Time-Resolved X-Ray Spectroscopies and Scattering with One Trillion Photons

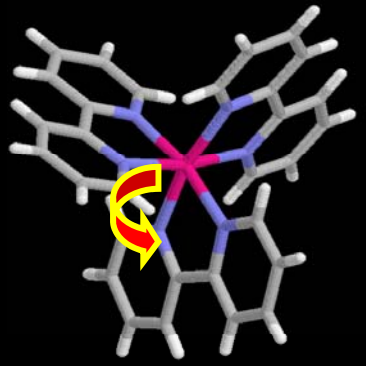
Christian Bressler

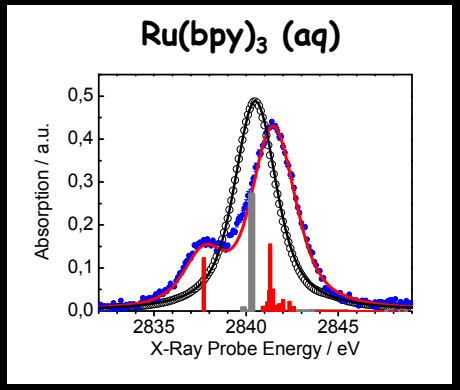
European XFEL

XDL Workshop "tickle and probe", Cornell University, June 21, 2011

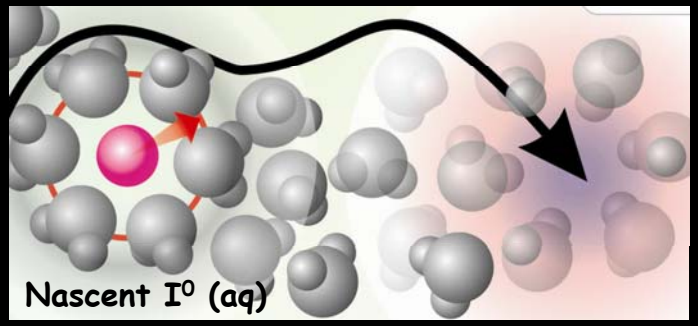
Dynamic Studies in Photochemistry

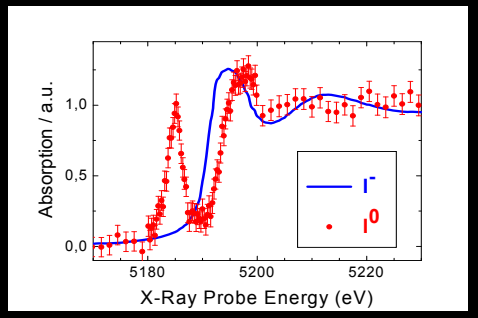
1. Intramolecular Charge Transfer



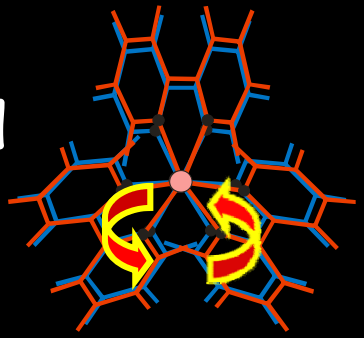


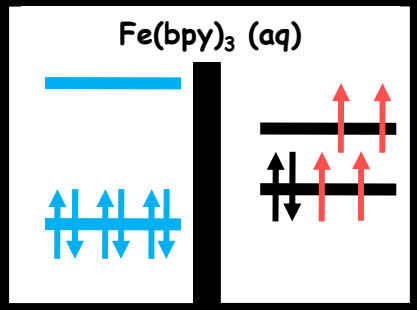
2. Towards Solvation Dynamics

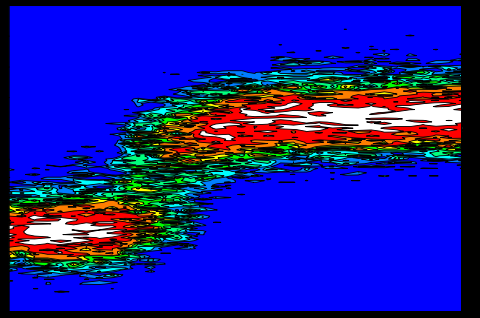




3. Light-Induced Spin Crossover

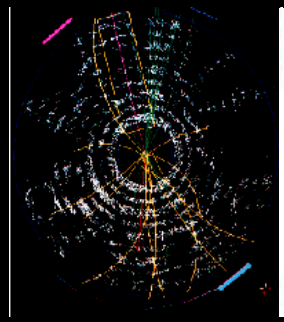


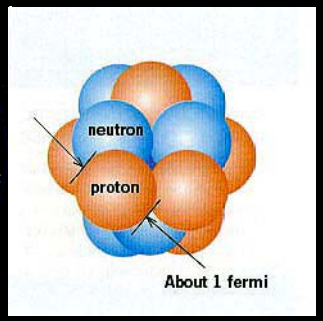




What are the fundamental timescales?

Chemistry and Biochemistry

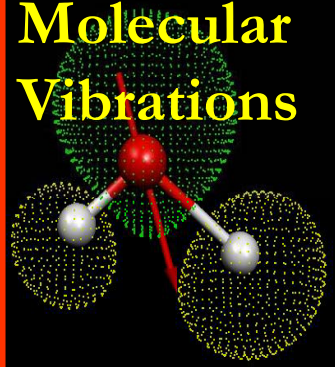




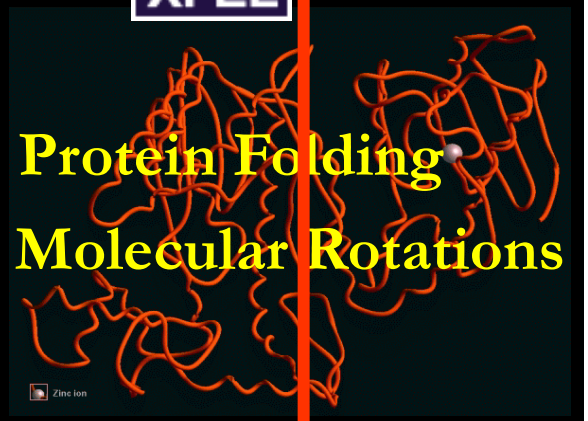
Strings, Cosmology

Particle Collisions

Photosynthesis
Vision
Molecular Vibrations



European XFEL

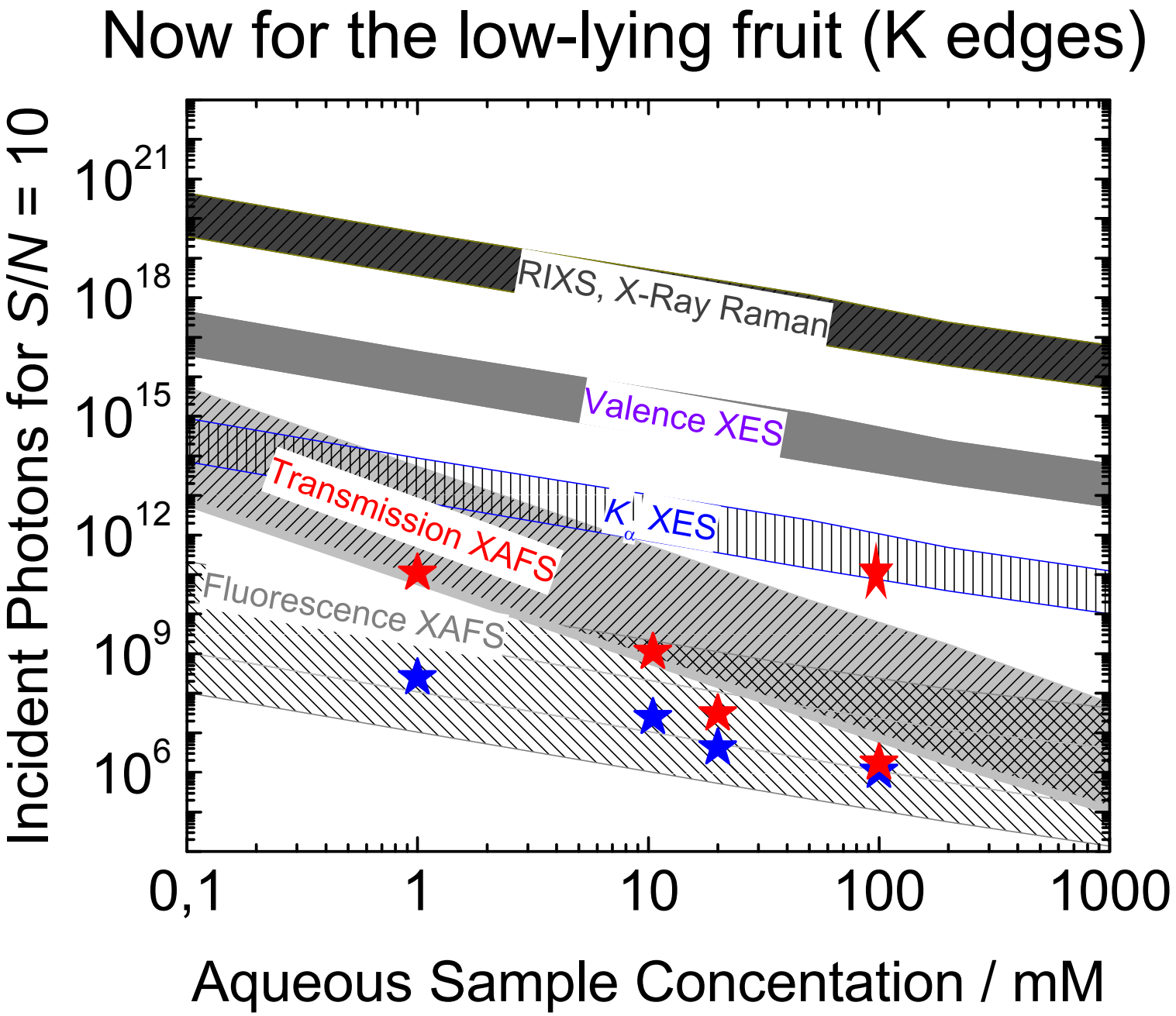


Protein Folding
Molecular Rotations

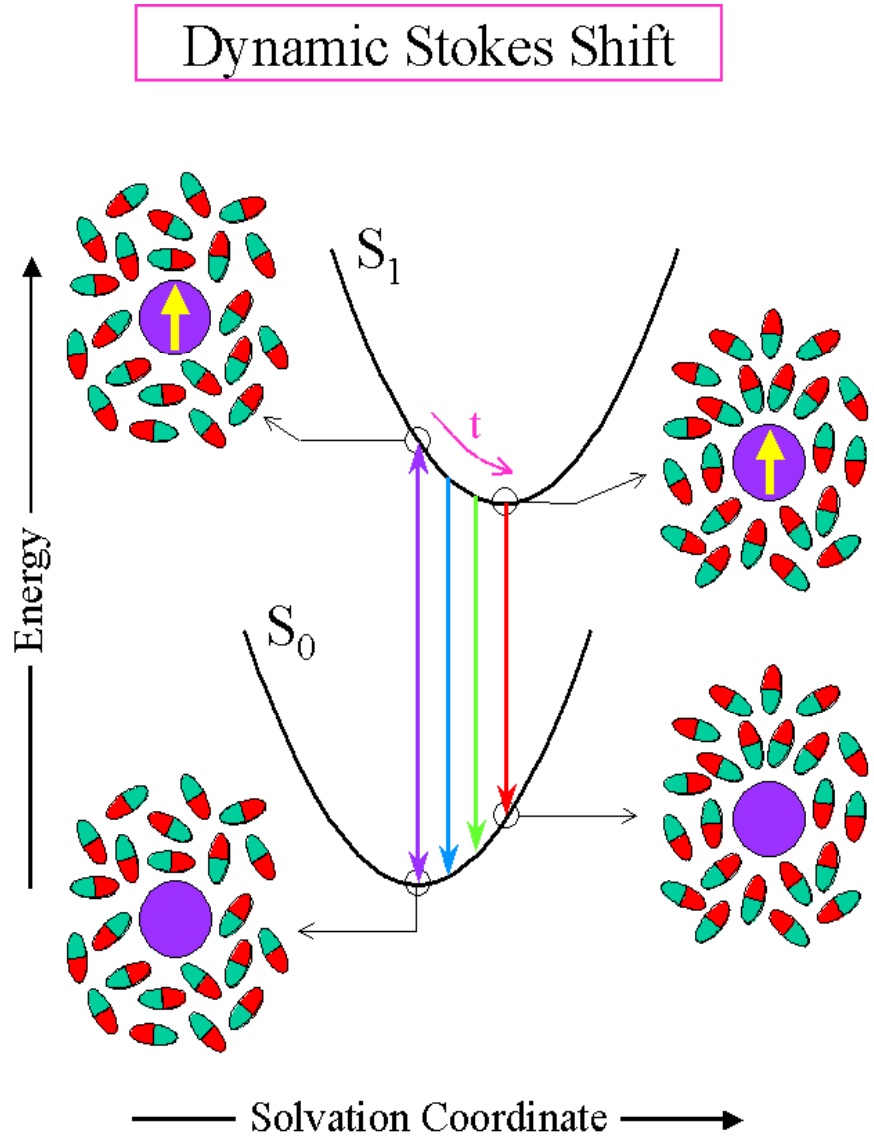
Electron dynamics

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

Time /seconds


Now for the low-lying fruit (K edges)
Incident Photons for S/N = 10
10^21
10^18
10^15
10^12
10^9
10^6
RIXS, X-Ray Raman
Valence XES
Transmission XAFS
Kα XES
Fluorescence XAFS
0,1
1
10
100
1000
Aqueous Sample Concentation / mM

