XFELs as molecular movie cameras

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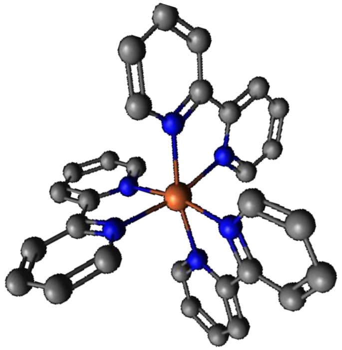
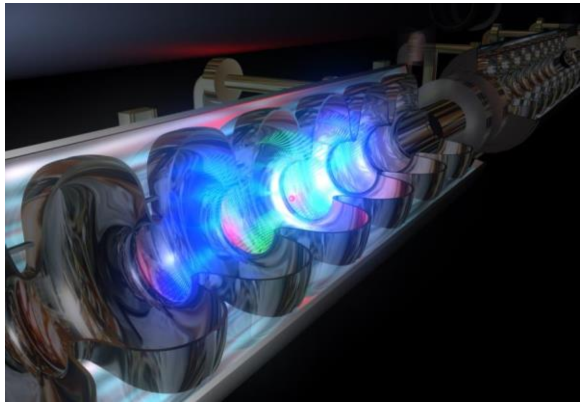
Klaus B. Møller
(DTU Chemistry)

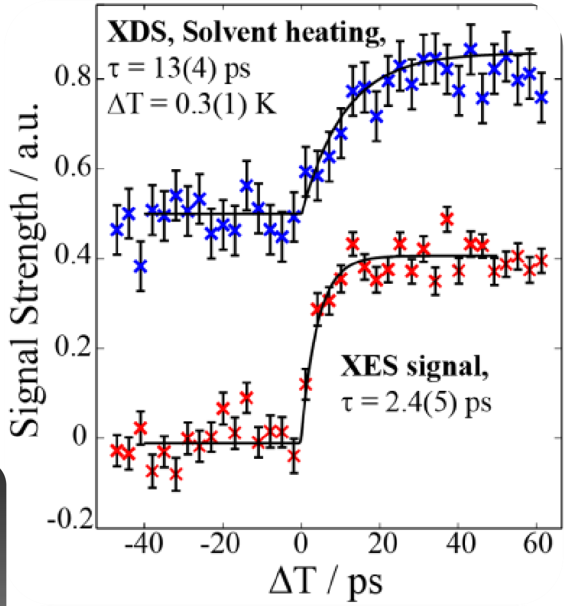
DTU

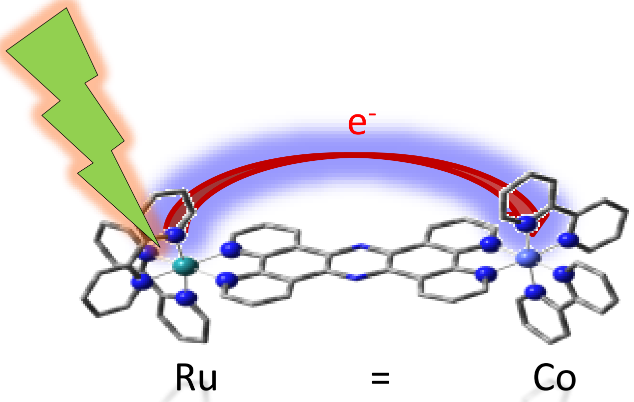
Contents

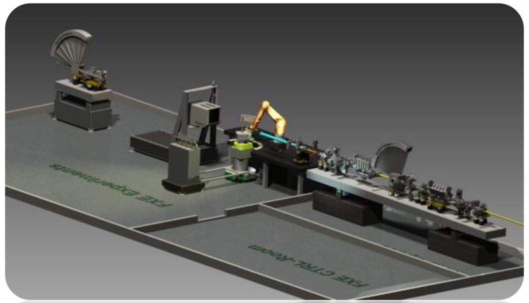




- Length and timescales for functional materials
- Ultrafast science at XFELs
- Optical pump – X-ray probe techniques
- Difference signals
- Structural information without crystals
- Ru=CO Donor-Acceptor systems
- Mapping coherent structural changes
- New materials

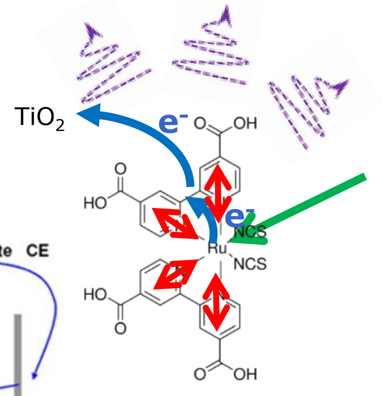






Timescales of functions in functional materials

Heat release to environment



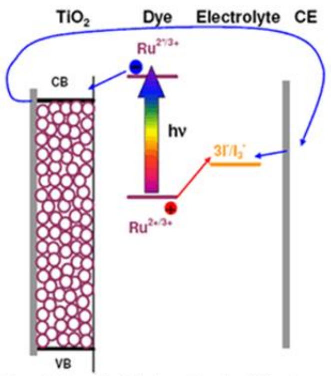
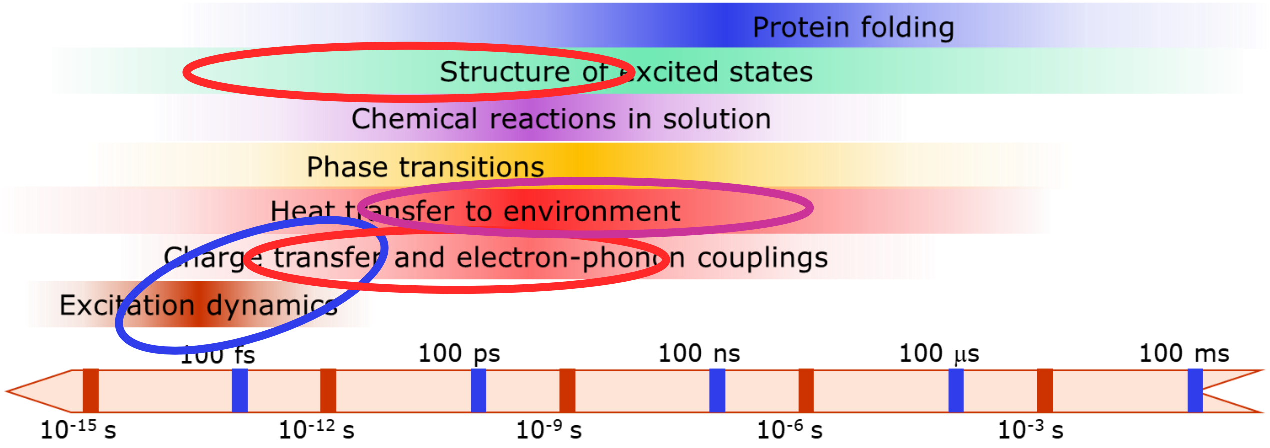
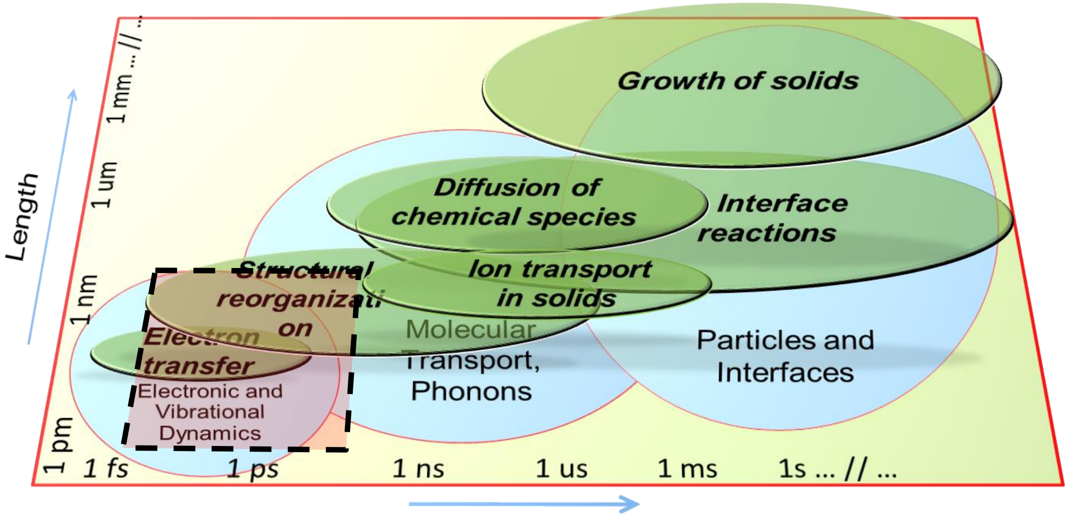


Figure 1. Schematic of electron pathway in a DSC system

'traditional' dye sensitizer for photovoltaics

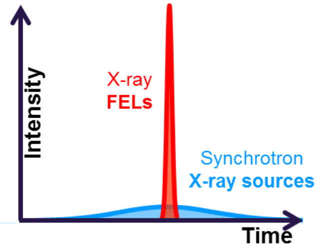


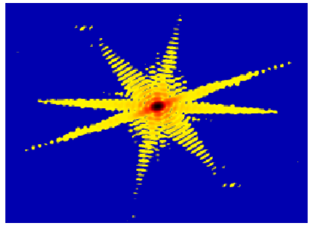
Time scale



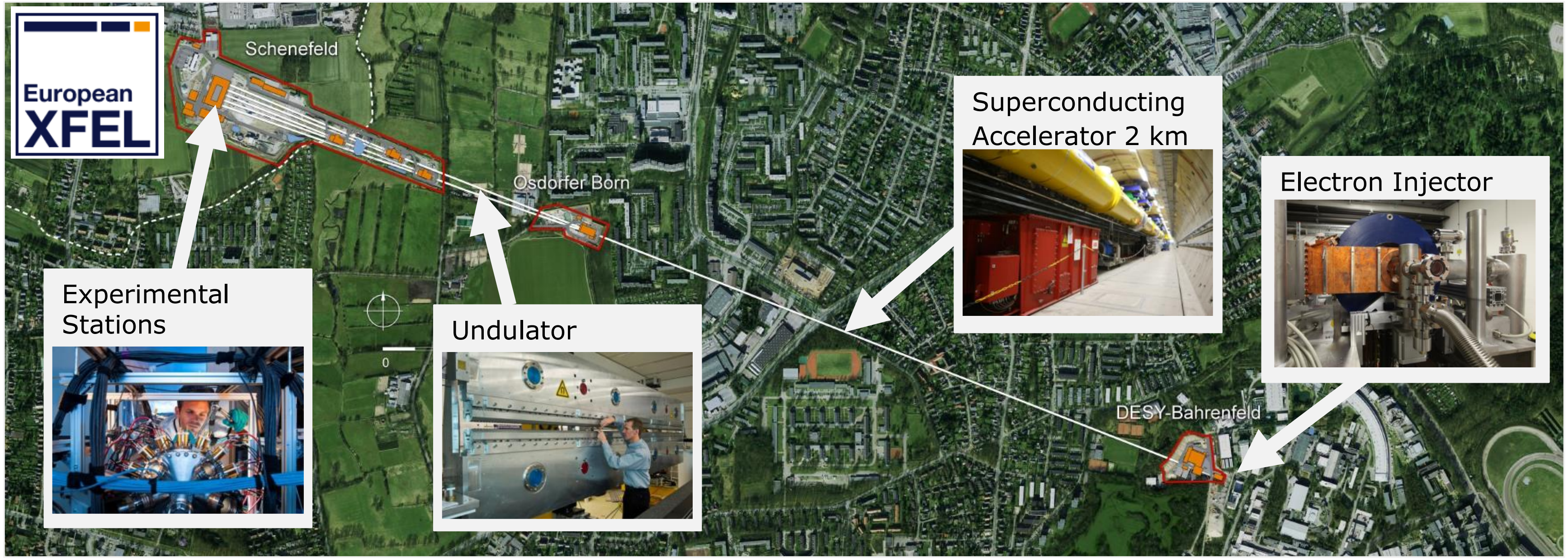
We need: 0.01-10 nm length scales and 10 fs – 100 ps timescales

