanding of the structure-function relationship is required for optimized molecular photocatalysts in water splitting schemes

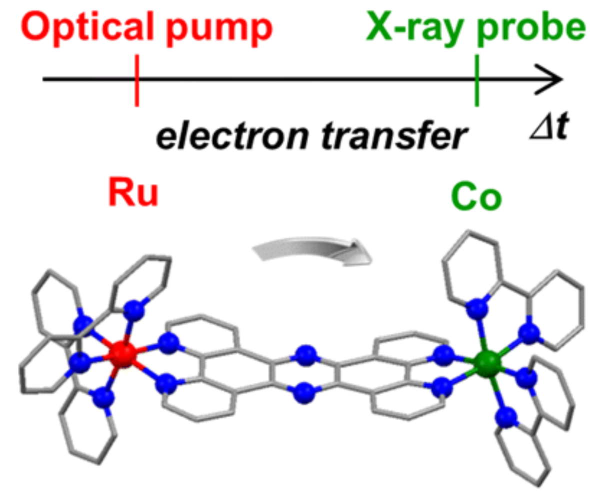
XAS studies in the ps-ns time domain



K-edge XAS spectra of Ru^{II}=Co^{III}

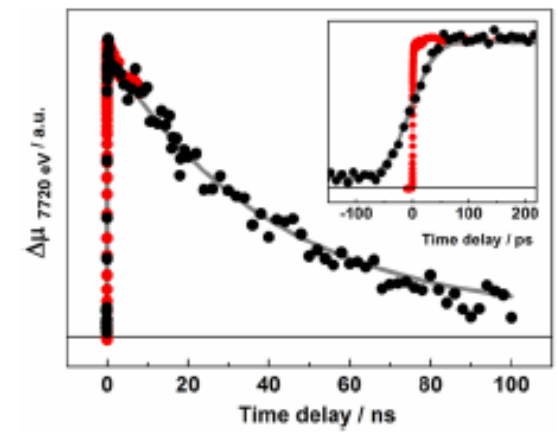
Difference spectra compared to a reference spectrum

XANES and EXAFS simulations using model structures extracted from DFT and x-ray crystallography



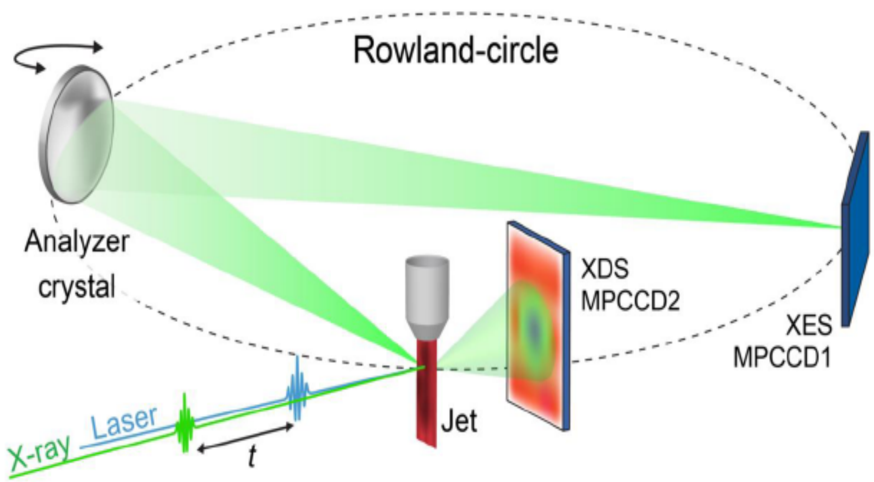
ΔR= 0.20 +/- 0.03 Å

$[(bpy)_2 Ru^{II} (tpphz) Co^{III} (bpy)_2] \times (PF_6)_5$

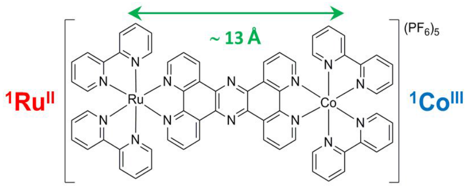


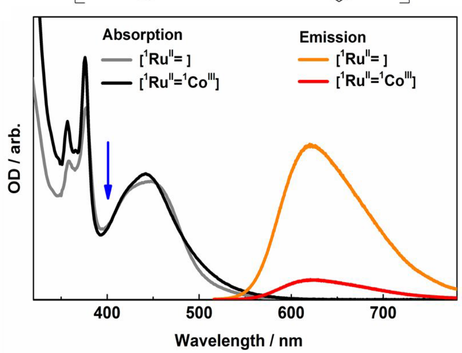
S. E. Canton et al., J. Phys. Chem. Lett., 2013