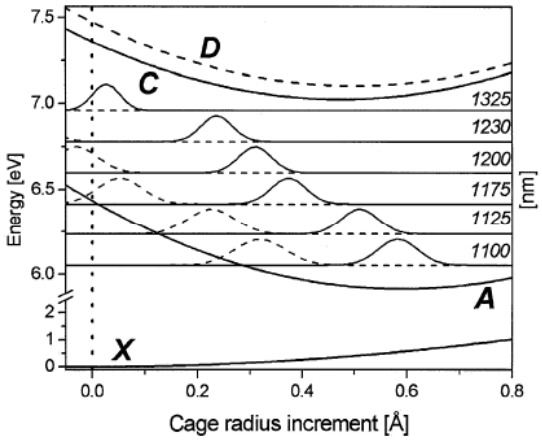
Towards Solvation Dynamics

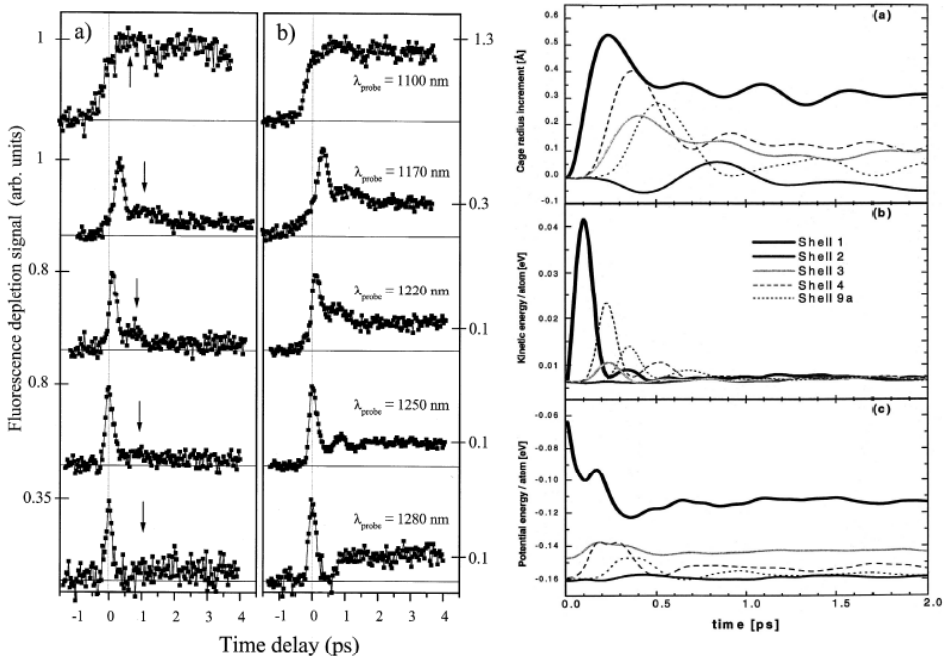


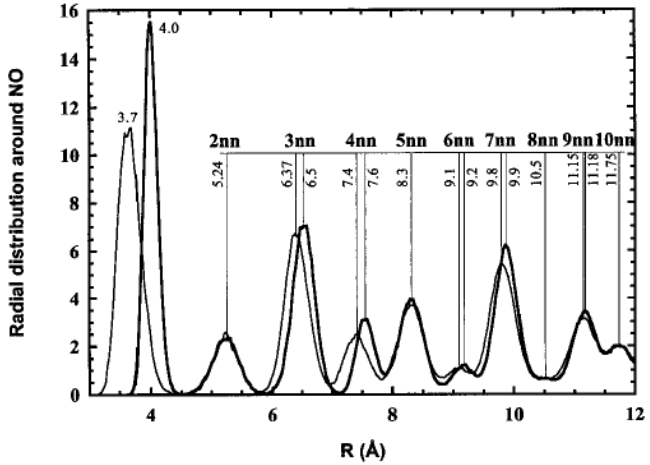
-Distinguish IVR from guest-host interactions

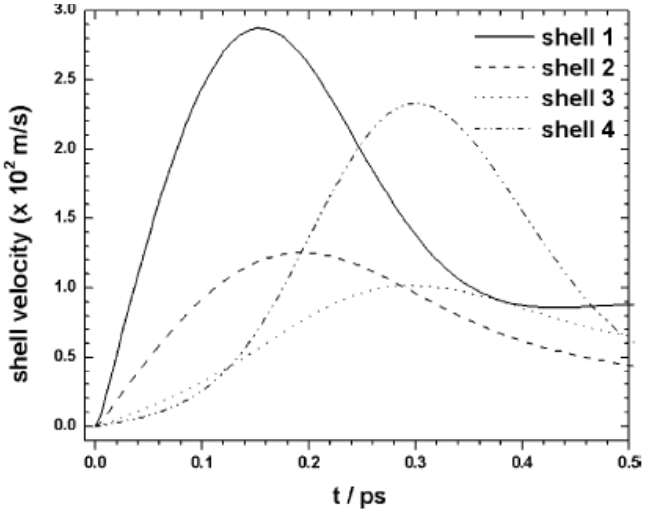
-Example: NO/Rg matrix

Rydberg NO in rare gas matrices: bubble formation









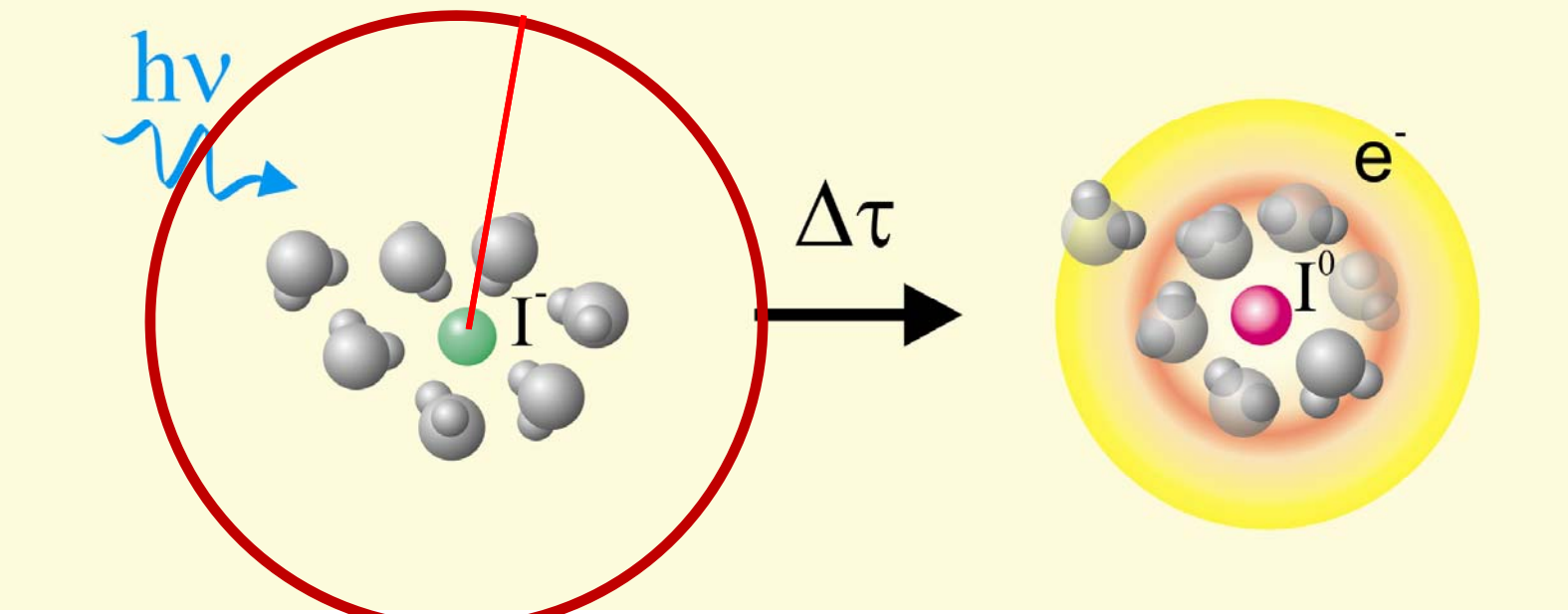
F. Vigliotti et al. / Chemical Physics Letters 362 (2002) 31–38

J. Chem. Phys., Vol. 114, No. 12, 22 March 2001

C. Jeannin et al. / Chemical Physics Letters 316 (2000) 51–59

Ultrafast Processes in the Condensed Phase (of any kind)

Speed of Sound: >10 Å/ps

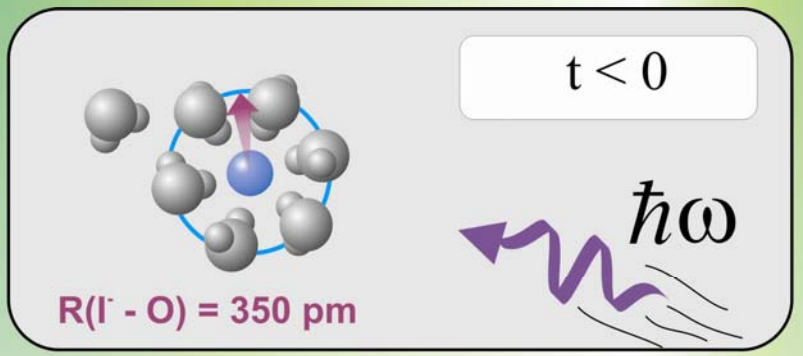


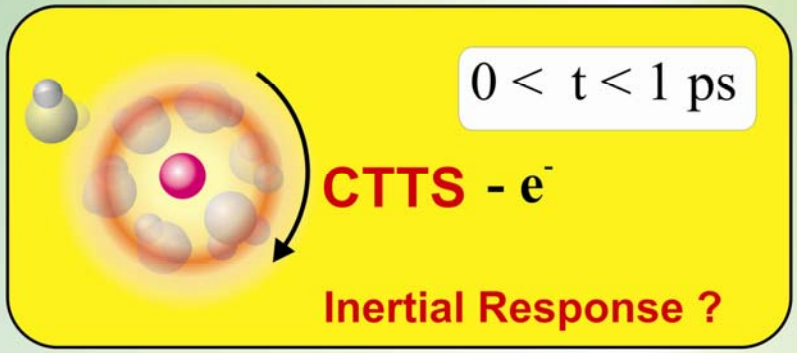
…→ca 100-1000 Solvent Molecules involved

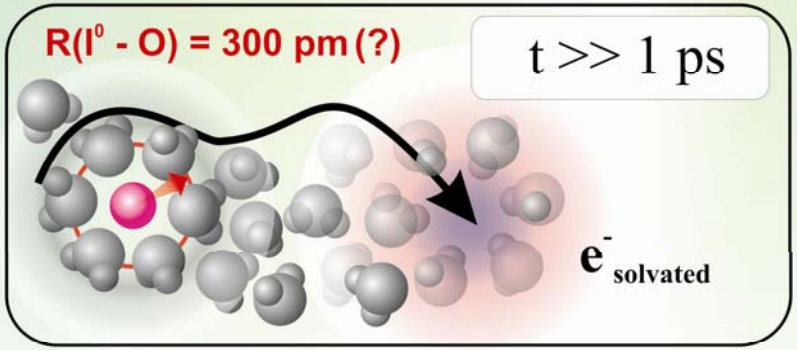
X-Ray Absorption Spectroscopy
Singles Out Reaction Center …

Electron Detachment Reactions (via XAFS)

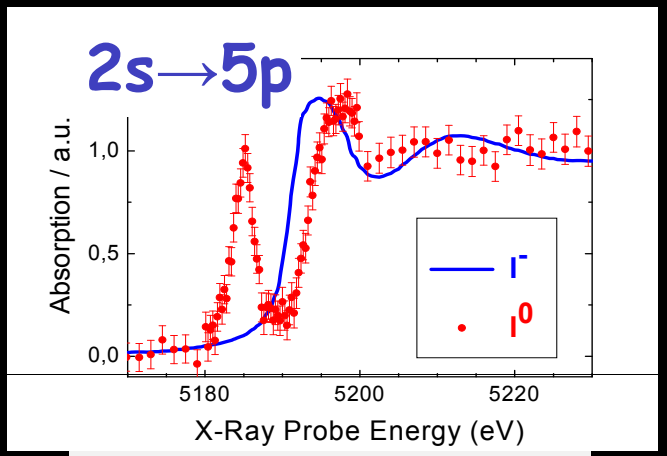
Condensed Phase Dynamics



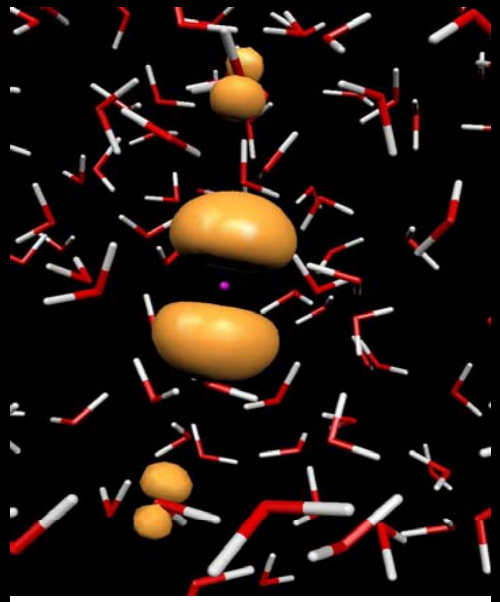




Nascent I atoms in solution

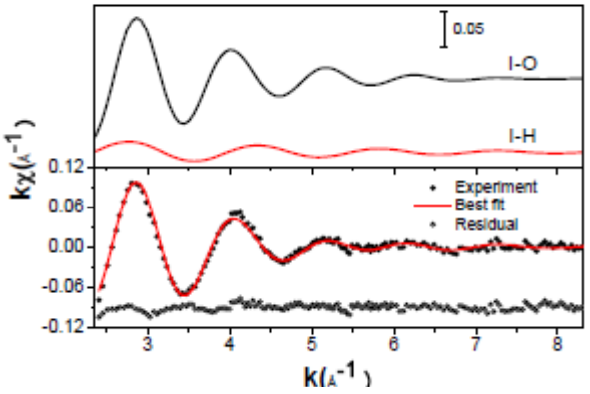


Pham *et al.*, JACS (2007)