XFELs: short and intense x-ray pulses

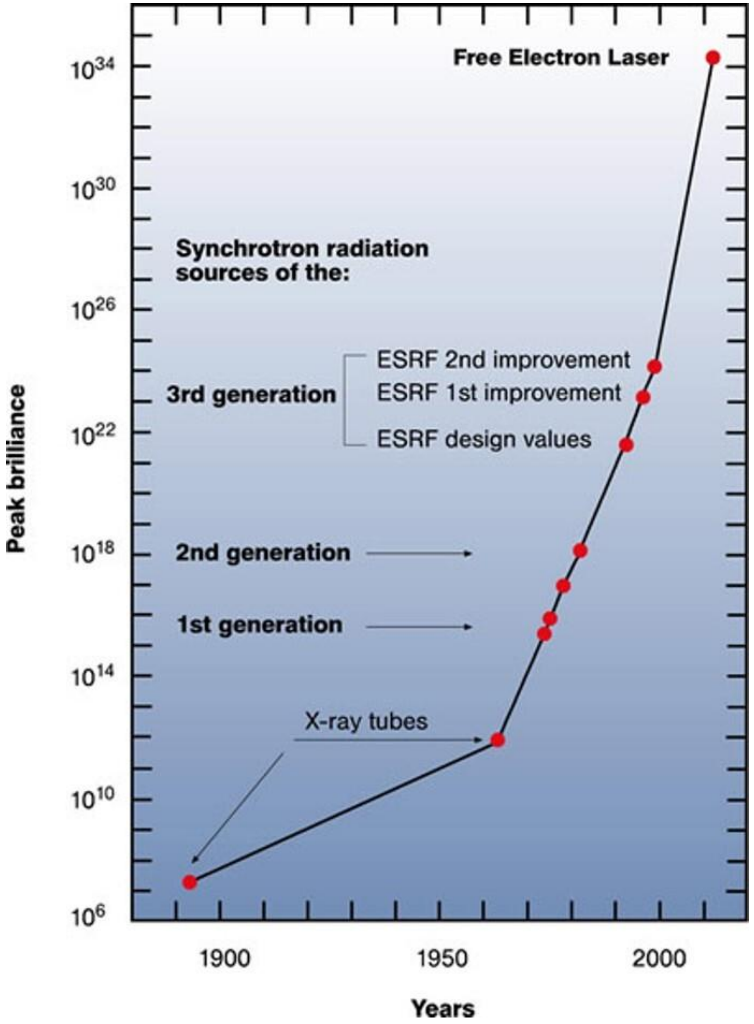




- XFELs pack the same x-ray power in 100 fs as most synchrotrons do in 1 second
- High peak brilliance (many photons per time on the sample, up to 10^{20} W/cm^2)
- Ultra short pulses (femtosecond time resolution, 'diffract before destroy', 1 – 100 fs)
- Coherence (imaging, correlation spectroscopy, Fully transverse, Partially temporal)



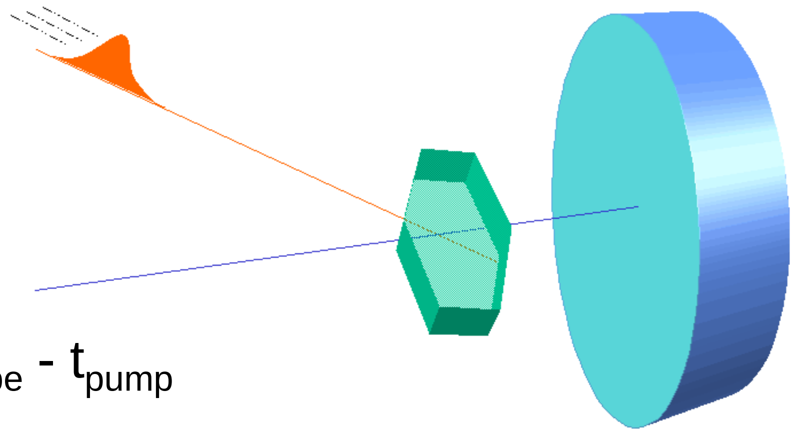
Peak brilliance



Short x-ray pulses: Capturing fast processes with pump-probe

Laser pump

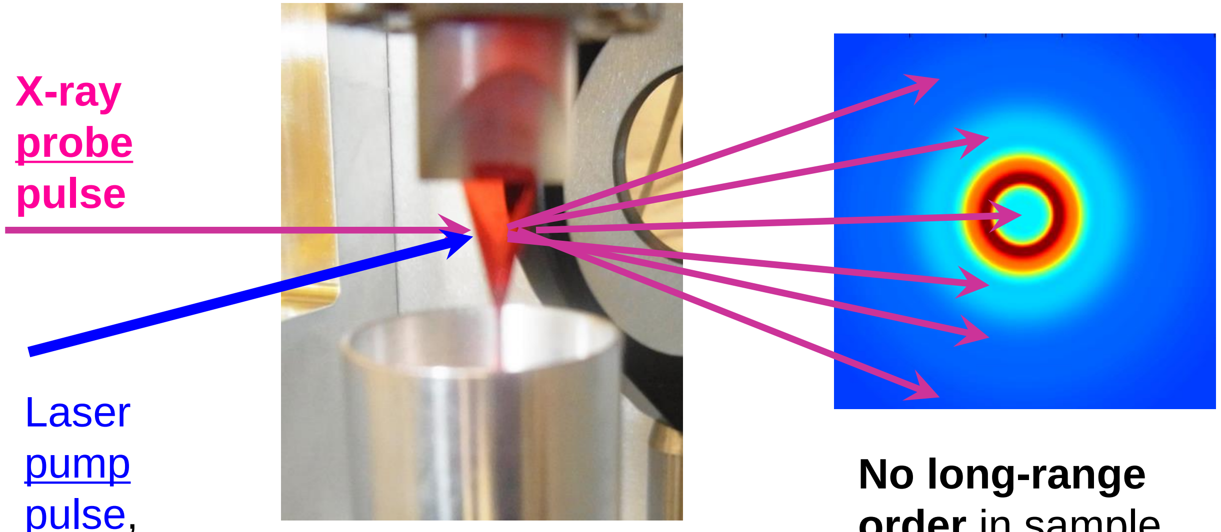
X-ray probe



$\tau = \Delta t = t_{probe} - t_{pump}$

Sample delivery – replenish sample between shots:

Fast-flowing 50-300 μm liquid jet, [c] = 1-100 mM

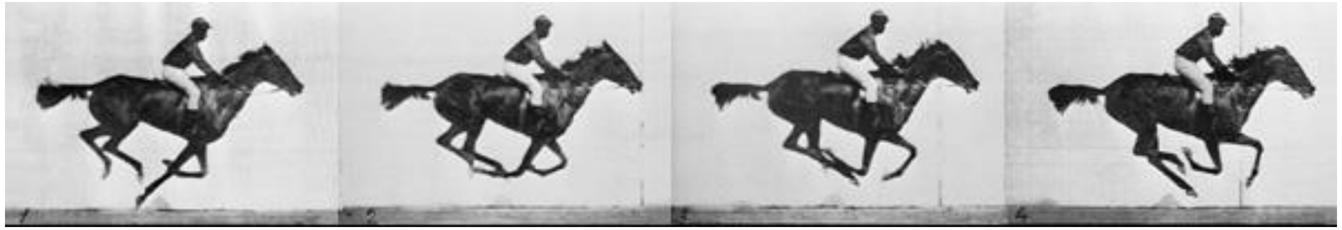


No long-range order in sample

-> only ”diffuse” scattering

Tracking processes while they occur

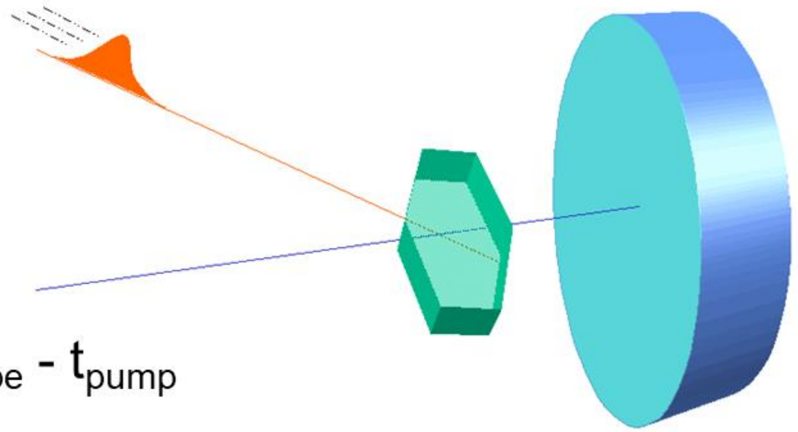
(Muybridge, Stanford 1878, the first film)



Short x-ray pulses:
Capturing fast processes with pump-probe

Laser pump

X-ray probe



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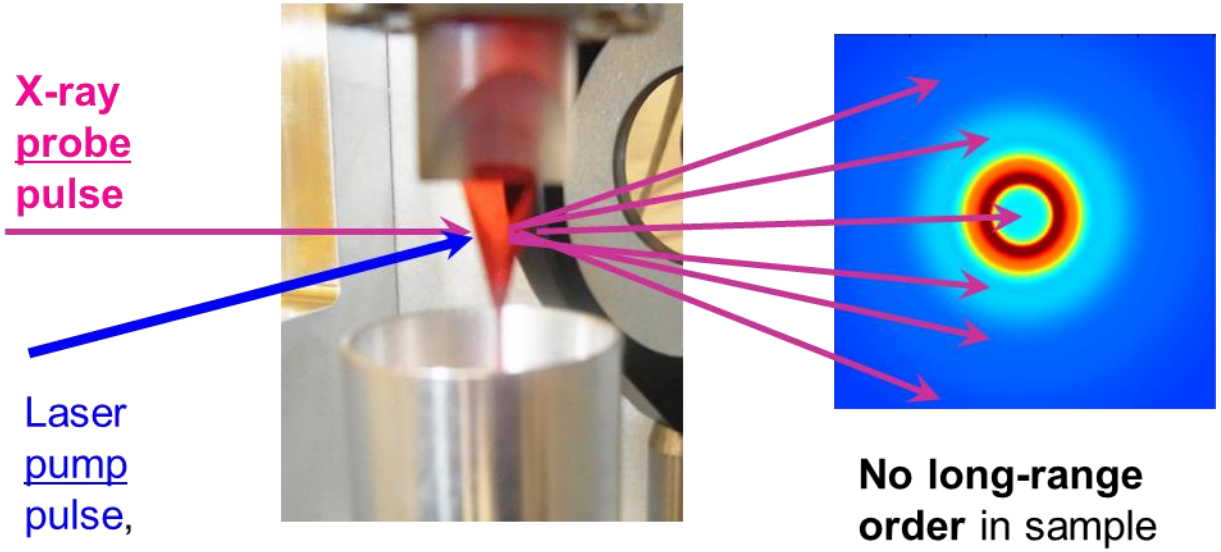
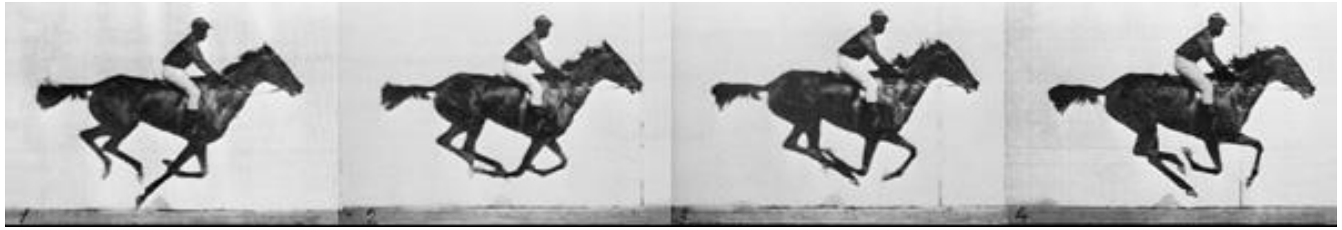


No long-range order in sample

-> only "diffuse" scattering

Tracking processes while they occur

(Muybridge, Stanford 1878, the first film)