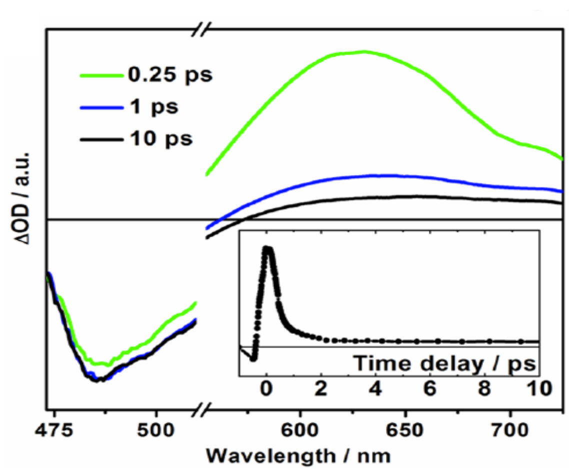
SACLA experiment – combined XDS and XES study



$[(bpy)_2 Ru^{II} (tpphz) Co^{III}(bpy)_2] \times (PF_6)_5$





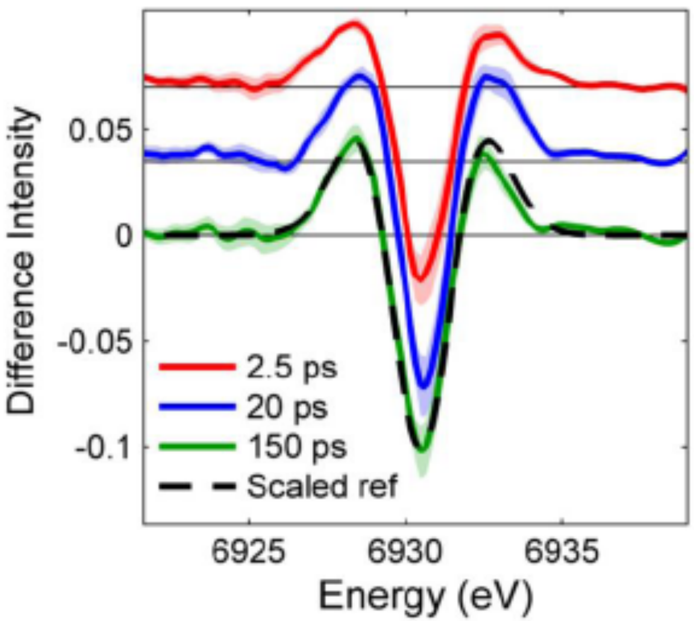


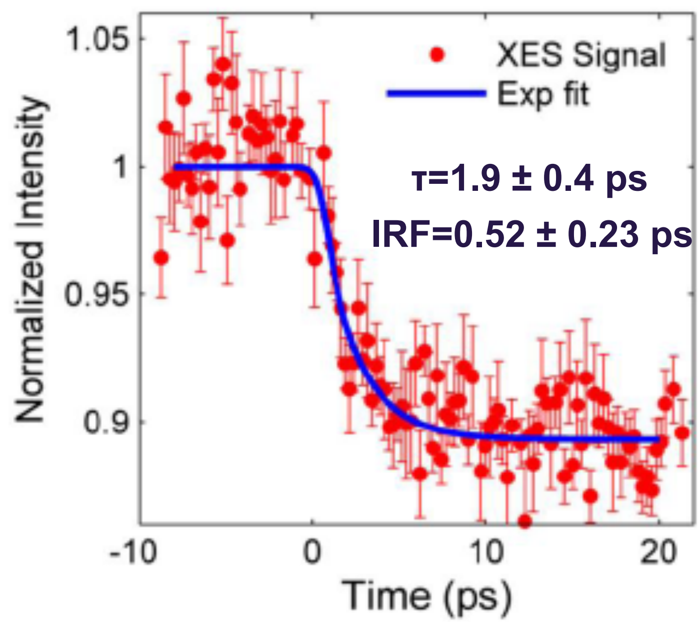
No dynamics at the redox site (Co atom) can be identified using the ultrafast optical spectroscopy → optically dark state!