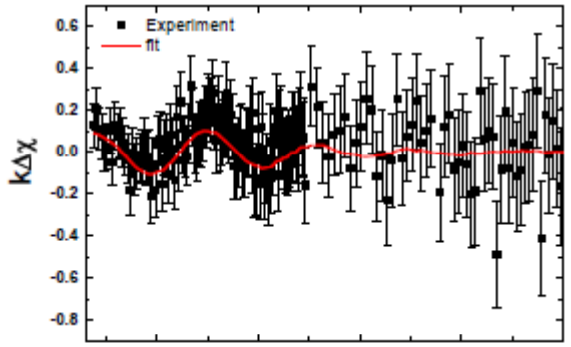


I. Tavernelli (EPFL)

EXAFS and XANES of nascent iodine radicals

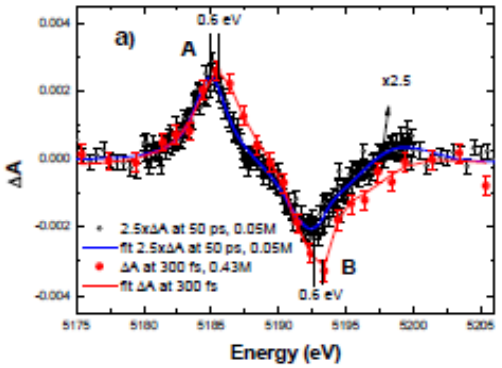


static

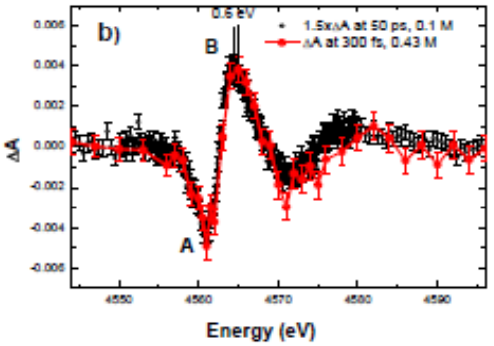


50 ps

300 fs
50 ps



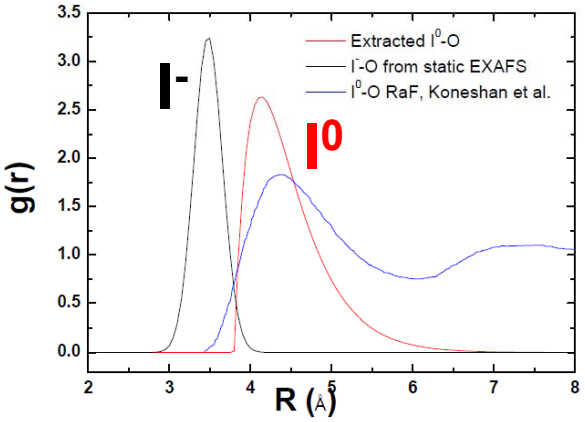
300 fs
50 ps

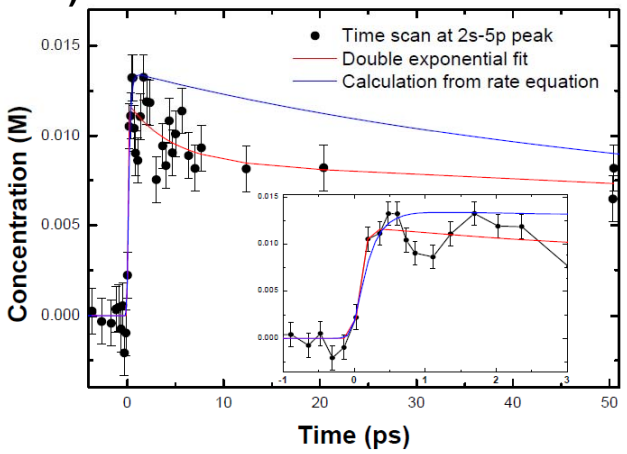


V.-T. Pham *et al.* Chem. Phys. (2010)

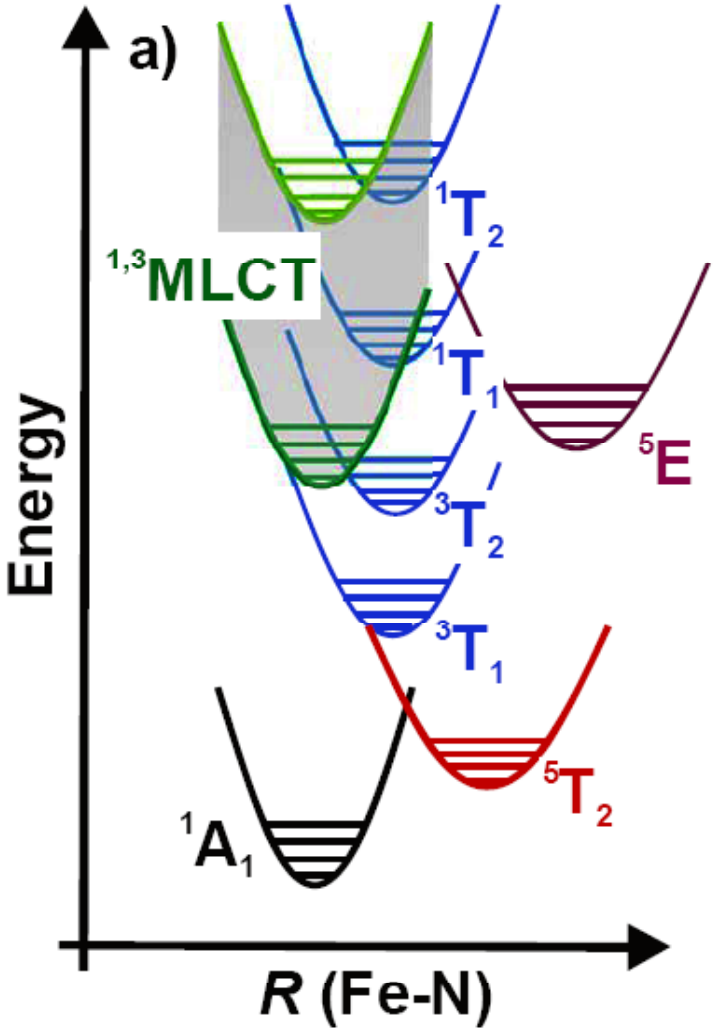
V.-T. Pham, PhD thesis (2010)

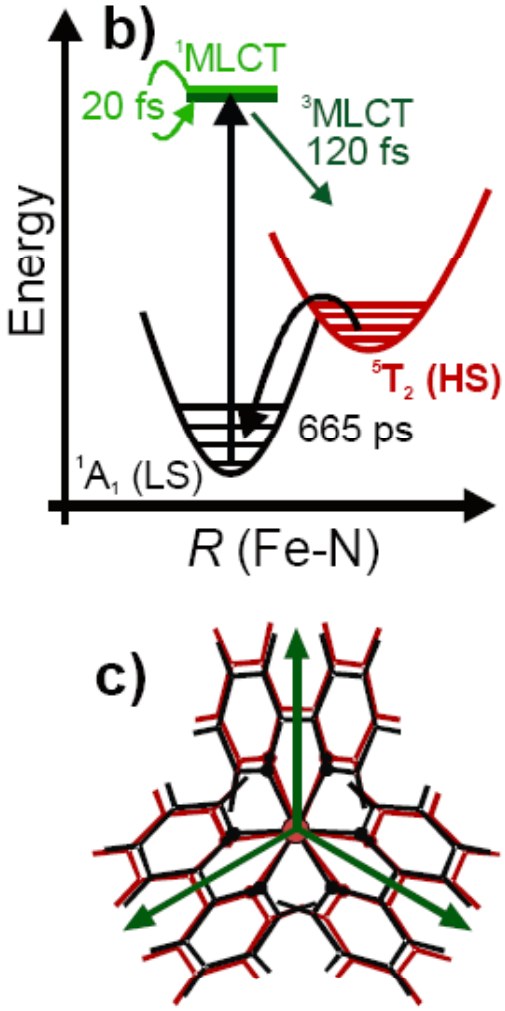
V.-T. Pham *et al.* Submitted (2011)

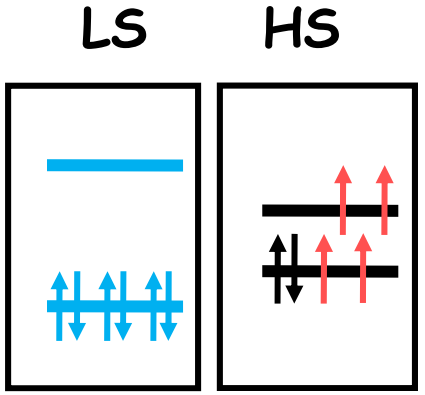


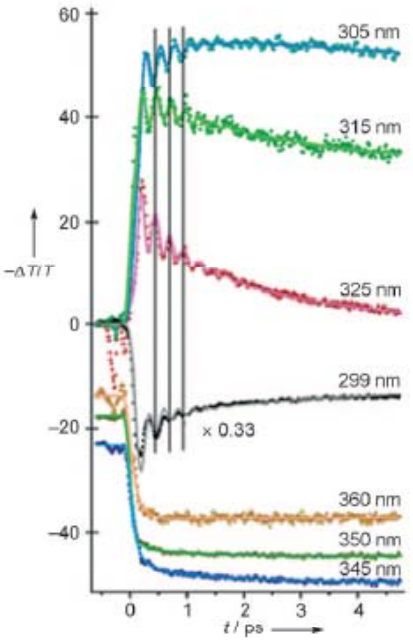


Now to something completely different….



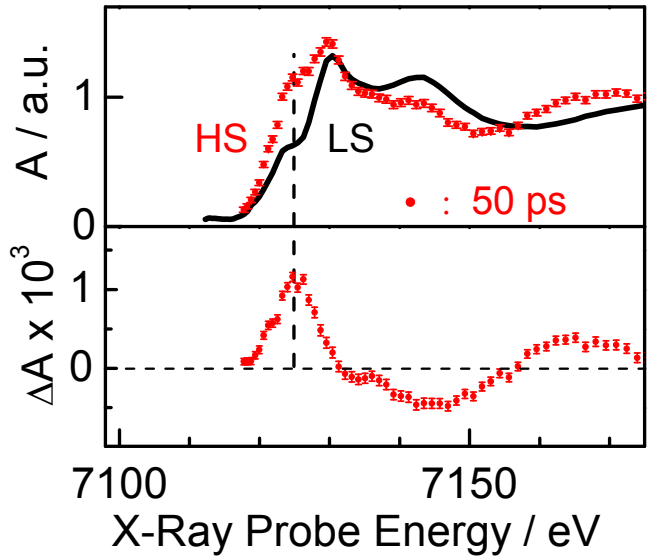


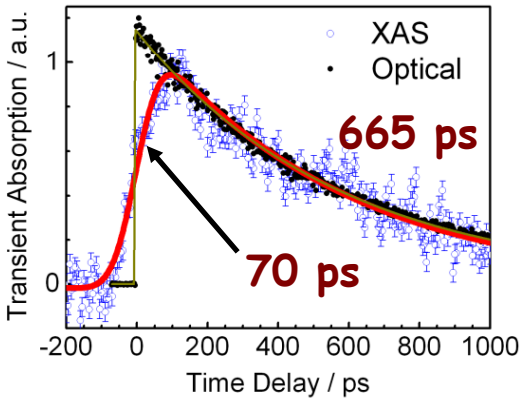




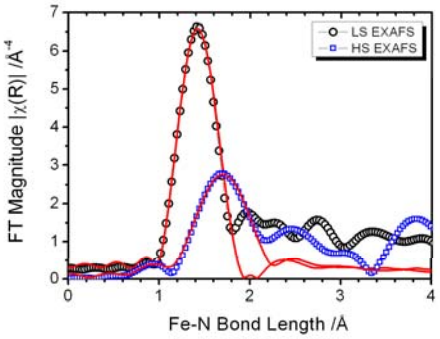
C. Consani *et al.*
Angew Chem (2009)

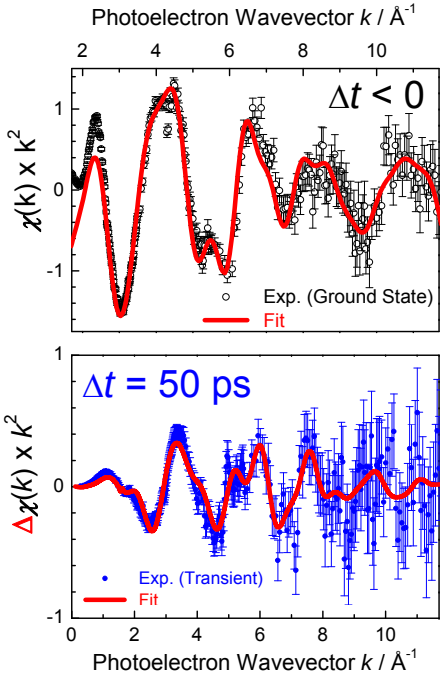
Towards Transient Structures via TR-XAFS