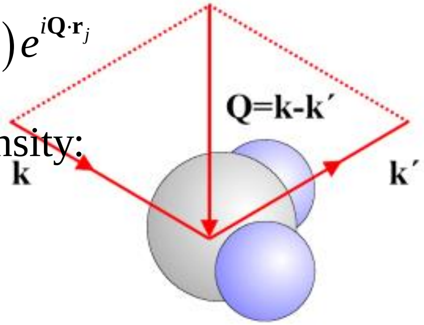
Scattering form a molecule - *without crystals*

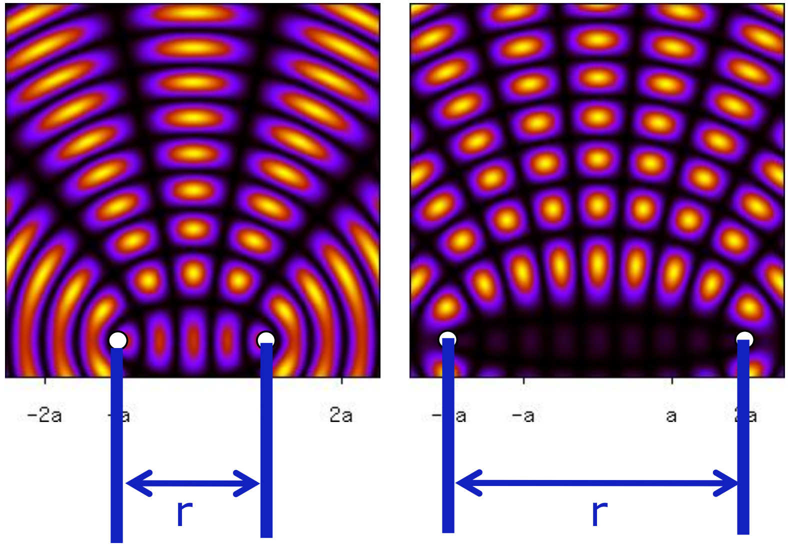
Total scattering length of the molecule is:

$$F^{mol}(\mathbf{Q}) = \sum_{\mathbf{r}_j} f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

Total scattered intensity:

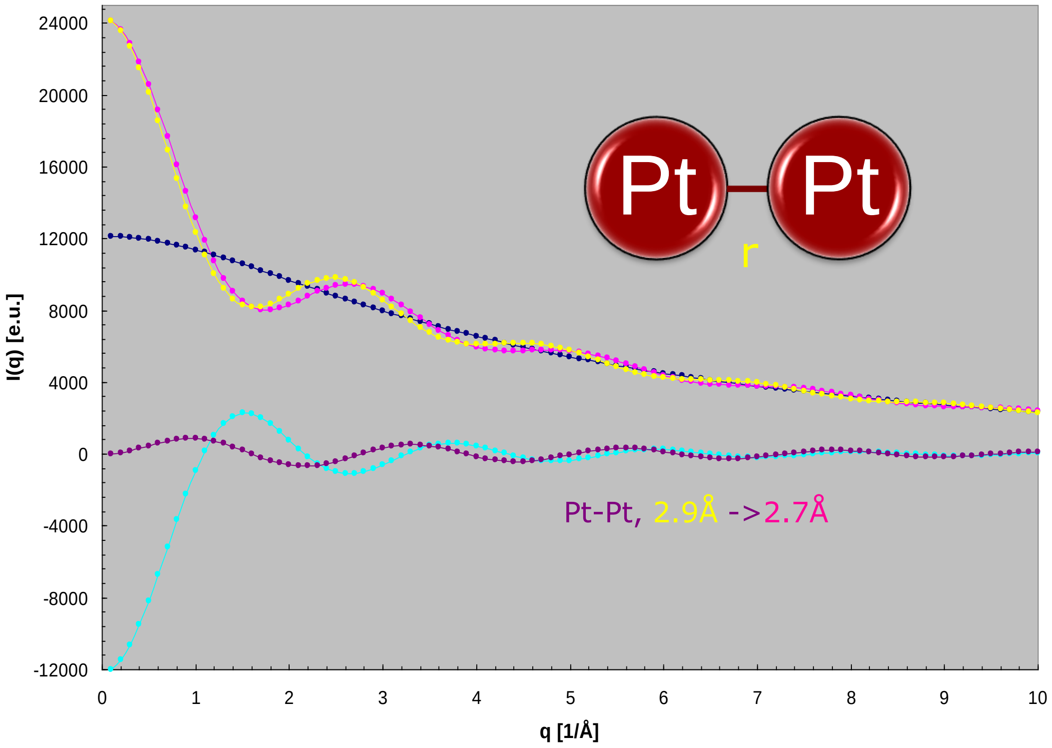
$$I(\mathbf{Q}) = \left|F^{mol}(\mathbf{Q})\right|^2$$



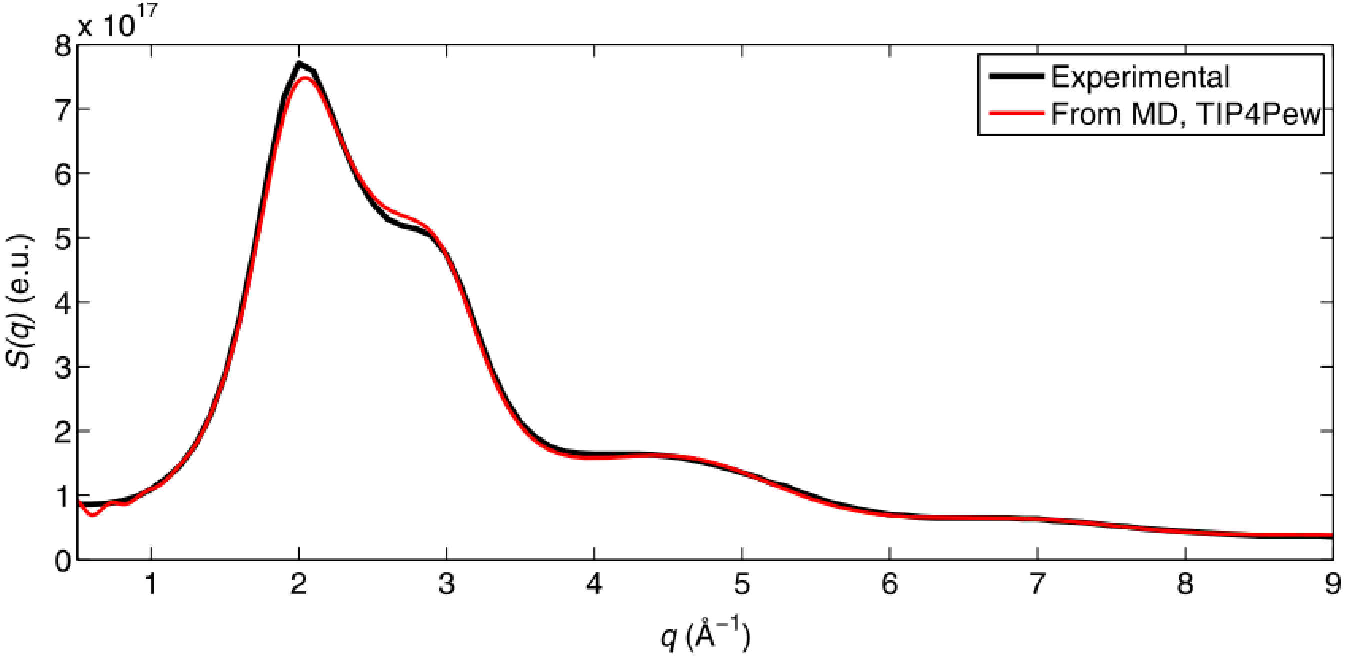


Randomly oriented molecules, the Debye formula:

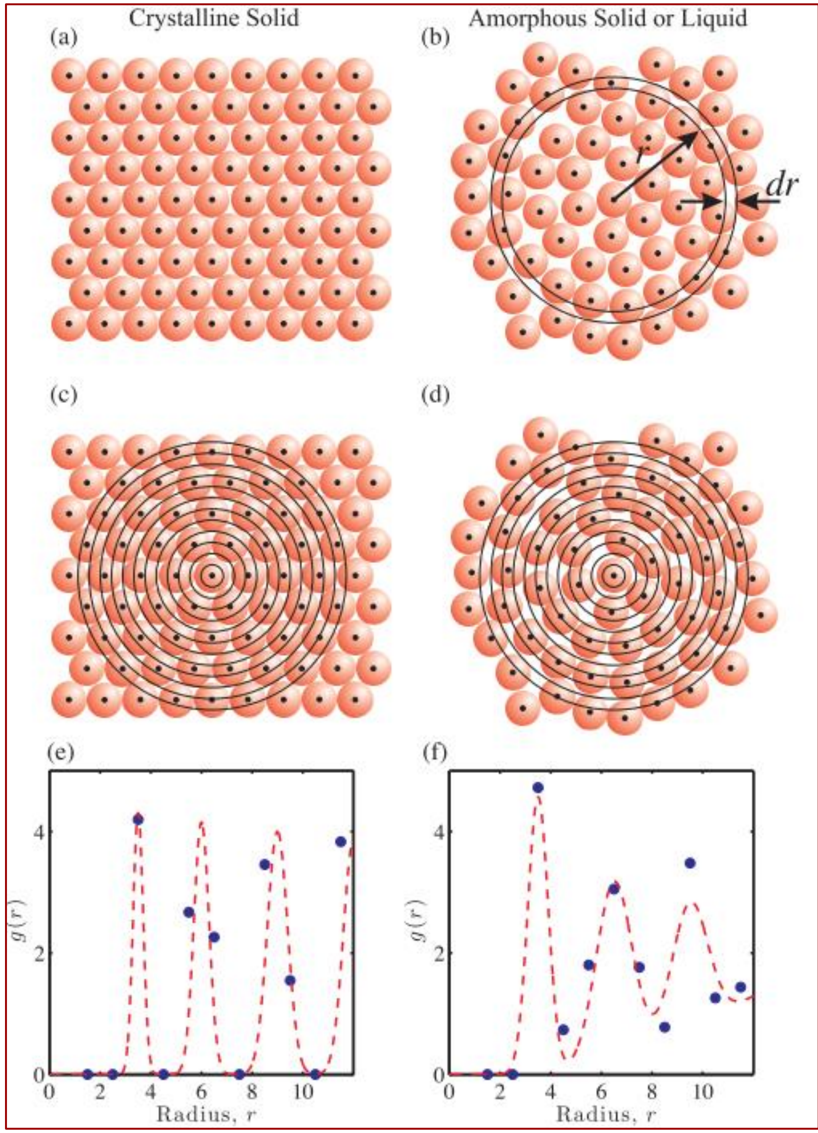
$$S(q) = \sum_{i,j} f_i(q)\, f_j(q) \frac{\sin(q\, r_{ij})}{q r_{ij}} \rightarrow \begin{cases} (\sum_i Z_i)^2 & \textit{for } q \rightarrow 0 \\ \sum_i f_i^2(q) & \textit{for } q \rightarrow \infty \end{cases}$$



X-ray scattering from liquids



Pair correlation function of a liquid



Scatttering from a liquid

$$S_v(q) = \sum_{l}^{v} N_l f_l(q)^2 + \sum_{l,m}^{v} f_l(q) f_m(q) \frac{N_l(N_m - \delta_{l,m})}{V} 4\pi \times \int_0^{R_{\mathrm{box}}} r^2 \left[g_{l,m}(r) - 1 \right] \frac{\sin(qr)}{qr} dr$$

e.g. Dohn, et al. *J. Phys. B At. Mol. Opt. Phys.* **2015**, *48* (24), 244010. https://doi.org/10.1088/0953-4075/48/24/244010.