European XFEL

X-ray Emission Spectroscopy

Kα XES for 3d metals → direct probe of the number of unpaired electrons→ oxidation and the total spin moment of the metal





Difference Kα spectra snapshot the time-dependent broadening of the emission

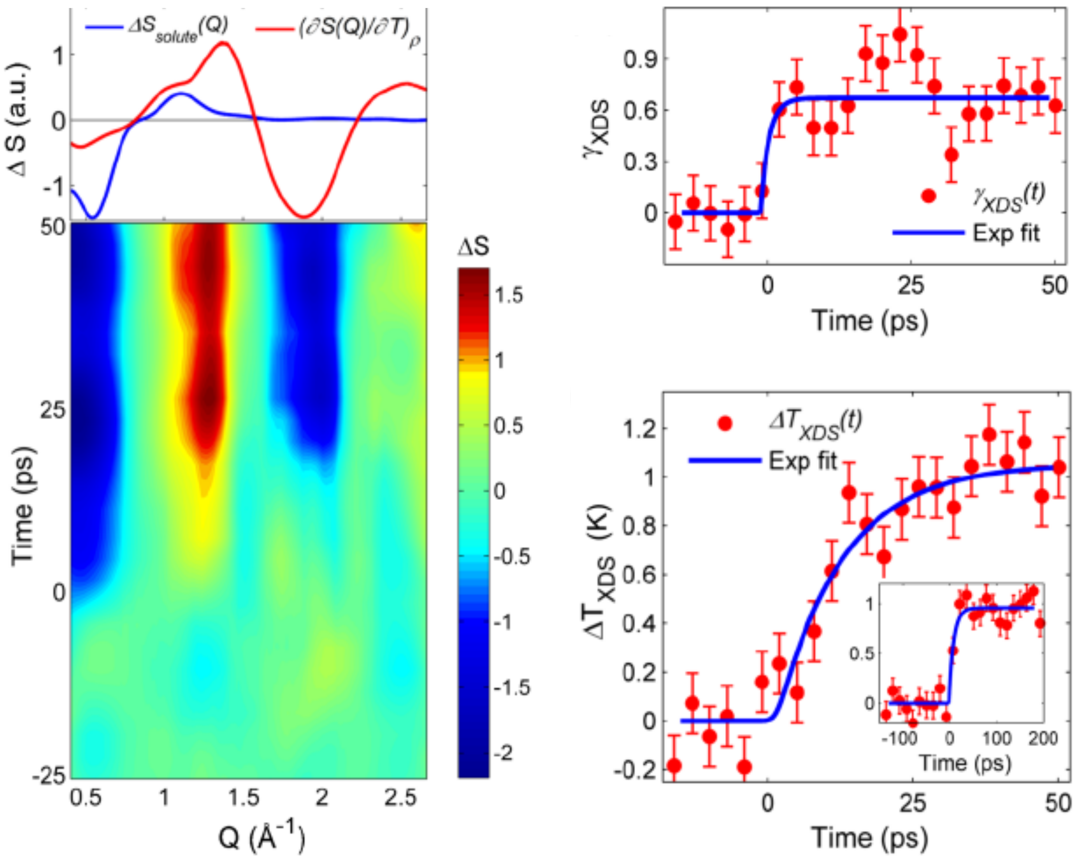
2p3d exchange interaction is weak and yields only the line broadening!

The measured value between the ground and excited state = 0.6 eV (ΔS=3/2, HS state)

S. Canton, *et al.*, accepted Nat. Commun. 2015

X-ray Diffuse Scattering

$$\Delta S_{Calc} = \alpha \Delta S_{Solute} + \Delta T \left.\frac{\partial \Delta S}{\partial T}\right|_{\rho}$$



The negative difference scattering signal at Q=0.5 Å^{-1} sets in instantaneously