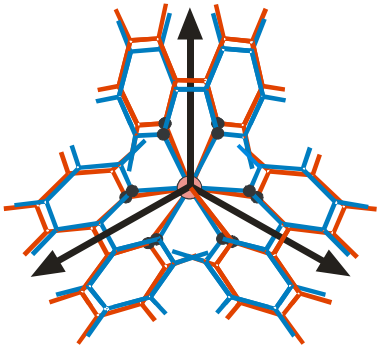




W. Gawelda *et al.*
Phys. Rev. Lett. (2007)

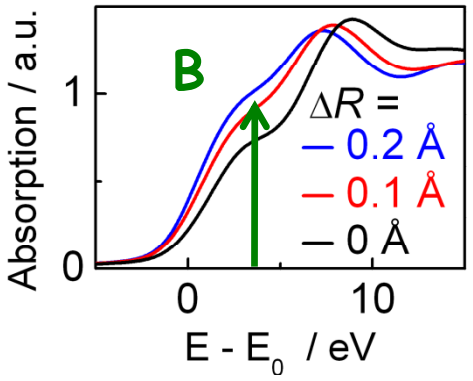




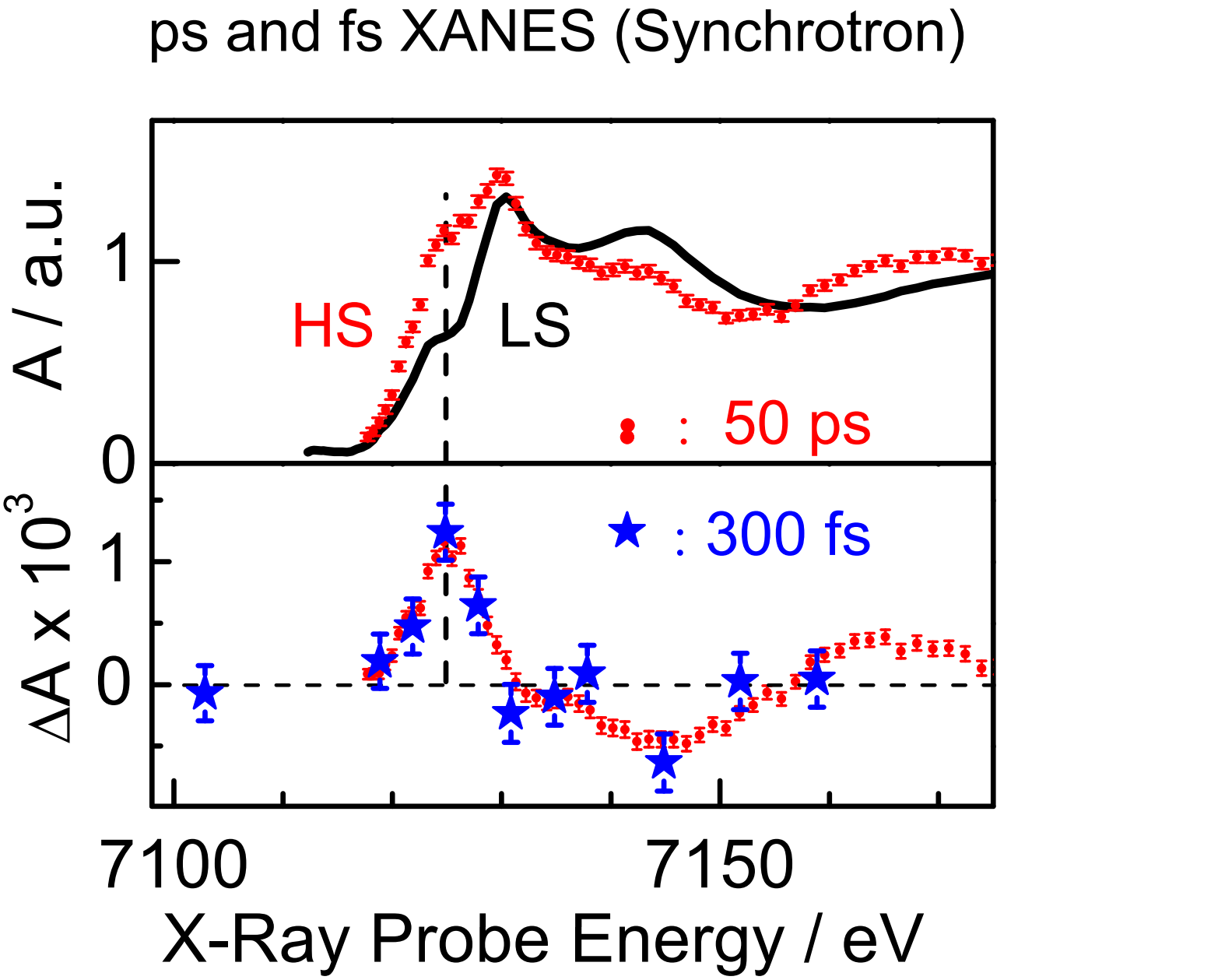


$\Delta R_{Fe\text{-}N} = 0.2 \pm 0.008$ Å

M. Benfatto (INFN Rome)

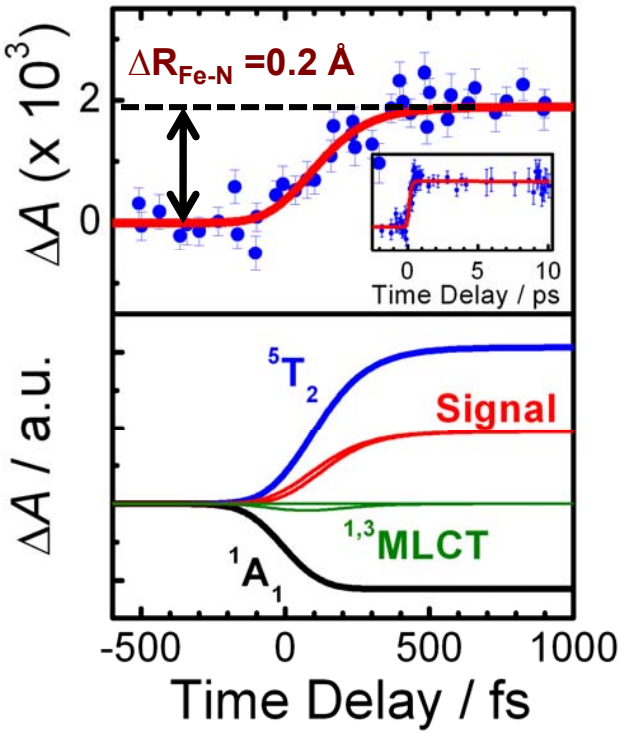


W. Gawelda *et al.*
J. Chem. Phys. (2009)



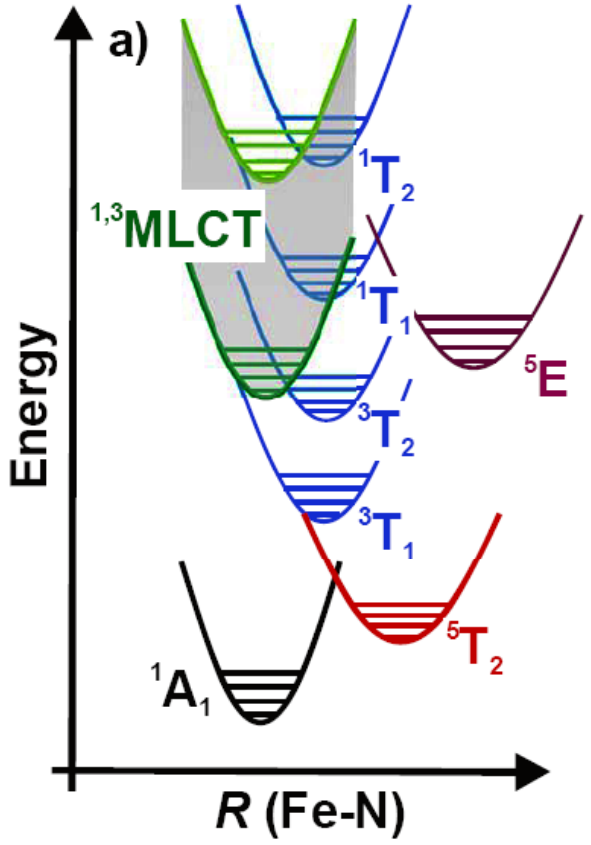
C. Bressler *et al.*, Science (2009)

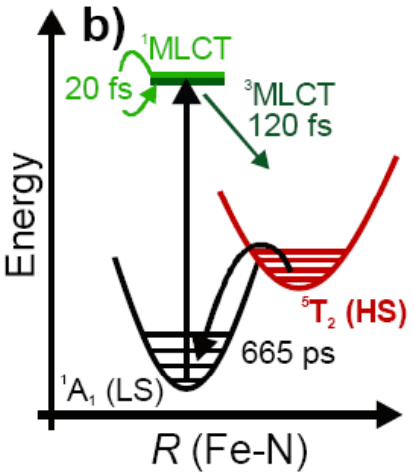
Identifying intermediate states...

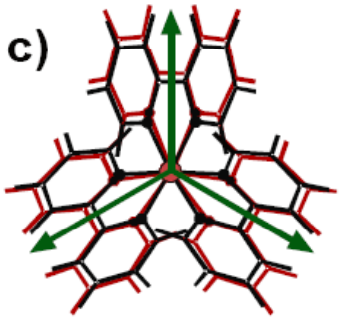


250 fs (instrument response):

140(30) fs hard x-ray pulse
115(10) fs laser pulse
<100(30) fs time zero drifts

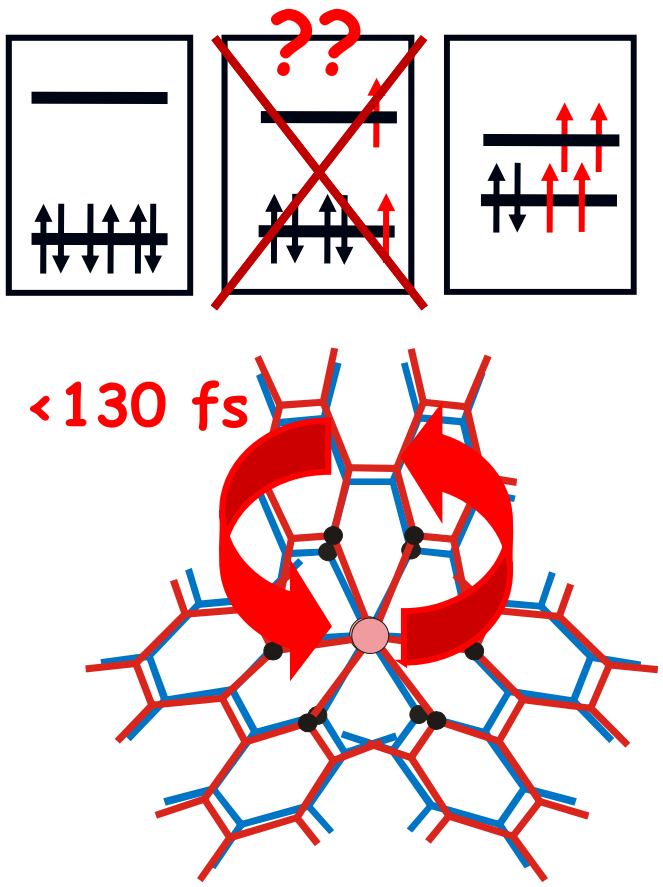


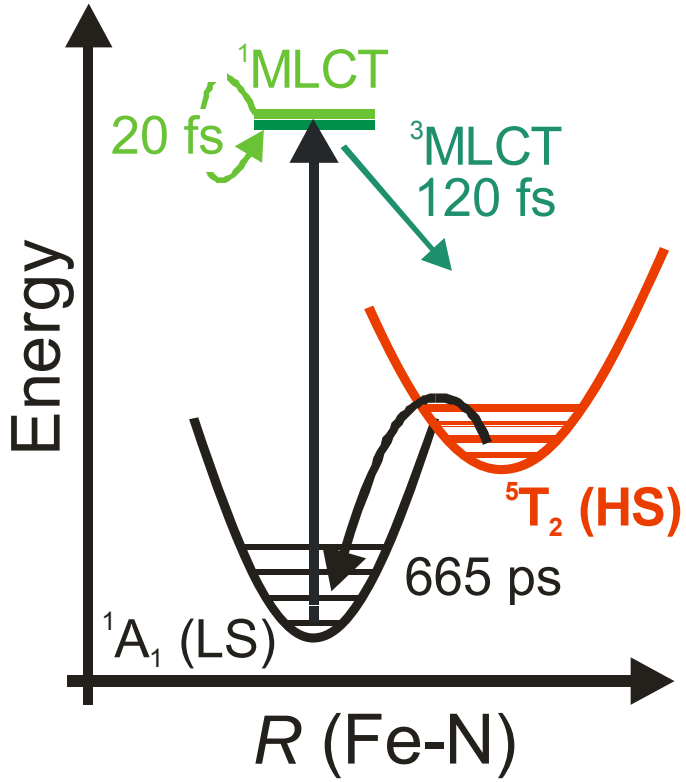




10-12 photons/pulse (2 kHz, 2 eV BW)

Combined optical and x-ray results



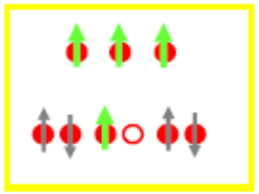


→ Need now a *Spin*-Sensitive Tool !!

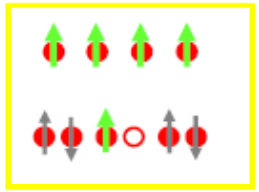
Spin sensitivity

Chemical sensitivity of Kβ Emission

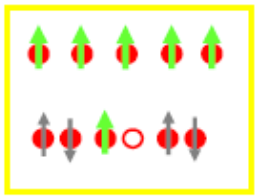
MnF_4: S=3/2

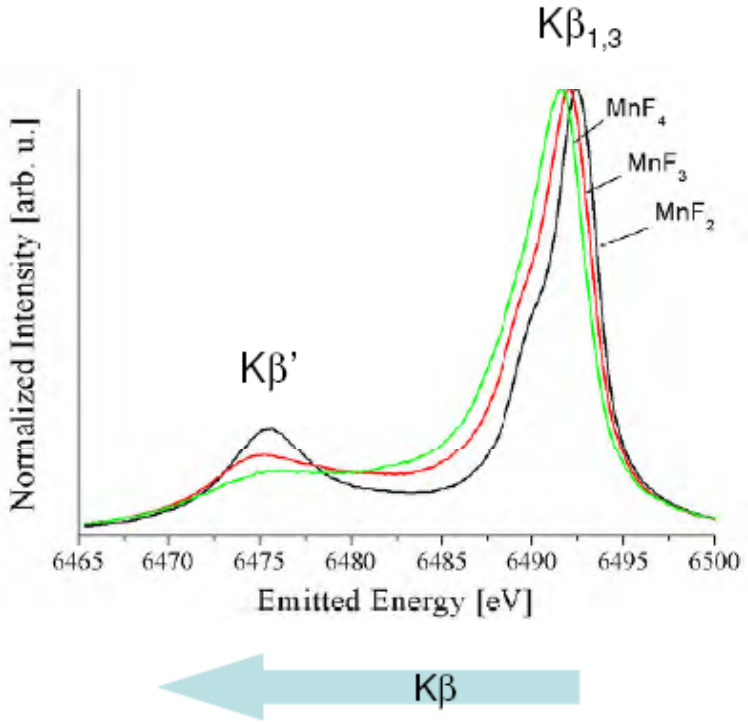


MnF_3: S=2

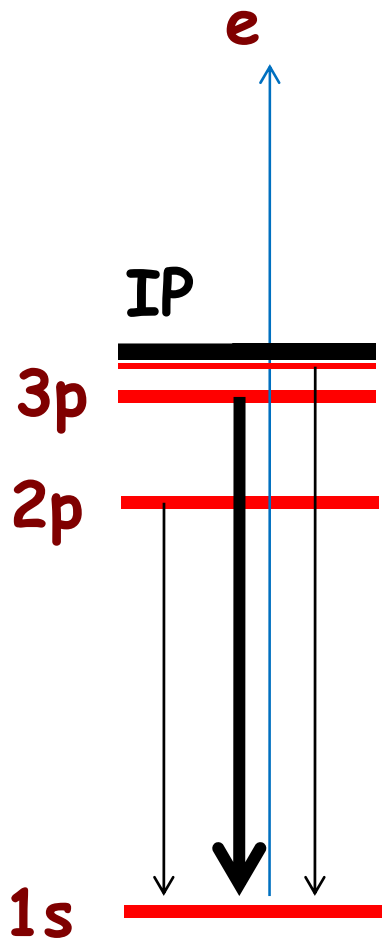


MnF_2: S=5/2



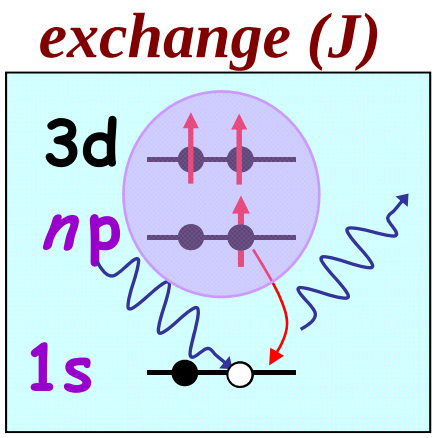


Wang et al. Phys. Rev. B 56, 4553 (1997)