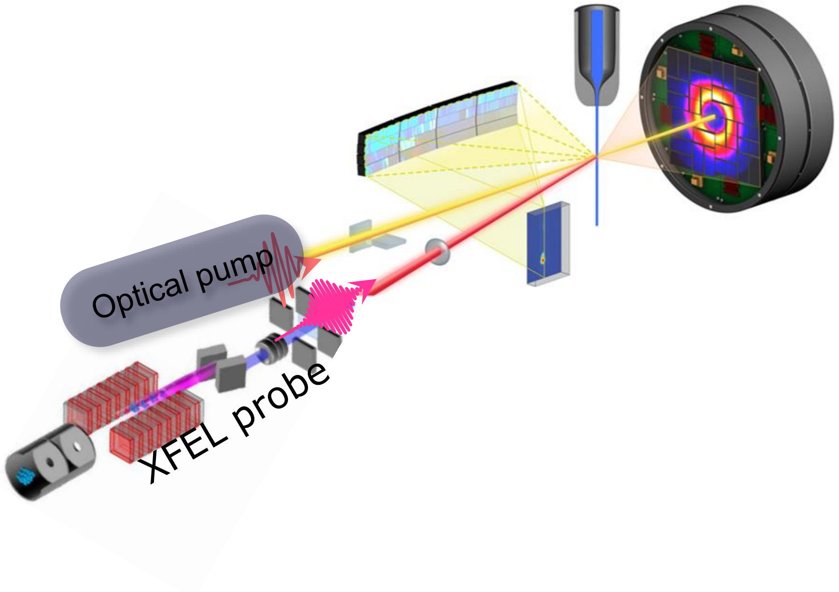
Als-Nielsen, J.; McMorrow, D. *Elements of Modern X-ray Physics*; Wiley, 2011.

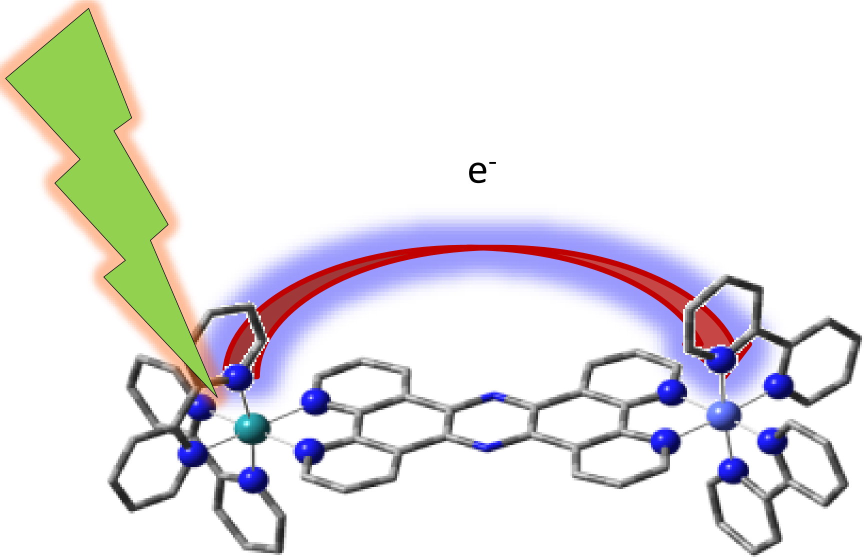
Full Ru=Co dynamics following photo-excitation

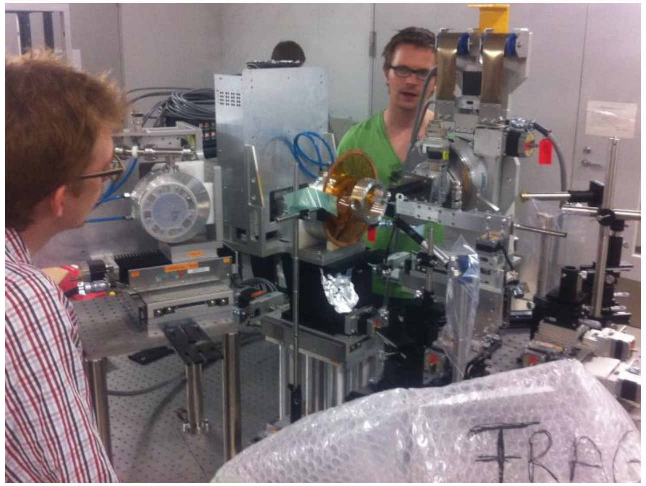
$[(bpy)_2Ru^{II}(tpphz)^{1}Co^{III}(bpy)_2](PF_6)_5$

Prototypical molecule for intramolecular (pre-)catalysts

Challenge: Co centre is ”optically dark”, rendering full characterization difficult



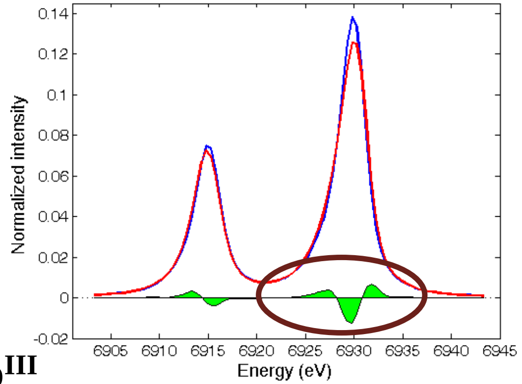


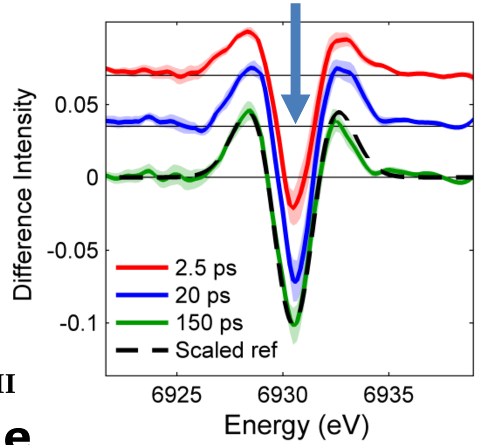


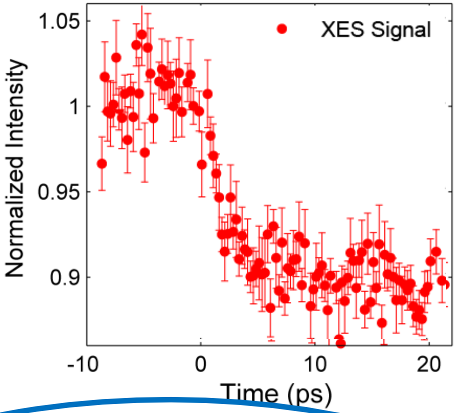
Experiment done at SACLA 2011, results Published 2015

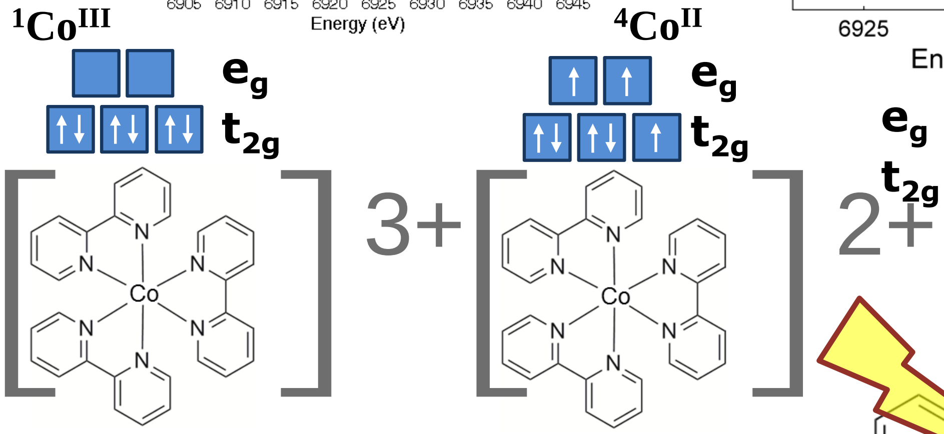
Collaboration with V. Sundström group, Lund University

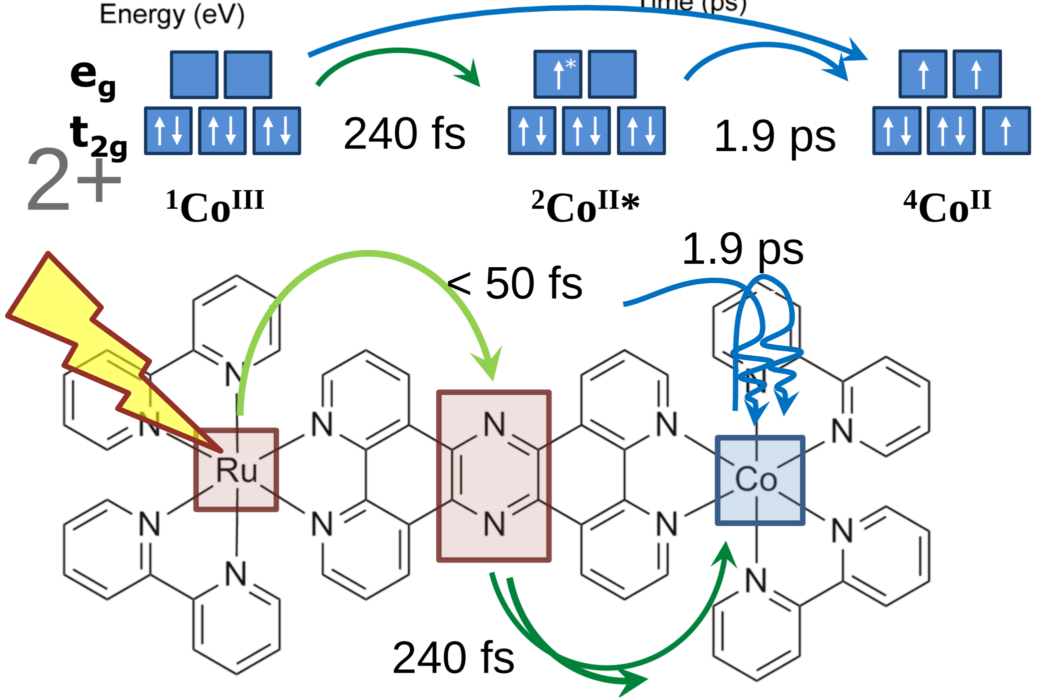
Experimental Analysis, Ru=Co – XES

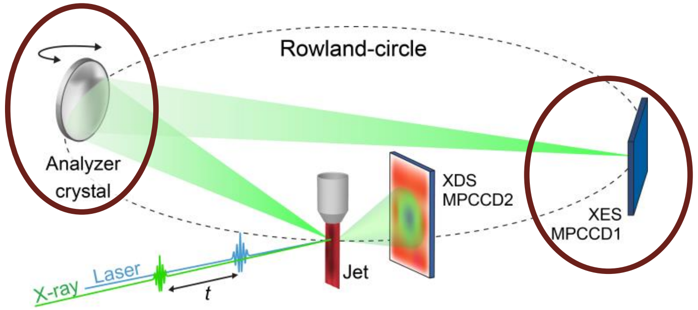








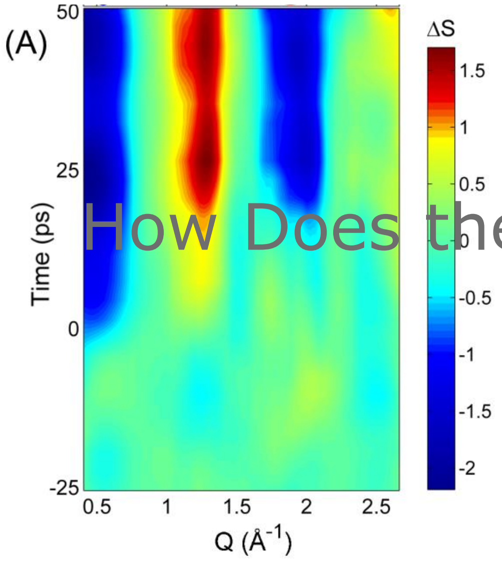




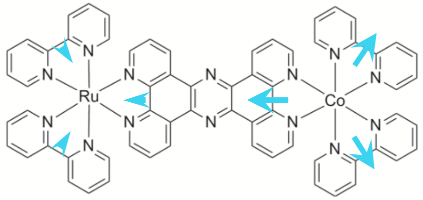
Canton, Kjær *et al* Nature Comm. 2015

Slides: K.S. Kjær

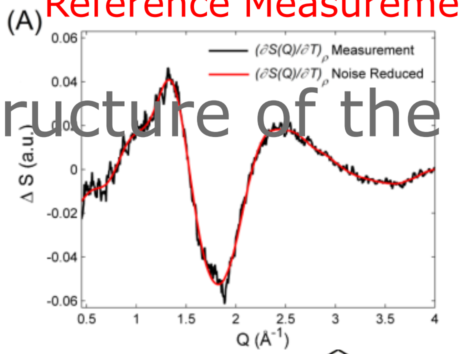
Experimental Analysis, Ru=Co – XDS (WAXS)