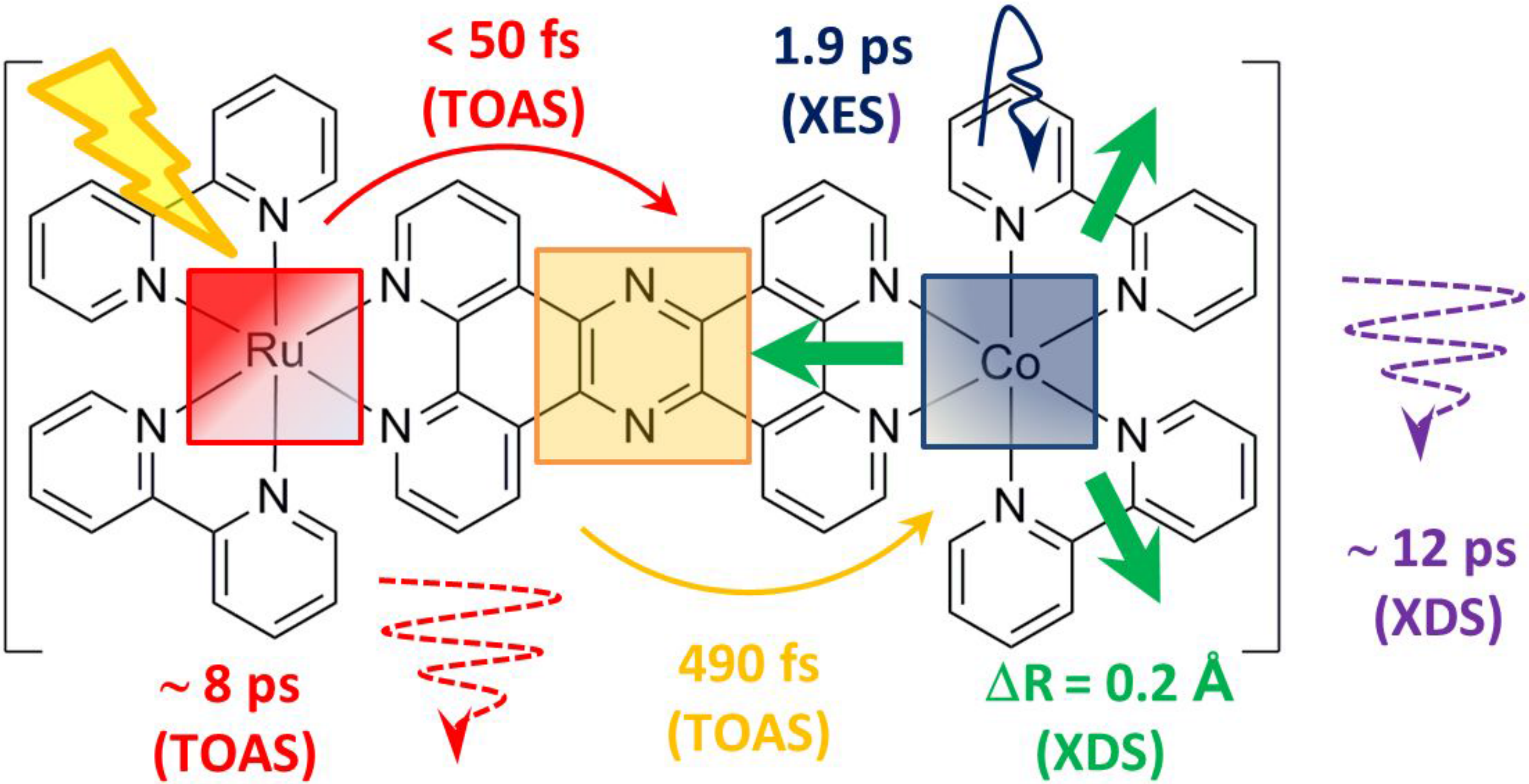
τ=2±0.5 ps

The positive and negative difference scattering signals larger Qs, i.e. Q=1.2 and 2.0 Å^{-1} grow slowly on 15-20 ps timescale