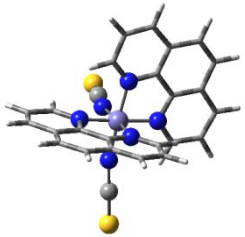


Courtesy: Pieter Glatzel (ESRF)

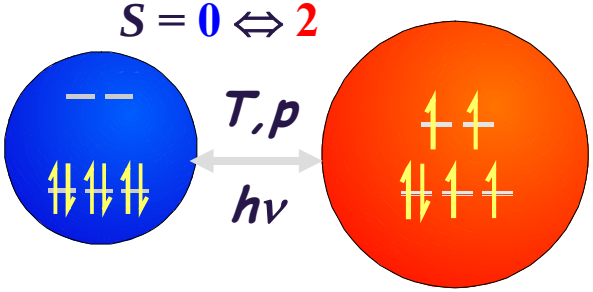
1s XES of a spin transition molecule

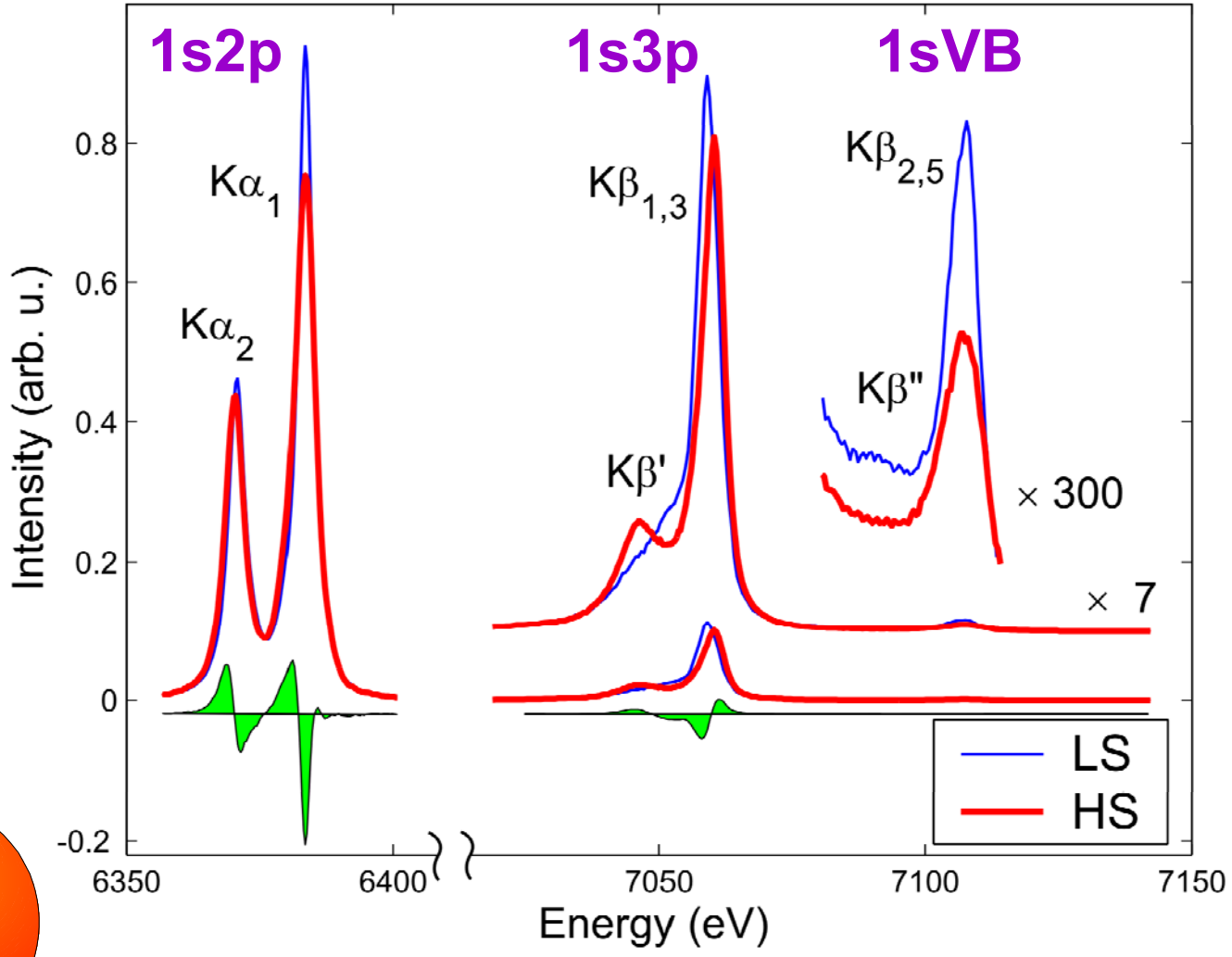


Fe^{II}— $3d^6$



$S = 0 \Leftrightarrow 2$

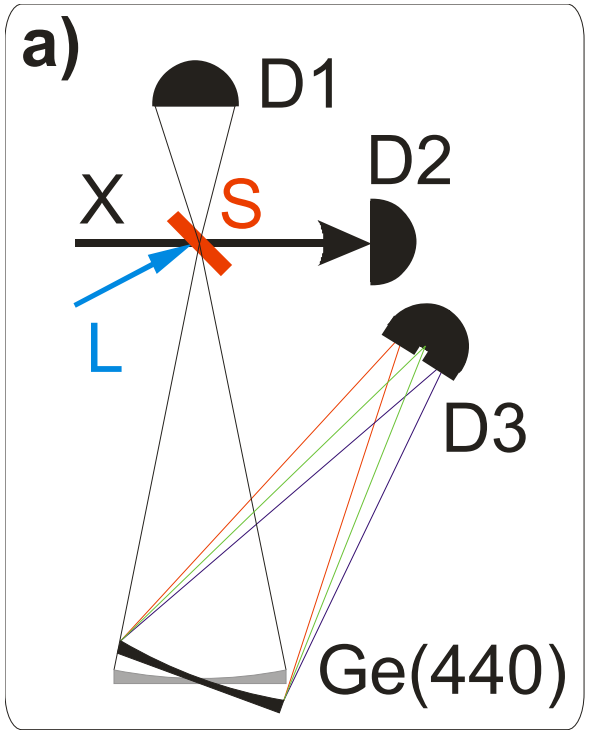


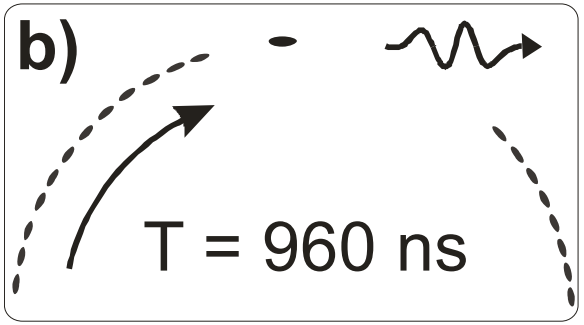


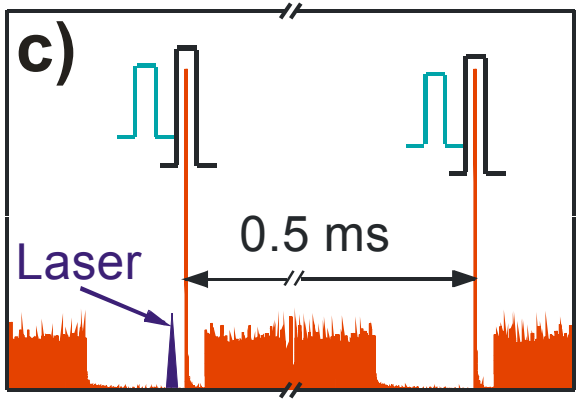
G. Vankó *et al., J. Phys. Chem.* B 110 (2006) 11647

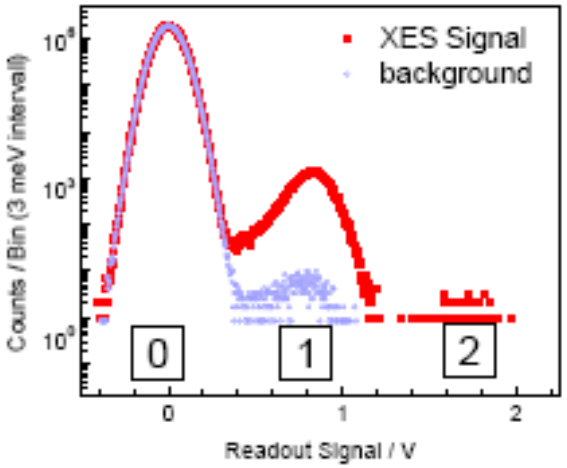
Towards ultrafast X-ray ***Emission*** Spectroscopy

10^3 – 10^6 ph/pulse (100 ps)
10-12 ph/pulse (200 fs)
10^{-3} ph/pulse (100 ps XES)



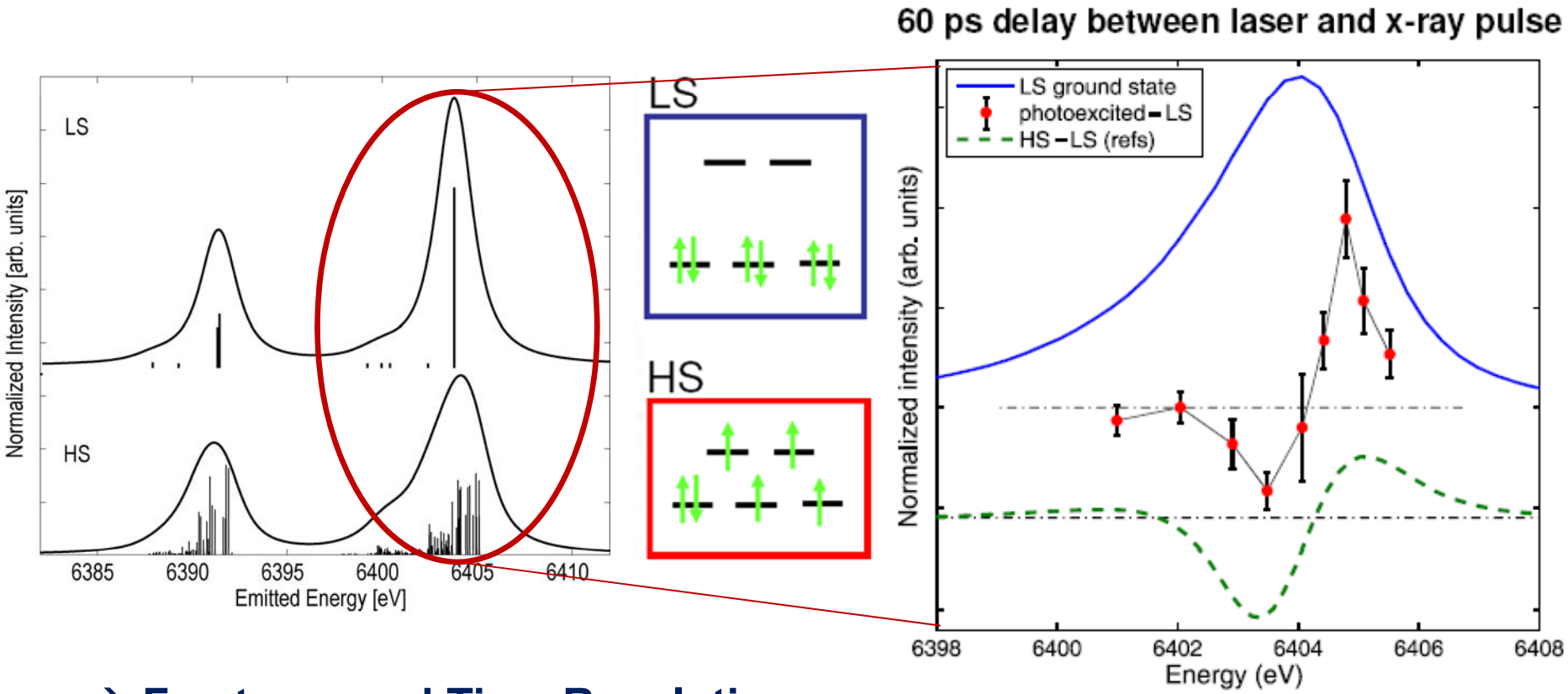






G. Vankó et al., Angew. Chem. Int. Ed. (2010)

Direct spin probing: first TR-XES (ps)



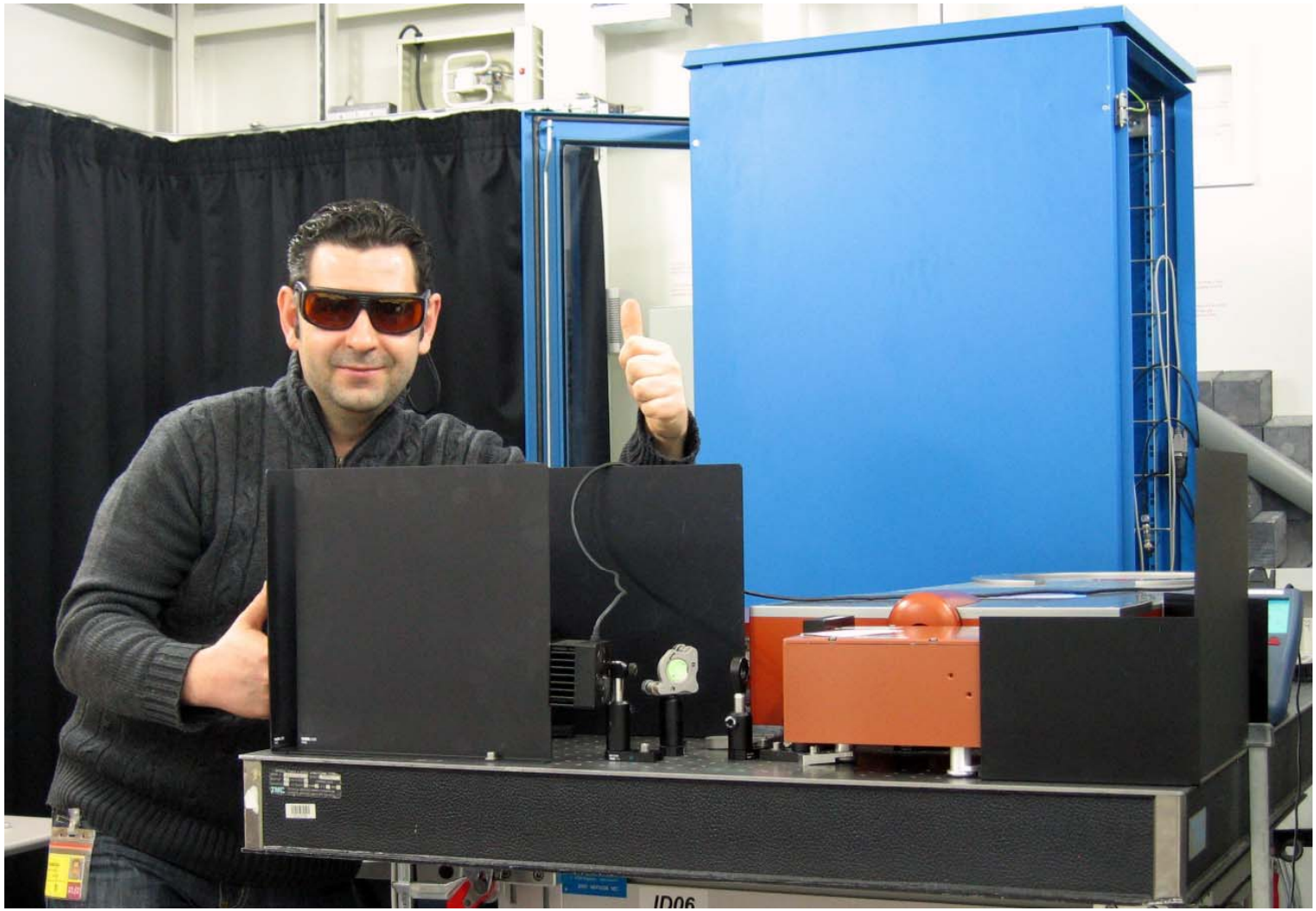
Direct measurement of change of Fe spin state.