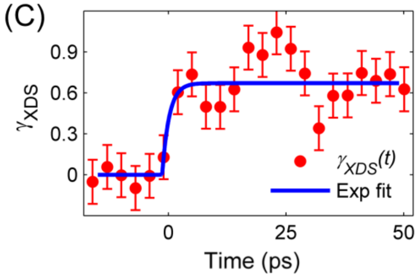


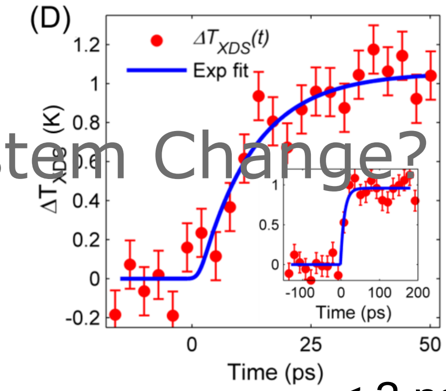
Simulated Signal From Calculated Structures



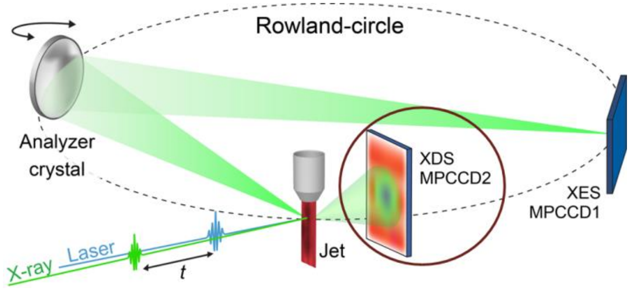
Reference Measurement

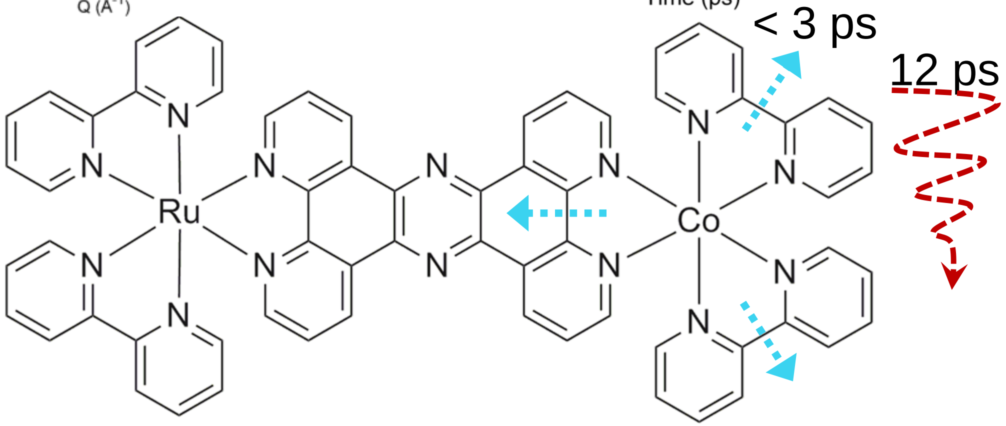






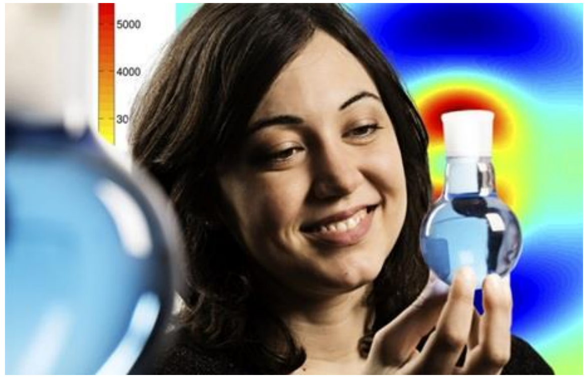
How Does the Structure of the System Change?



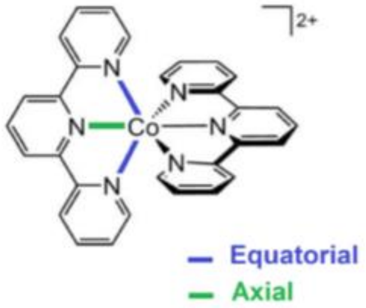


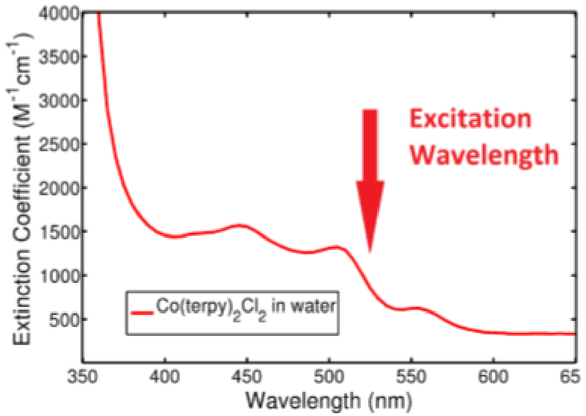
Canton, Kjær *et al* Nature Comm. 2015

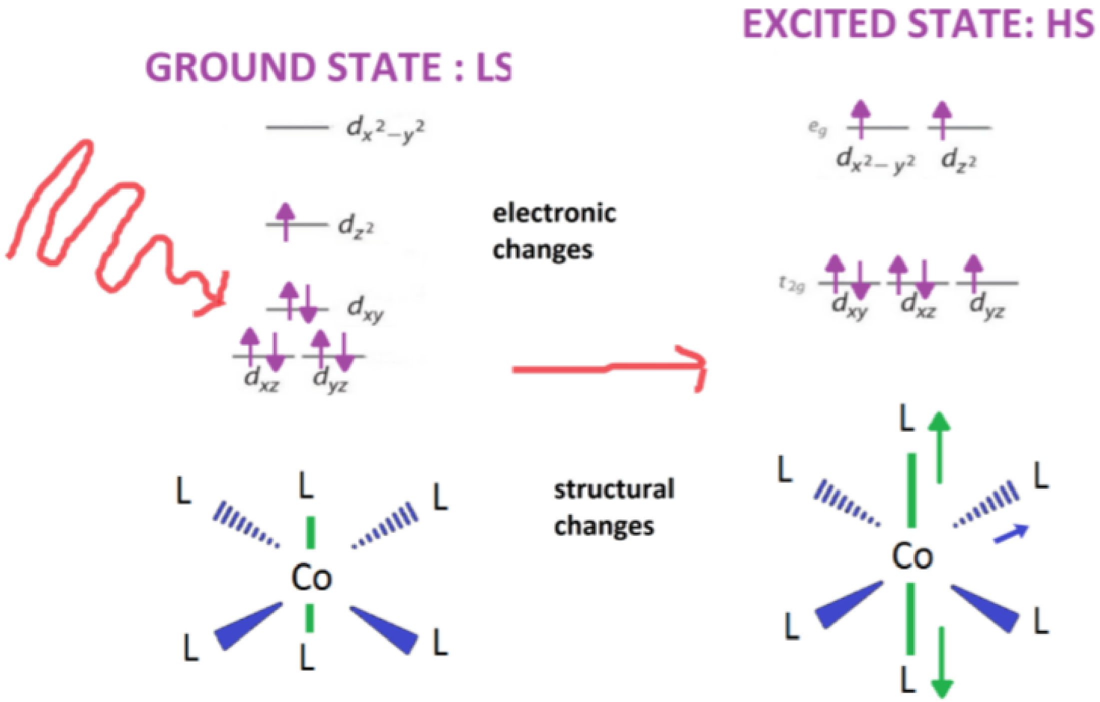
Zoom in on structural dynamics of Co(terpy) at LCLS



Elisa Biasin







$\Delta d_{Co\text{-}Naxial} \sim 0.16$ Å

$\Delta d_{Co\text{-}Nequatorial} \sim 0.08$ Å

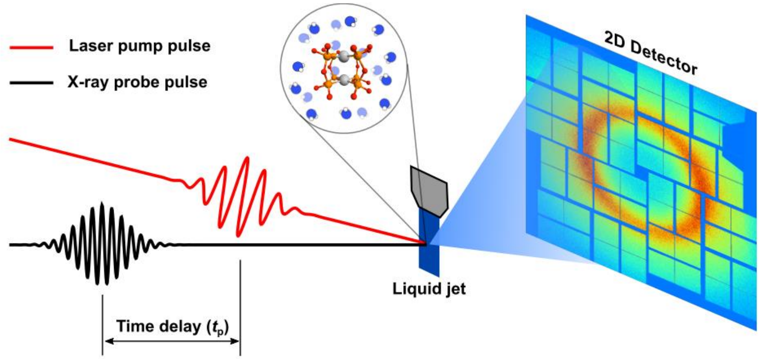
	LS	HS
$d_{Co\text{-}Naxial}$ (Å)	1.902	2.058
$d_{Co\text{-}Nequatorial}$ (Å)	2.08	2.16
η	0.91	0.95

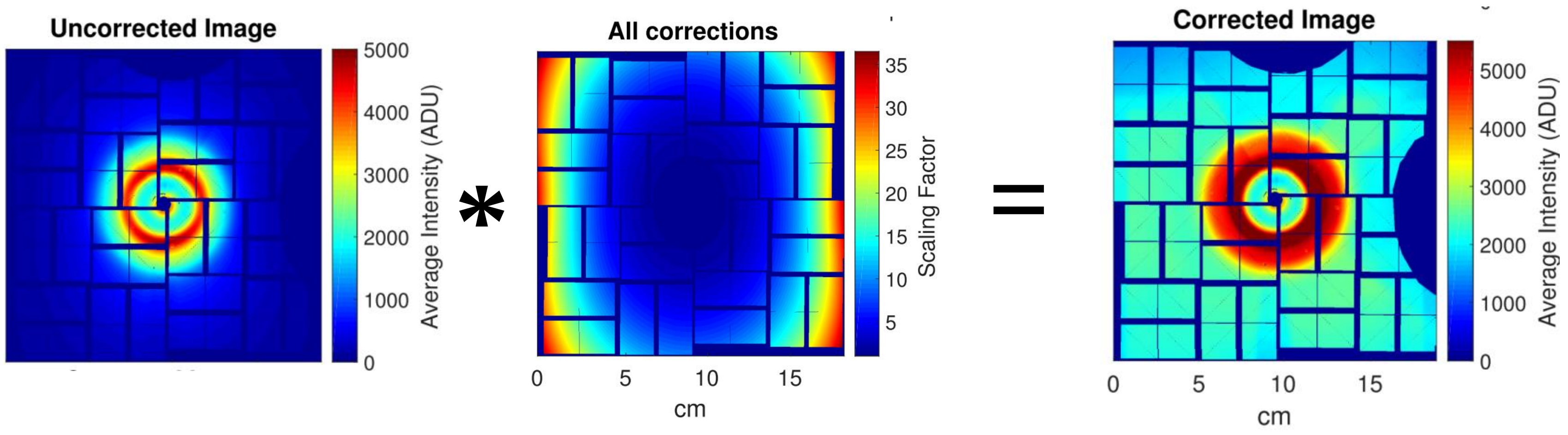
DFT model of LS and HS structure as basis for solute structure model