τ=12±3 ps

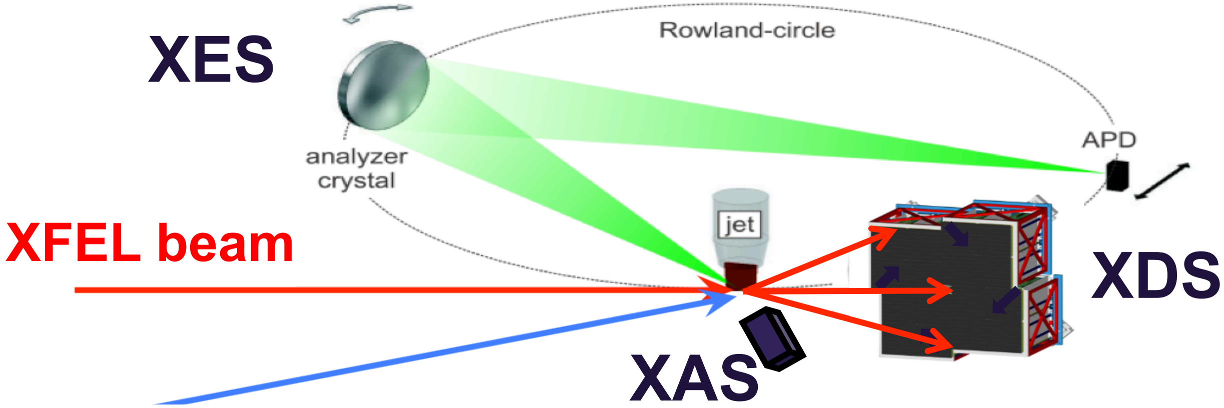
S. Canton, *et al.*, accepted Nat. Commun. 2015

The full reaction cycle revealed with complementary tools

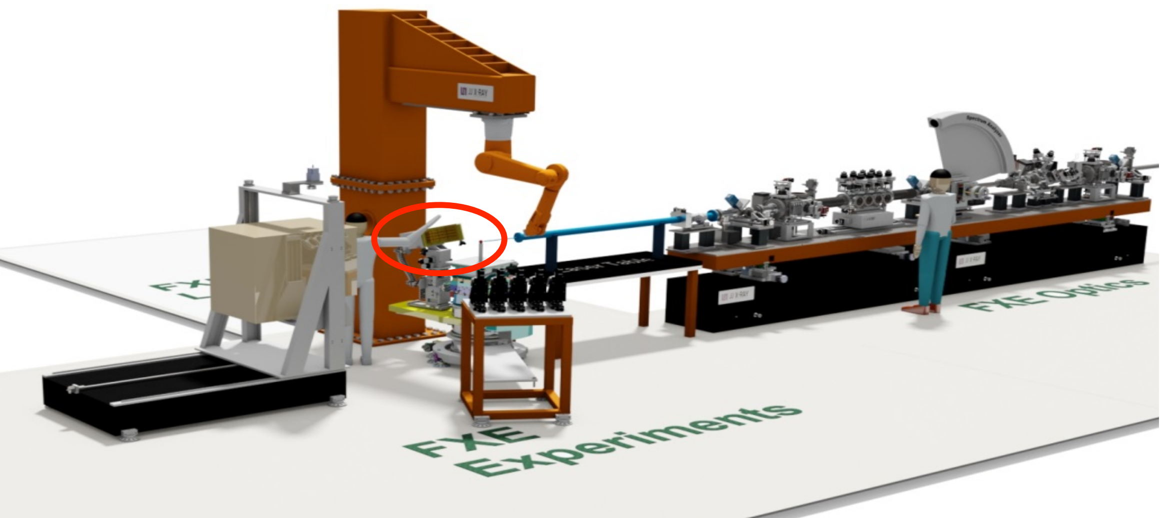


S. Canton, *et al.*, accepted Nat. Commun. 2015

Summary: Towards A High-Speed Molecular Camera for tracking chemical reaction dynamics



Von Hamos (2014)



A Suite of Simultaneous X-Ray Tools available:

- *XAS (w/DAFS)*
- Non resonant XES
- Resonant XES (RIXS)
- X-Ray Raman Scattering
- XDS
- …

Please check our posters on Friday: Poster # 90 and #219

FXE instrument Workshop: Tomorrow, 13:30-18:00 CFEL SemRoom III (Bldg. 99)

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Lund University
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Villy Sundström

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Zoltán Németh

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Lars Mewes

SLAC/LCLS
Kelly Gaffney
Marco Cammarata
Henrik Lemke
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EU-CRISP
CUI Hamburg
Uni Hamburg
PIER Hamburg
IMPRS-UFAST

Thank you for your attention!