→ Femtosecond Time Resolution
→ Ideally suited for single wavelength XFEL experiments
→ MHz repetition rates !!!!

G. Vanko et al., Angew. Chem. Int. Ed., (2010)

European XFEL

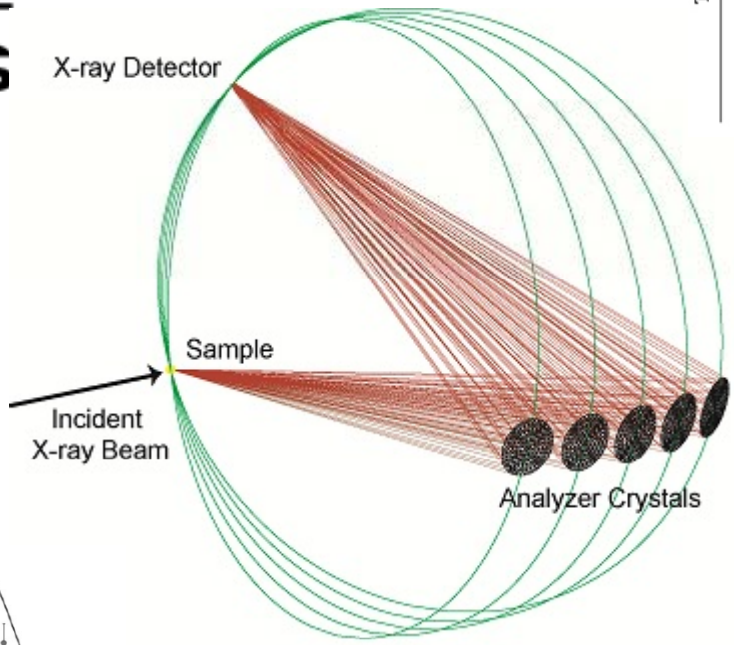
Ready to Pump-Probe at MHz rep-rates!!

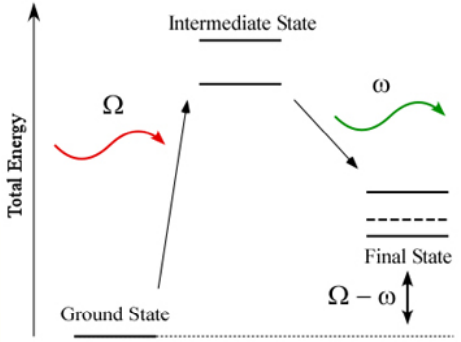


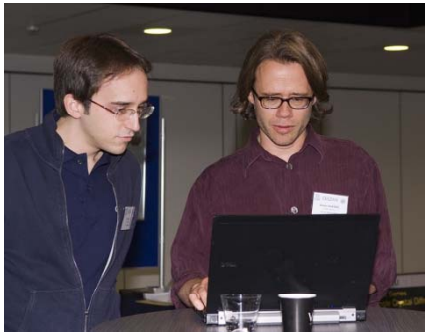
ID26 – X-ray Emission/Absorption Spectroscopy

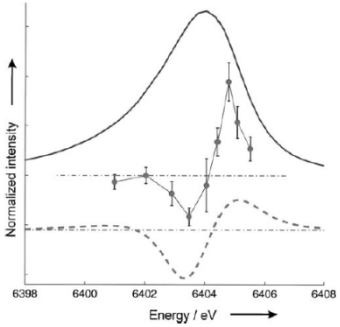
XAFS

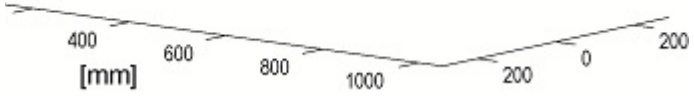
XES

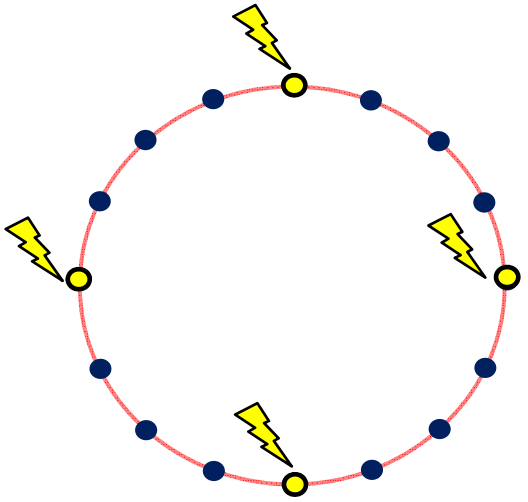






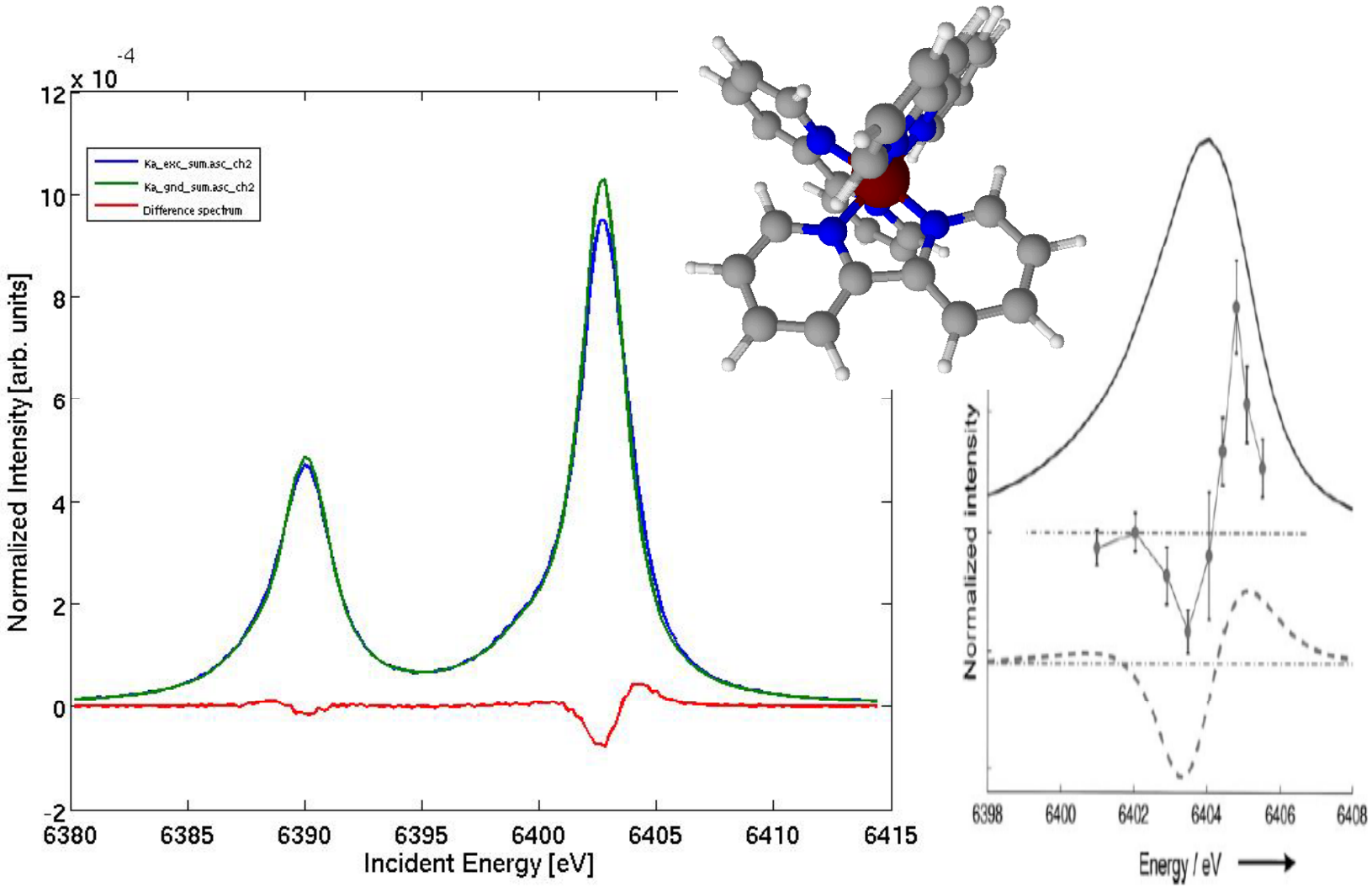






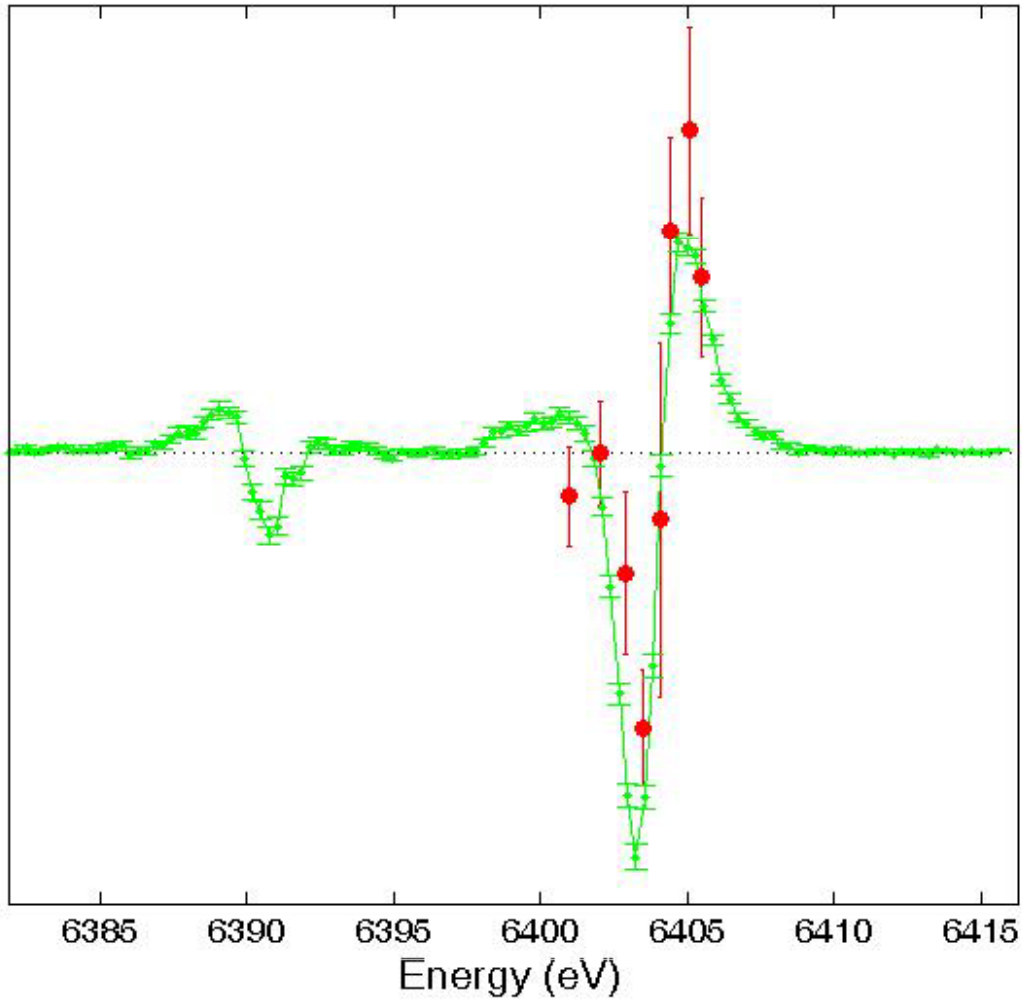
1.4 MHz

ID26/ESRF (March 2011)



APS, sector 7 (March 2011)

Picosecond K alpha XES at APS



1 kHz pp studies at SLS

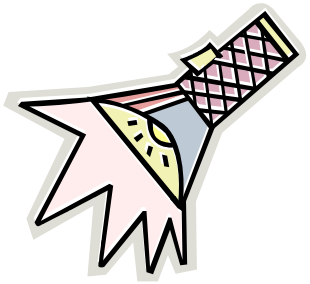
(Angew. Chem. 2010)