Need better data to discern differences

Slide: E. Biasin

Disentangling detector data

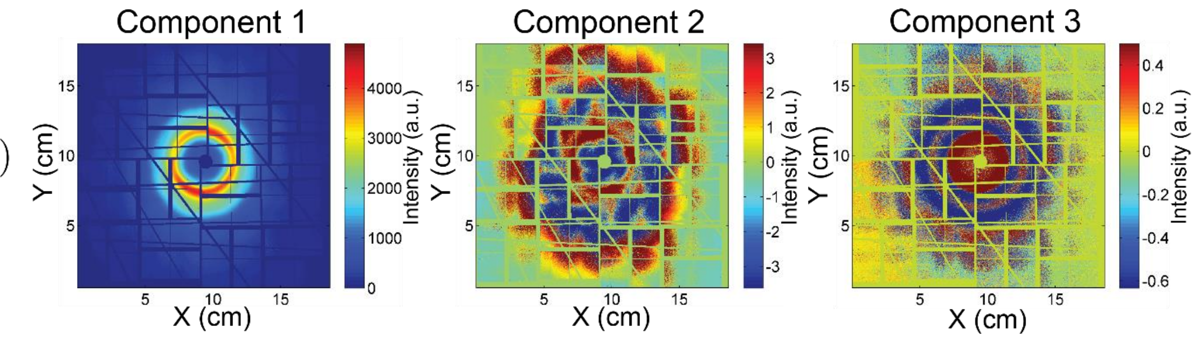




As-acquired detector data need Corrections:

- Geometry & polarization
- SVD-based linearization of detector response as function of $E_{X\text{-}ray}$ and $I_{X\text{-}ray}$

-> 150 differences images averaged per 10 fs time bin



Intensity depd. Intensity depd. Energy dependent

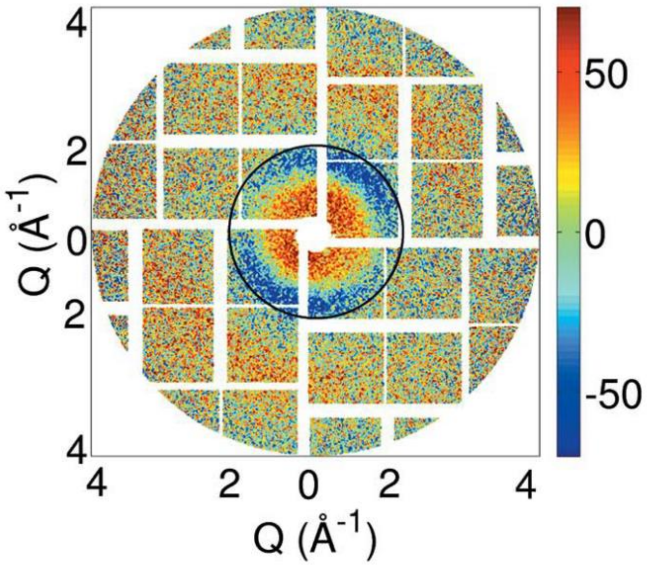

Faraday Discussions

Cite this: *Faraday Discuss.*, 2015, **177**, 443

PAPER

Disentangling detector data in XFEL studie of temporally resolved solution state chemistry

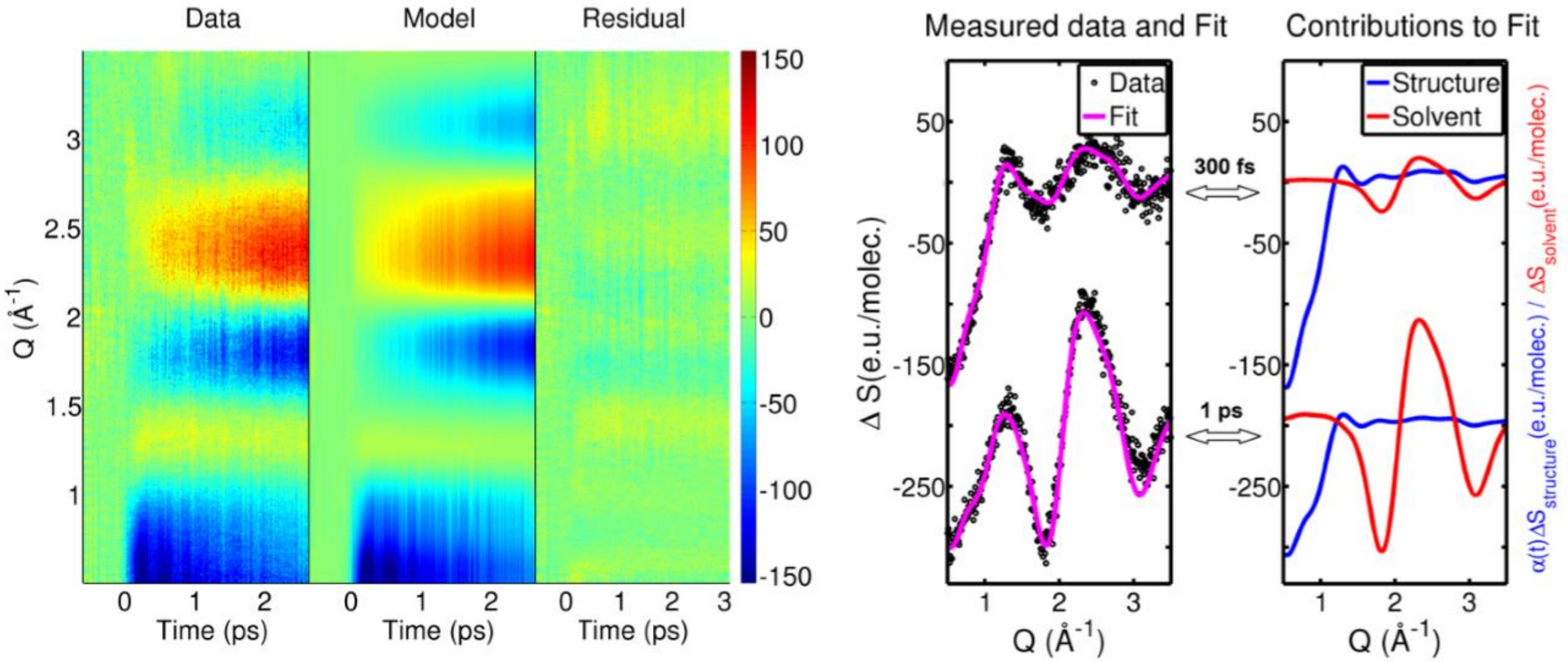
Tim Brandt van Driel,[a] Kasper Skov Kjær,[ab] Elisa Biasin,[a] Kristoffer Haldrup,[a] Henrik Till Lemke[c] and Martin Meedom Nielsen*[a]



Results

Solvent cage effects calculated by MD and included in the structural model of the solute

$$\Delta S_{model}(Q,t) = \alpha(t)\Delta S_{Structure}(Q, d_{Co-N}(t)) + \Delta T(t)\frac{\partial S(Q)}{\partial T}\bigg|_{\rho}$$

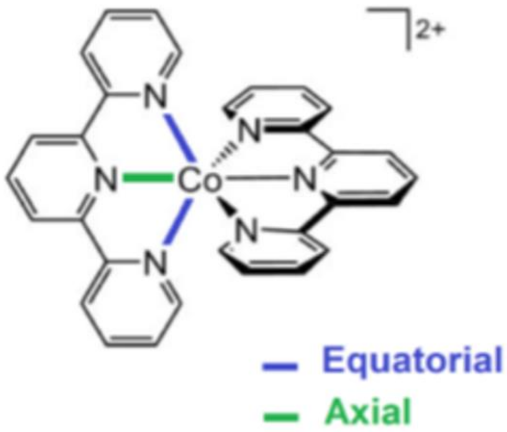


Slide: E. Biasin

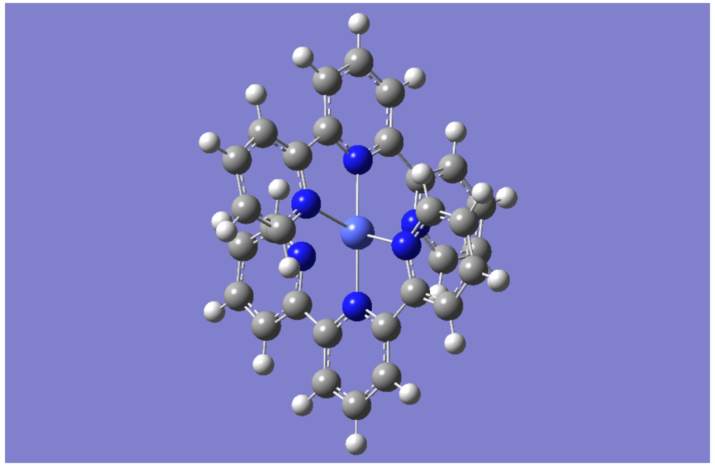
$[Co(terpy)_2]^{+2}$:: structural dynamics

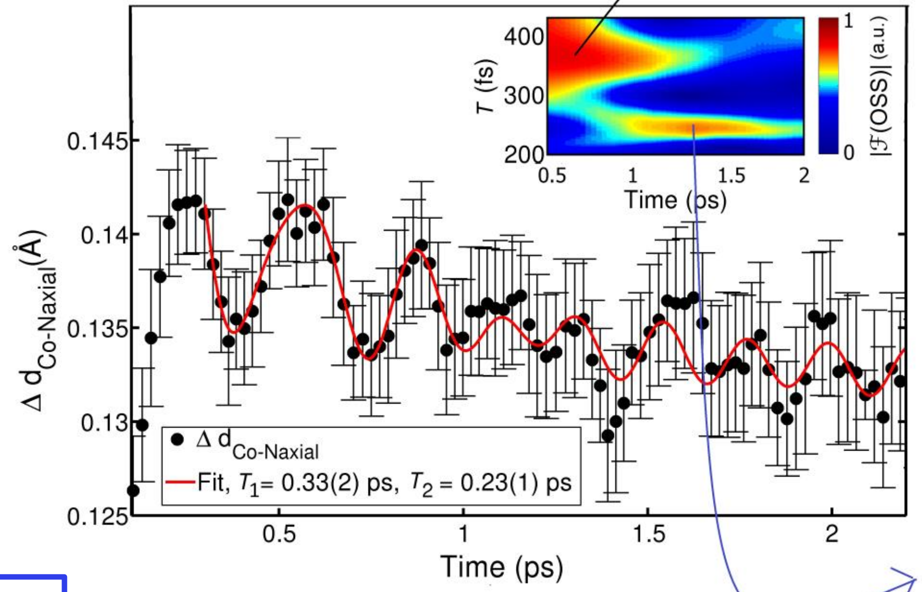
Comparison with DFT-calculated vibrational modes of the HS state

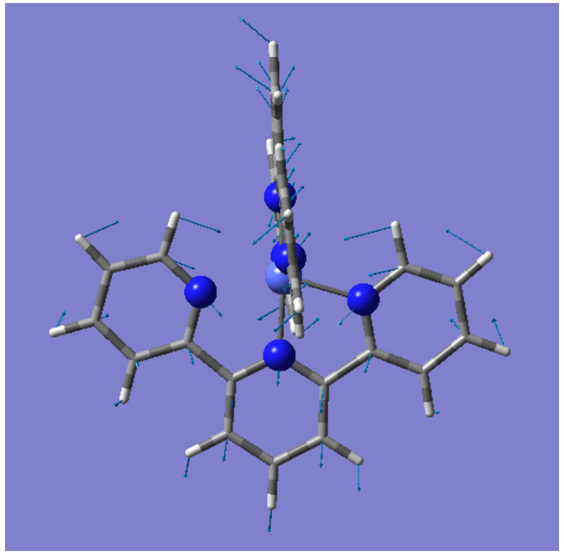
$$\Delta S_{model}(Q,t) = \alpha(t)\Delta S_{Structure}(Q, d_{Co-N}(t)) + \Delta T(t)\frac{\partial S(Q)}{\partial T}\Big|_{\rho}$$



breathing-like mode
92 cm^{-1} (360 fs)





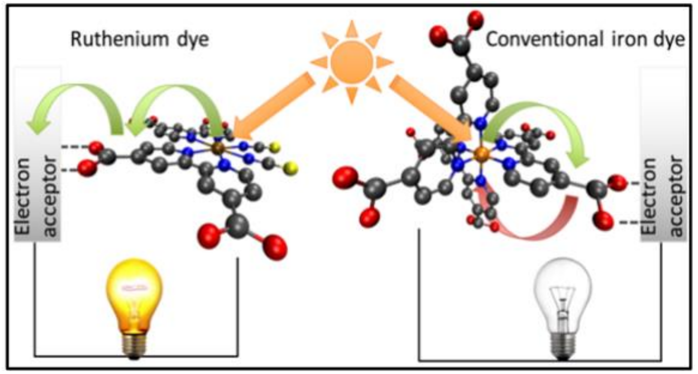


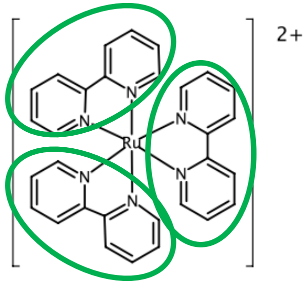
pincer-like mode
146 cm^{-1} (230 fs)