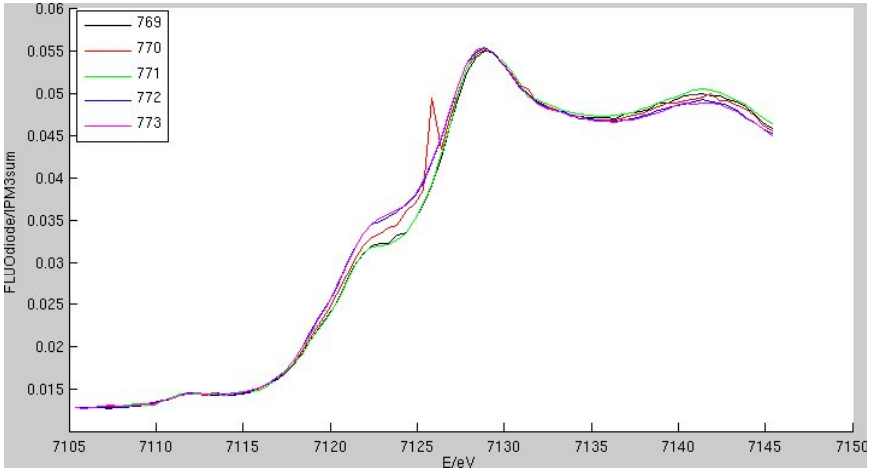
0.13 MHz at APS

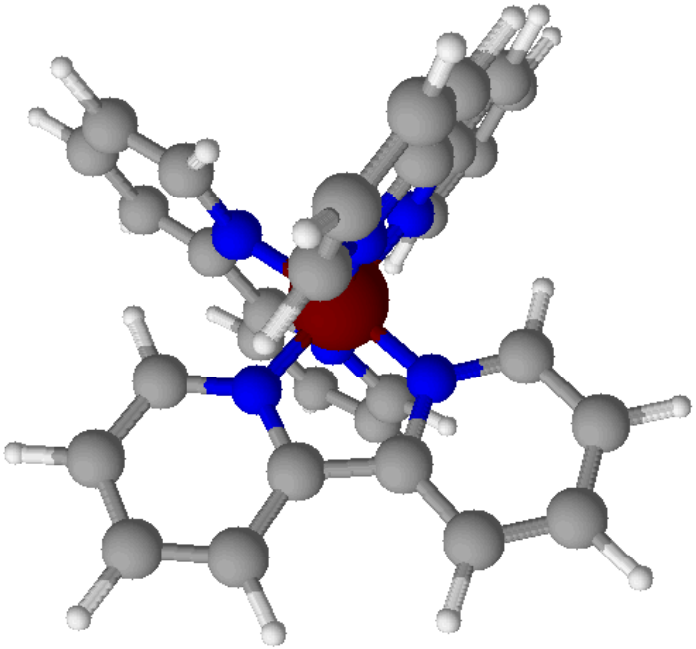
back to the future:

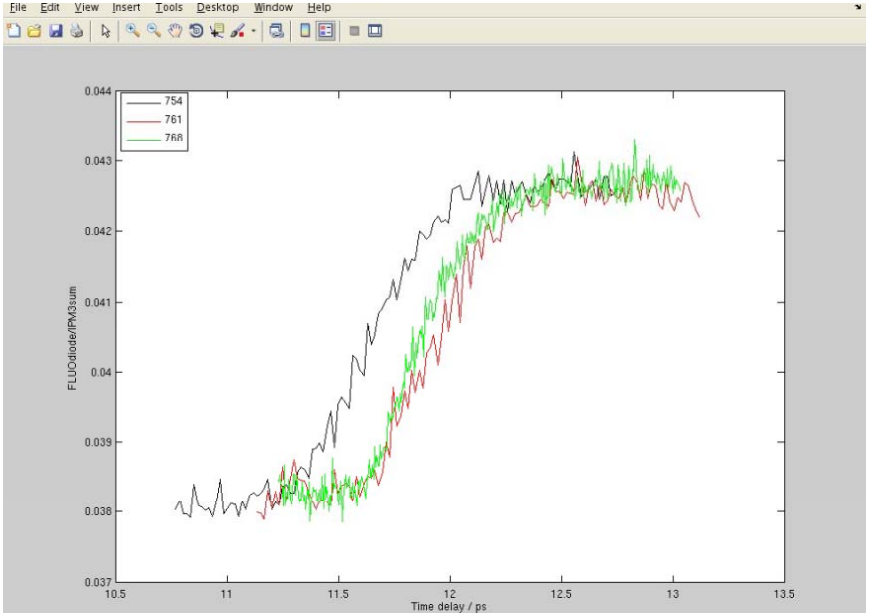
- Entering the femtosecond time scale (again)
  Linac coherent light source (LCLS)
- Credits: D. Fritz, M. Cammarata (SLAC)

XPP Commissioning (LCLS, Oct 2010) (Cammarata)