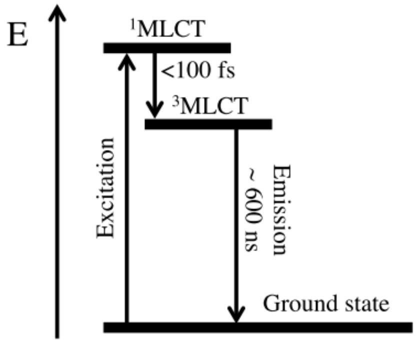
E. Biasin et al Phys Rev Lett. 2016

Possibly the first 'molecular movie' of a molecule in an environment

Ruthenium vs. Iron photosensitizers



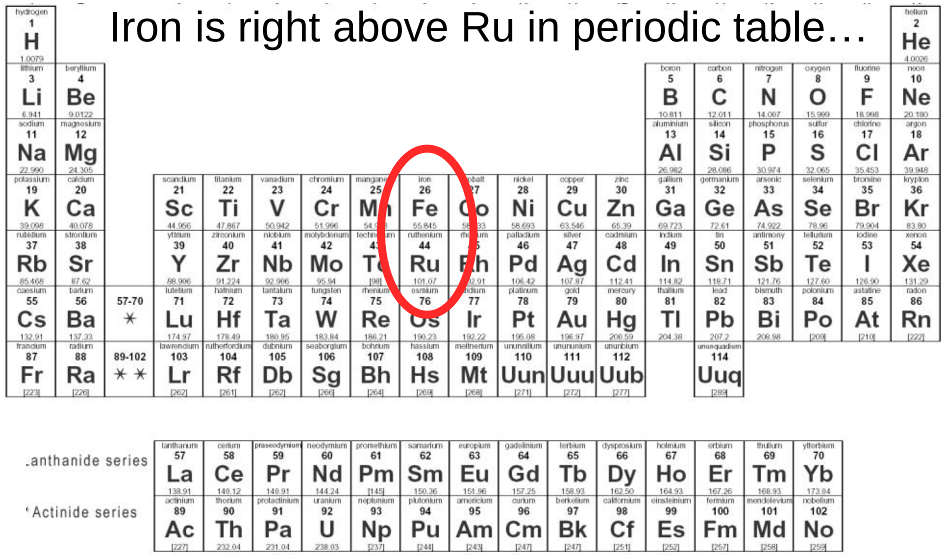




Long-lived Metal-to-Ligand Charge Transfer (MLCT) state allows efficient extration of electrons in Ru-based compounds for solar-energy harvesting (Graetzel et al.)

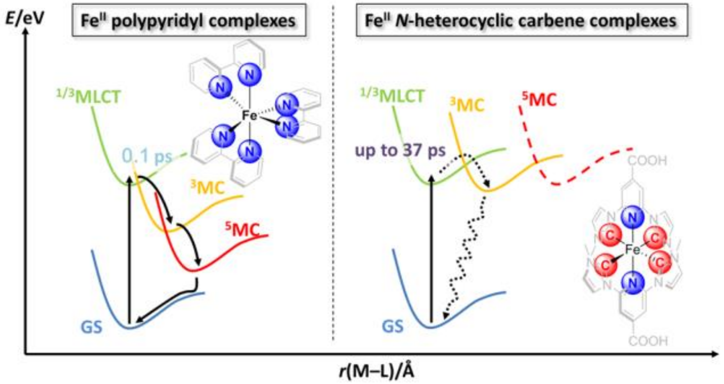
-Unfortunately, Ru is scarce and expensive...

Iron is right above Ru in periodic table…

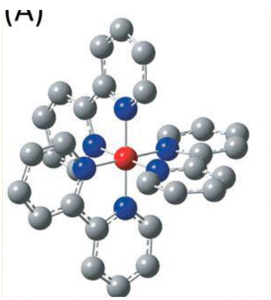


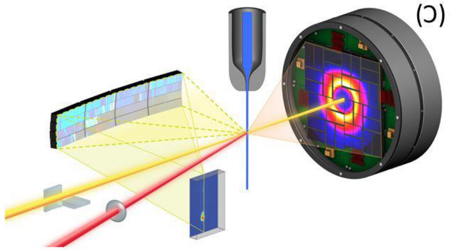
… but Fe has a much shorter excited state life time than Ru – too short for efficient charge extraction

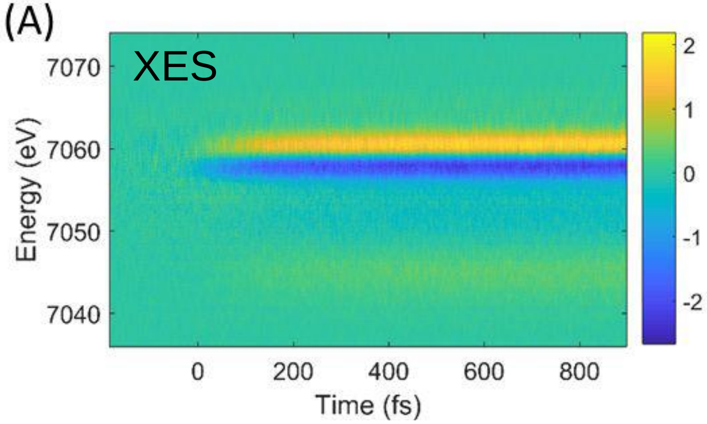
Can we identify and modify the properties of iron-based compounds to enable Fe-based photo-sensitizers

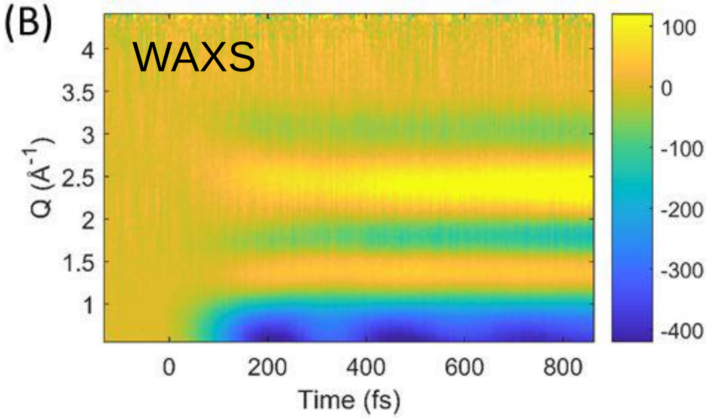


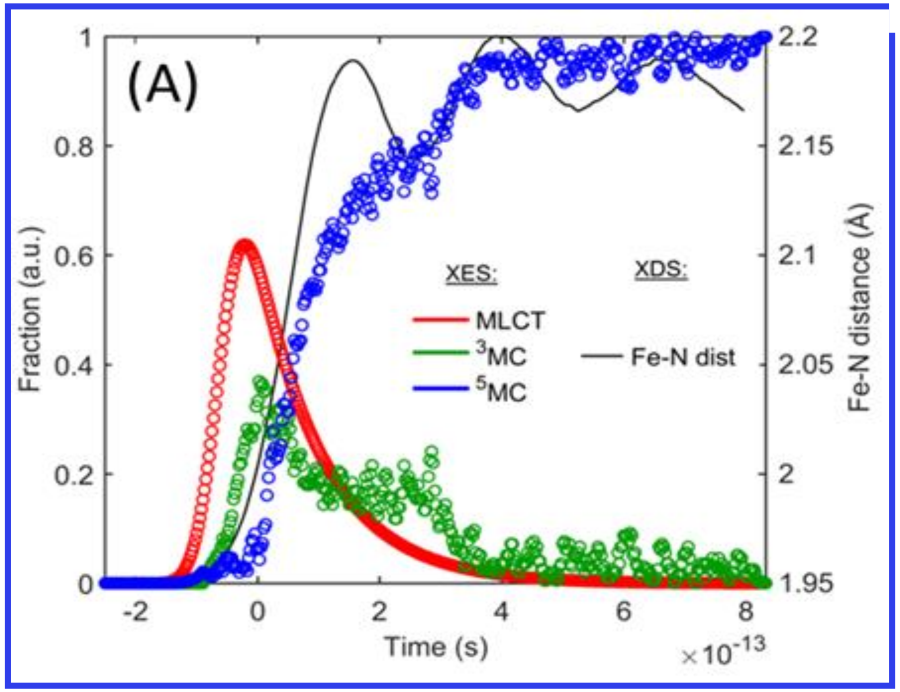
Combined XES and scattering on $Fe(bpy)_3$

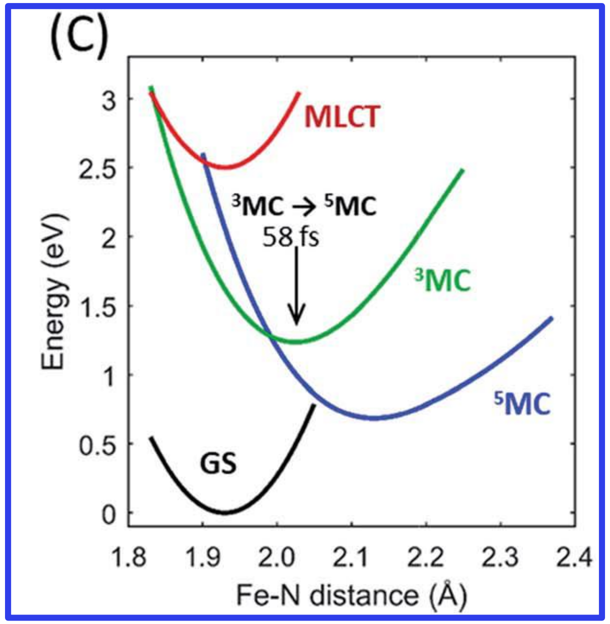


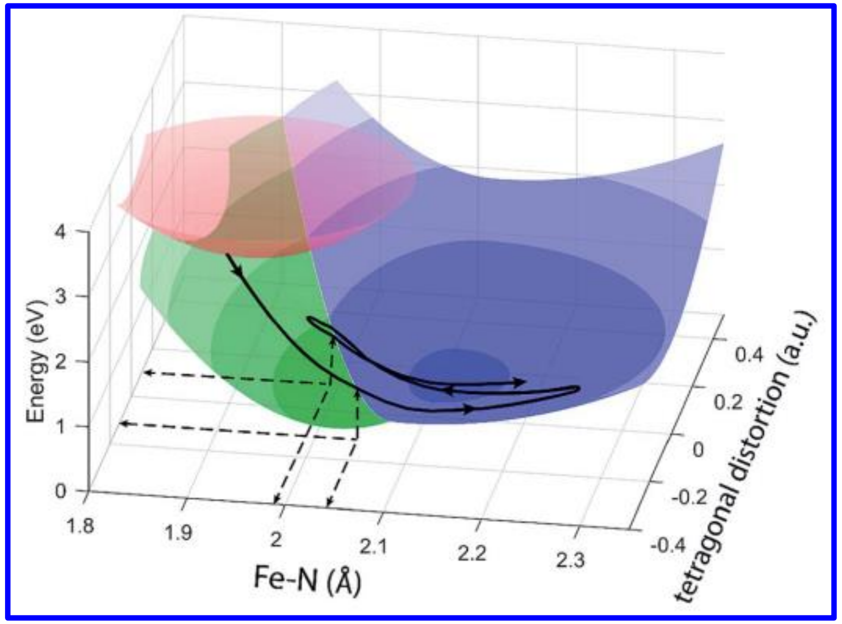






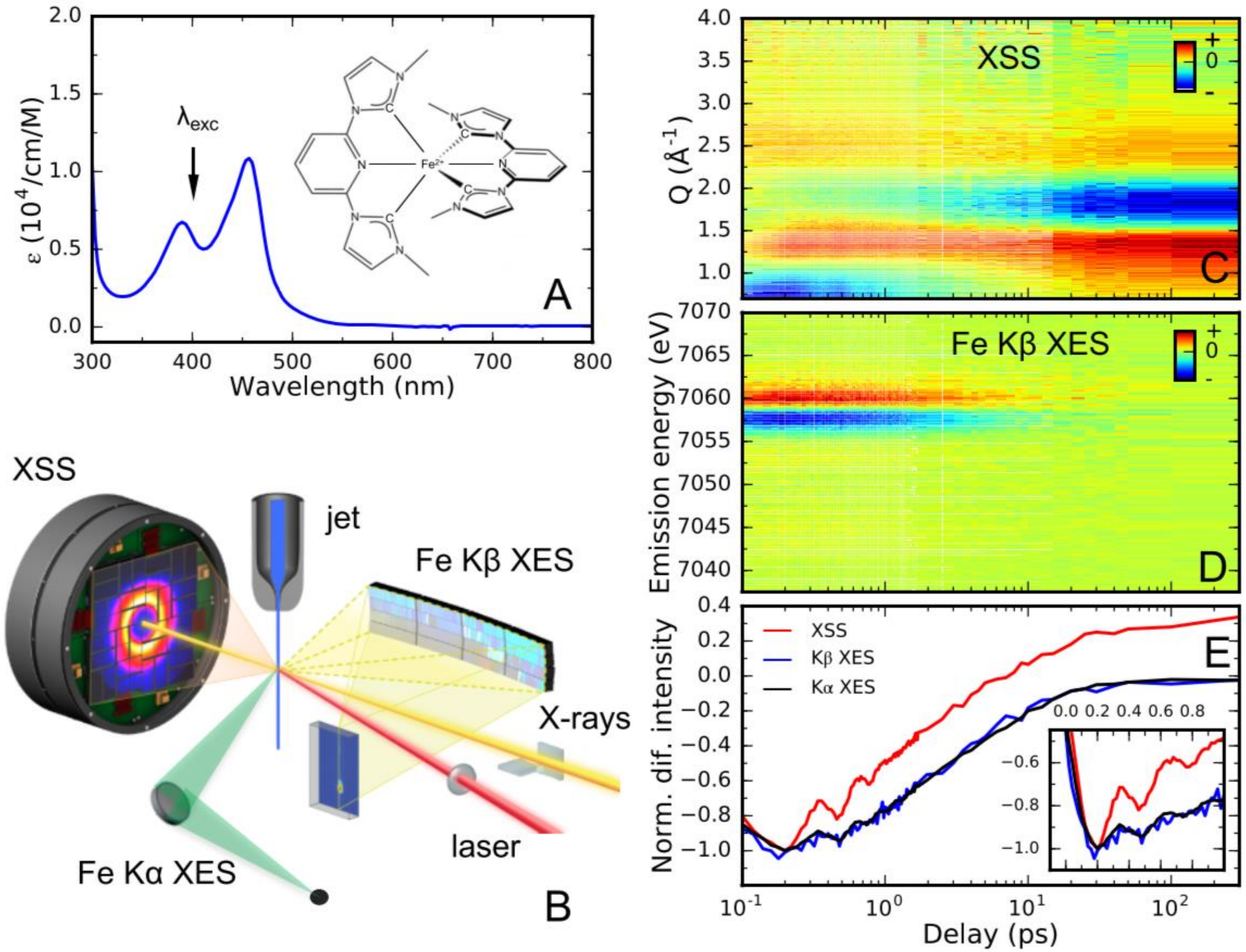


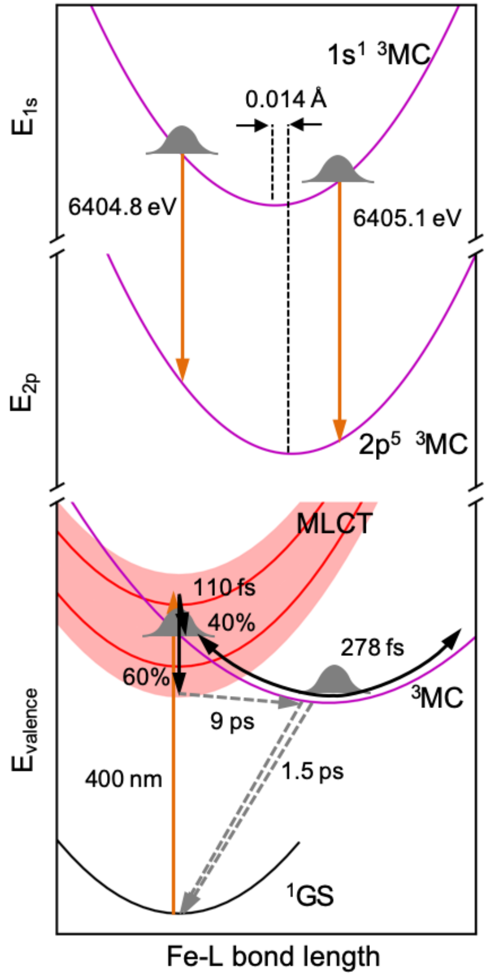


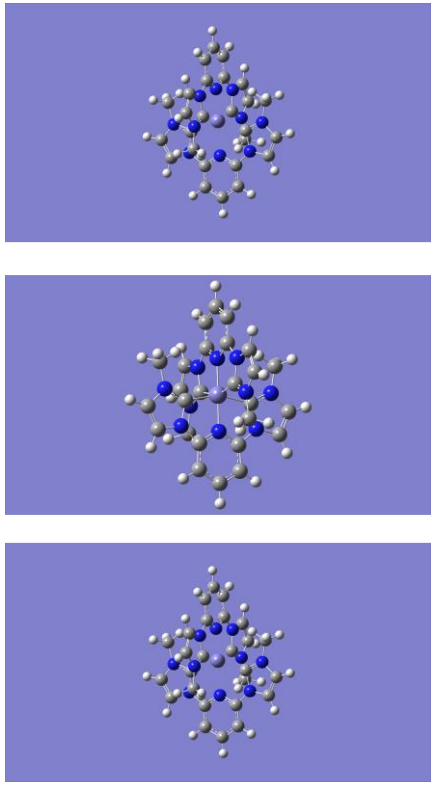


Kjær et al, Chem Sci 2019

Combined XES and scattering on FeCAB







XES structural sensitivity due to core-level vibronic coupling between 1s and 2p core-ionized states

FeCAB systems made at Lund Univ.

Kunnus et al, Nature Commun, 2020

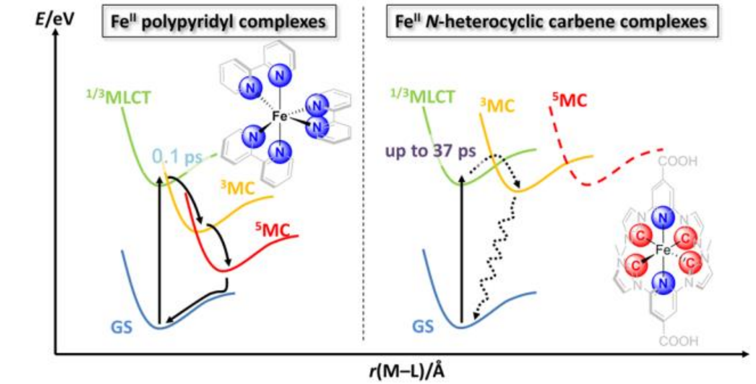
Summary

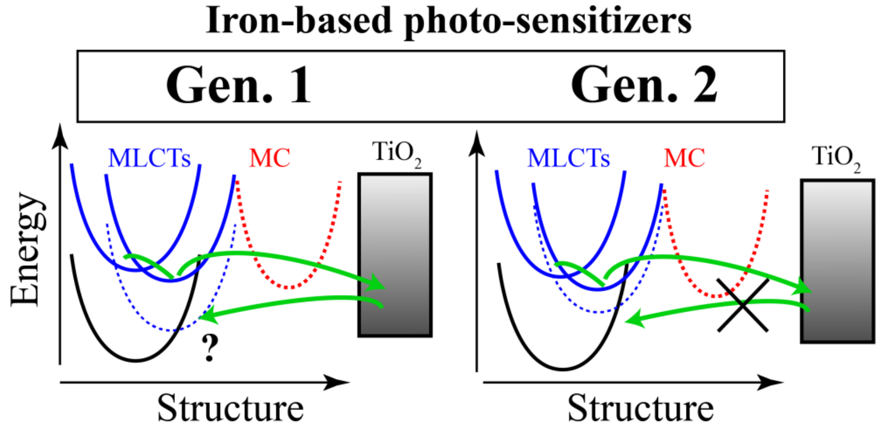
Novel iron-based compounds for use as photo-sensitizers appear promising, and share some of the properties of ”conventional” ruthenium-based sensitizers

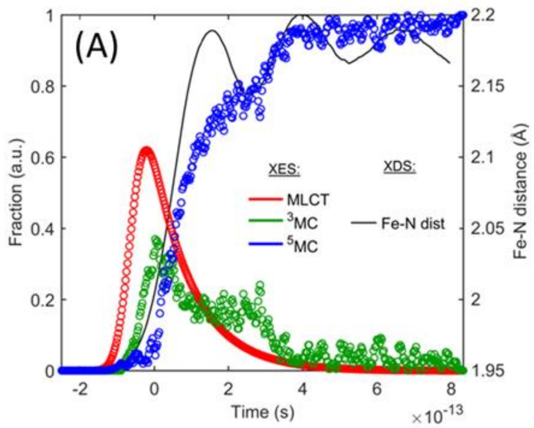
Quantitative information on the excited-state potential landscape(s) is necessary for rational design of even-better compounds

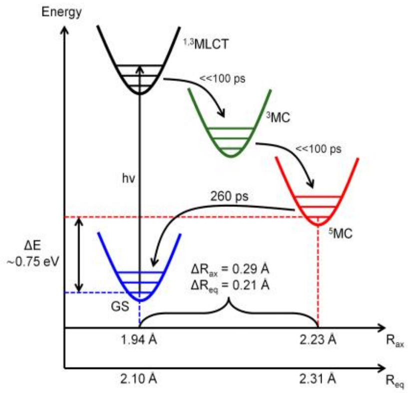
Combined studies, where the complementarity of XES and XDS is utilized, yields access to:

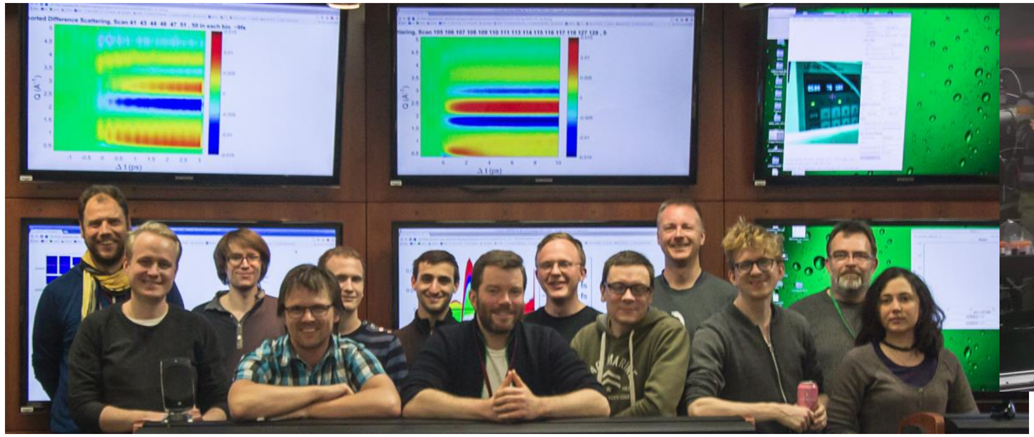
- Time-dependent electronic configuration
- Time-dependent structure
- Energy release to solvent
- Details of the solvent-solute interactions



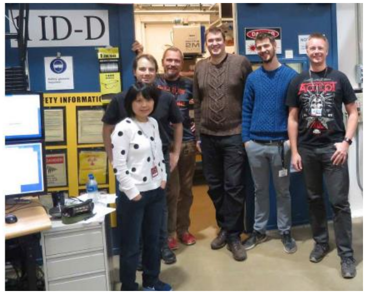








Thank you for your attention



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SLAC/Gaffney

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