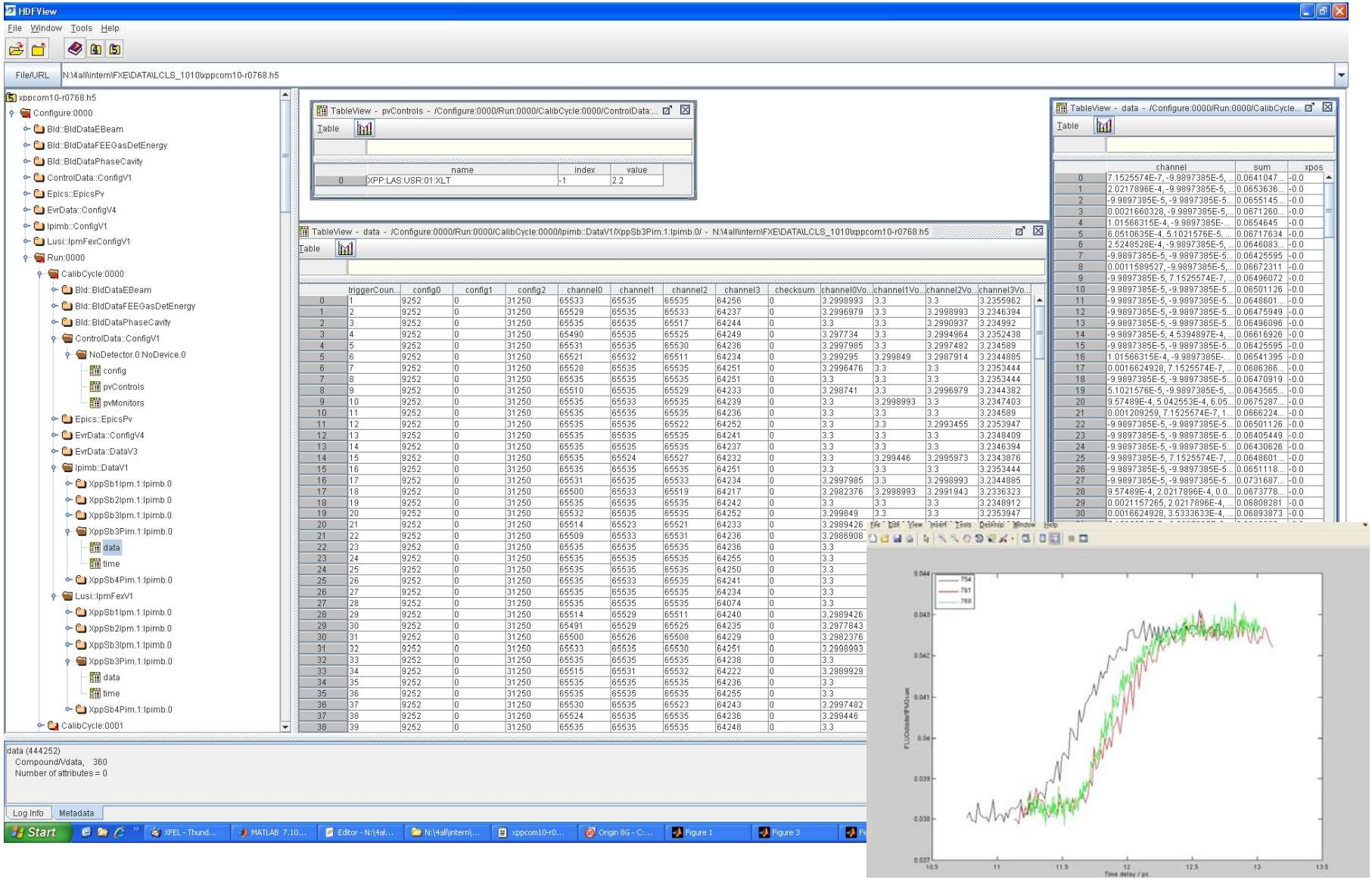




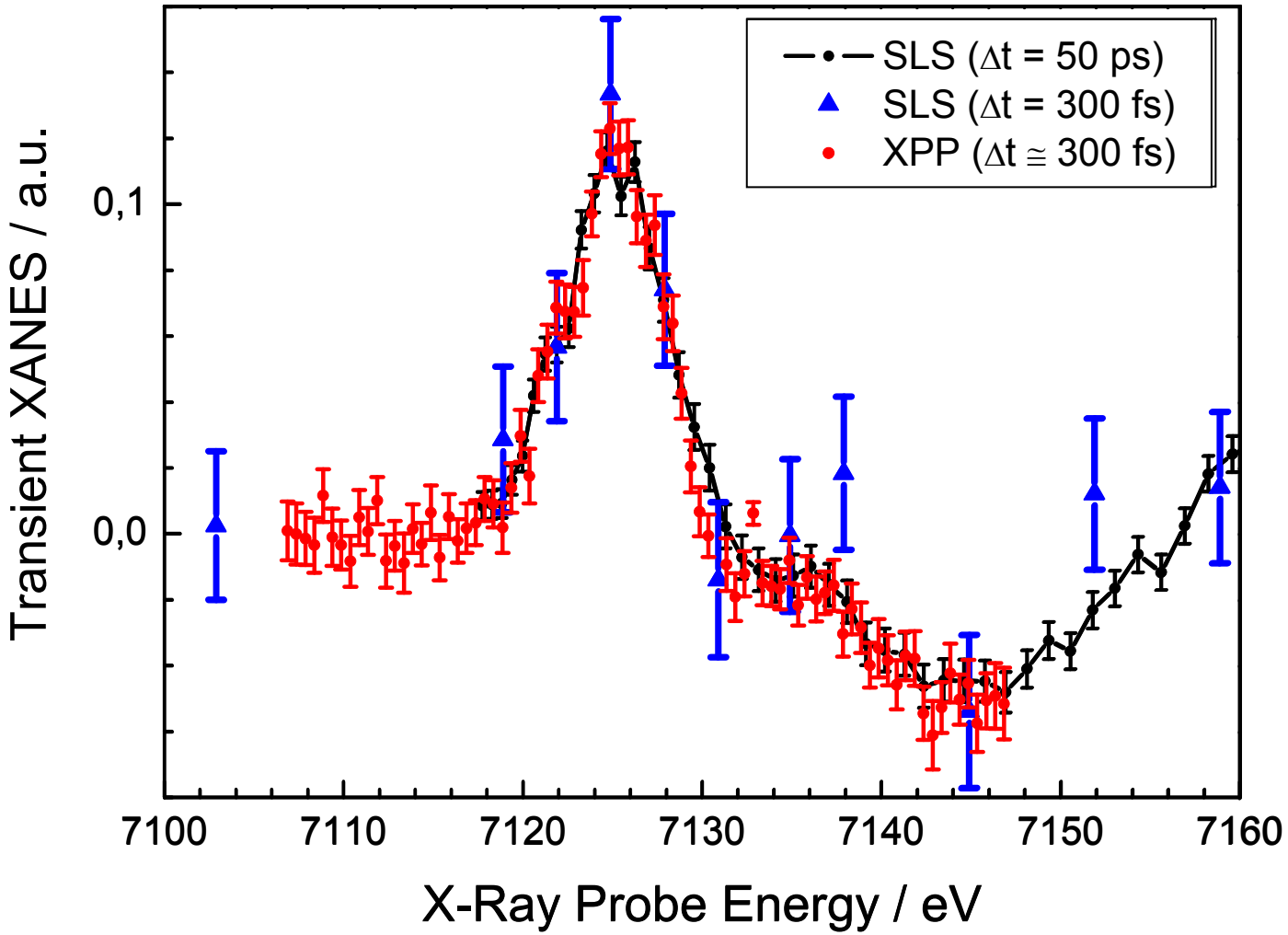




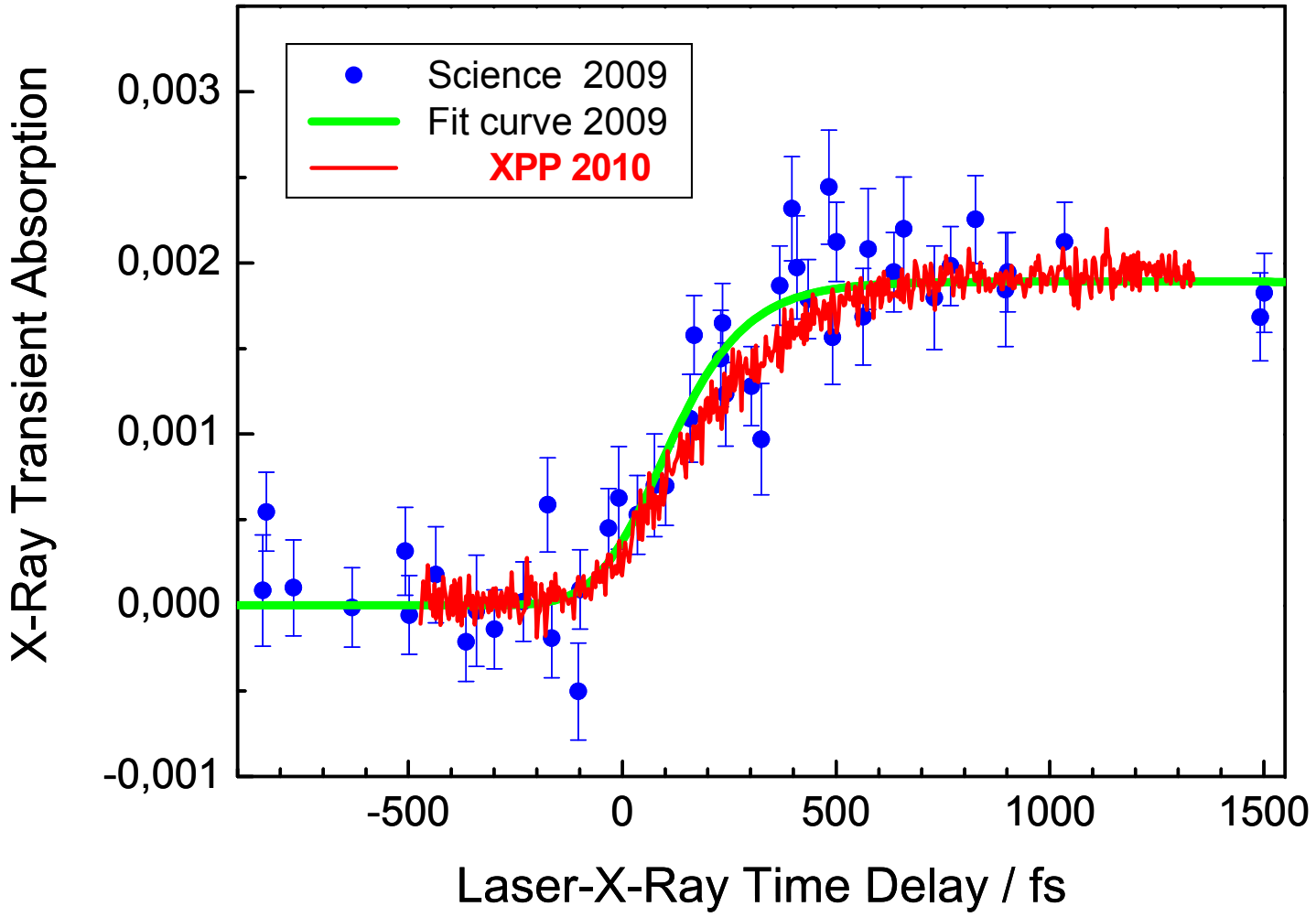
One single „File“ (10 min scan) at LCLS



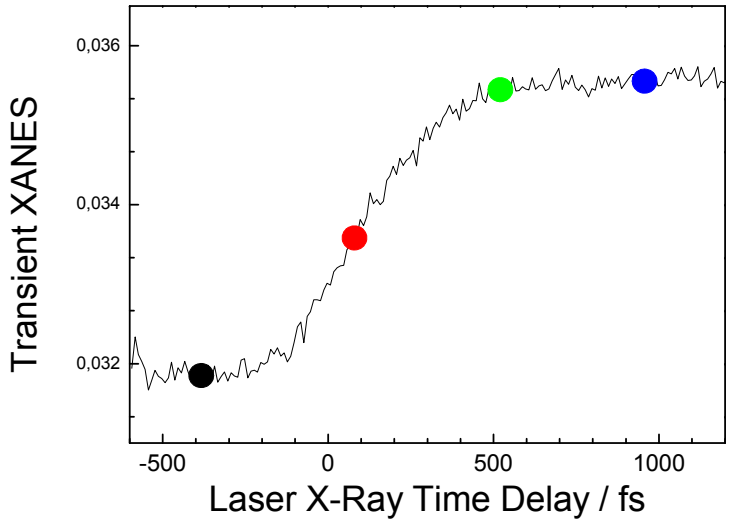
Oct 2010: XPP commissioning

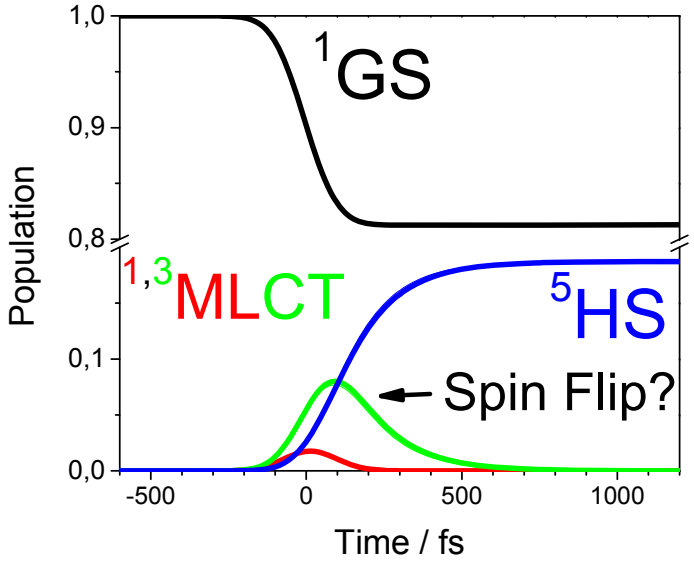


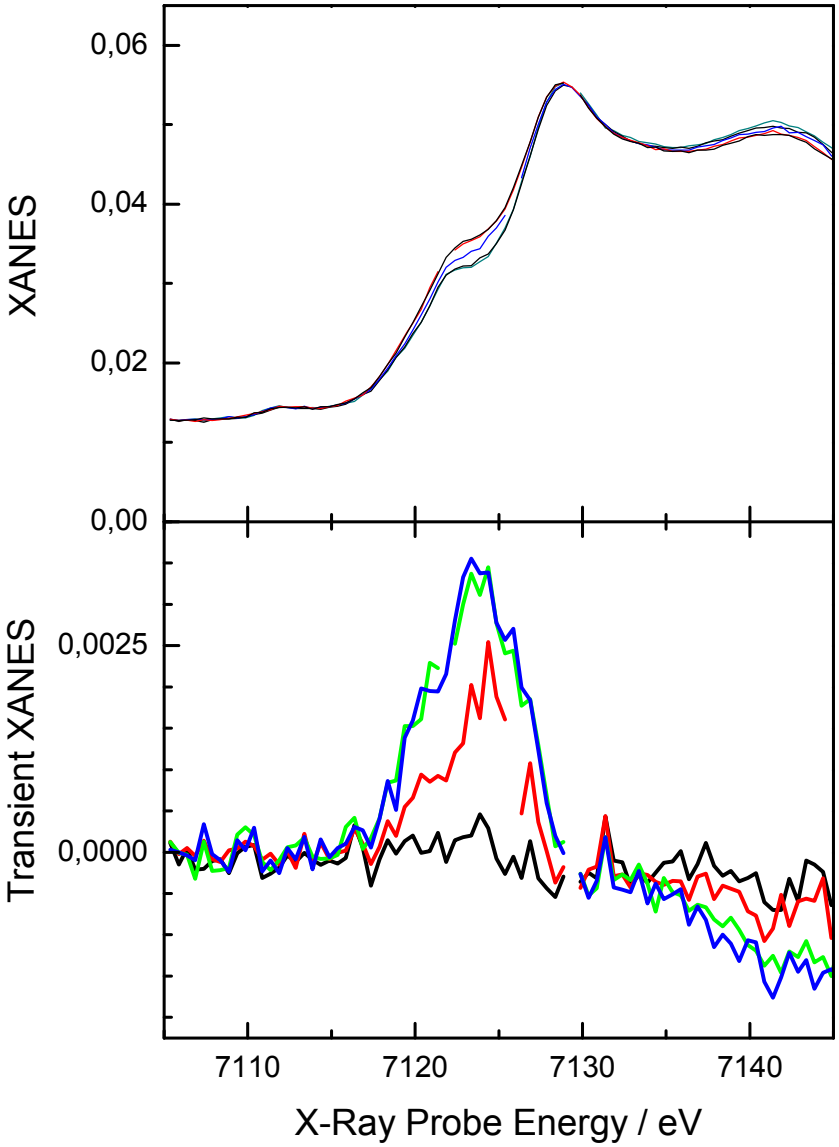
Real-Time Traces



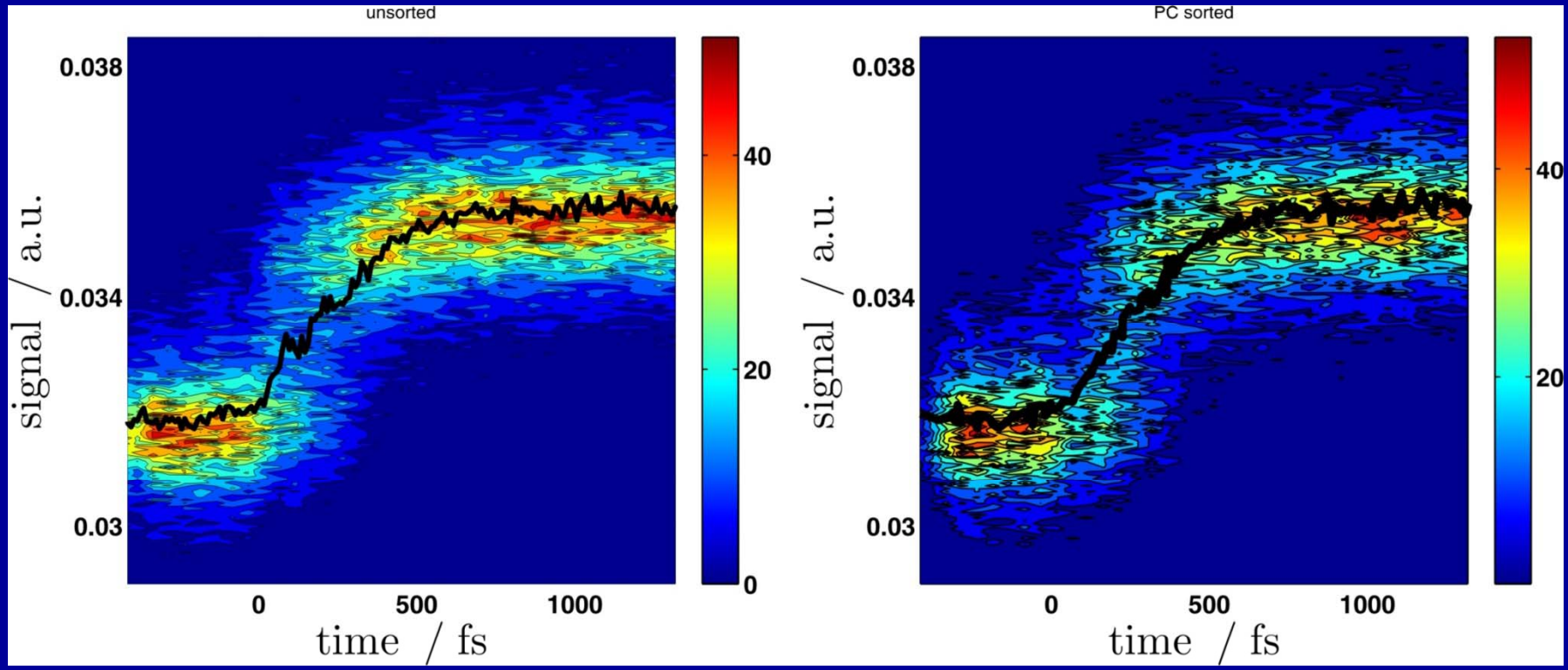
Transient Spectra around Time Zero



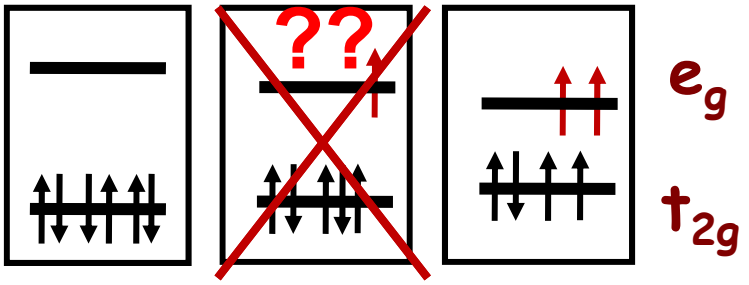


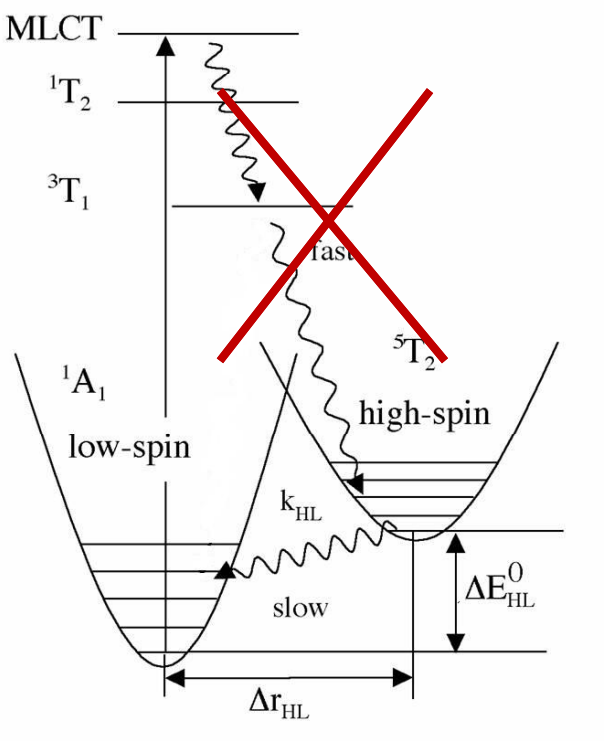


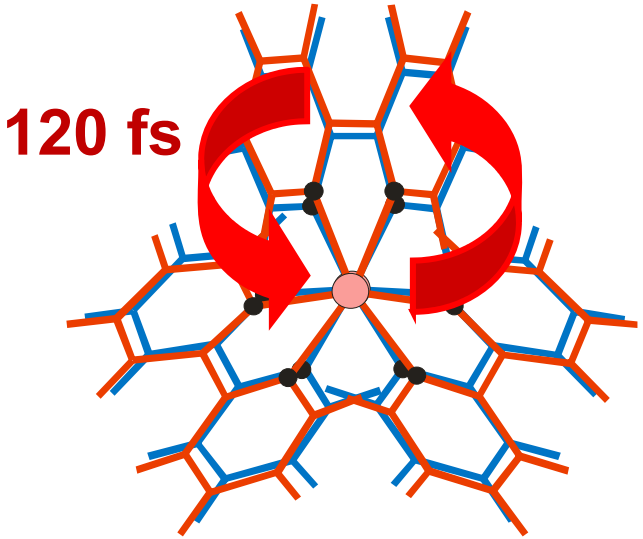
Looking into the raw data…

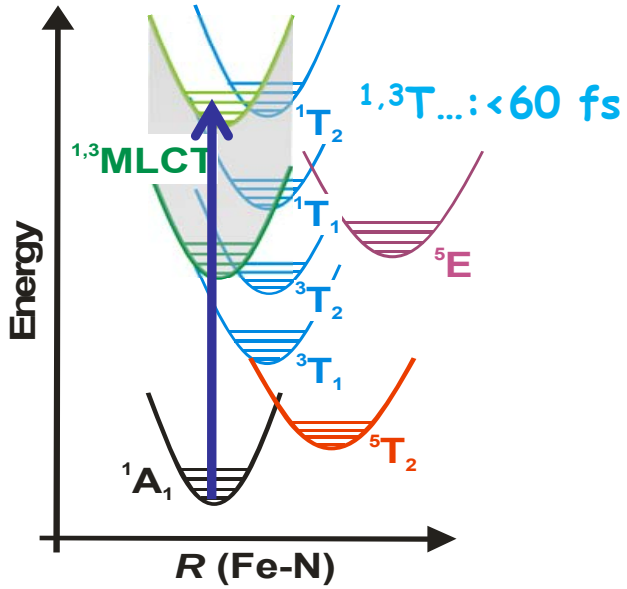


Summary of combined optical/XAS studies





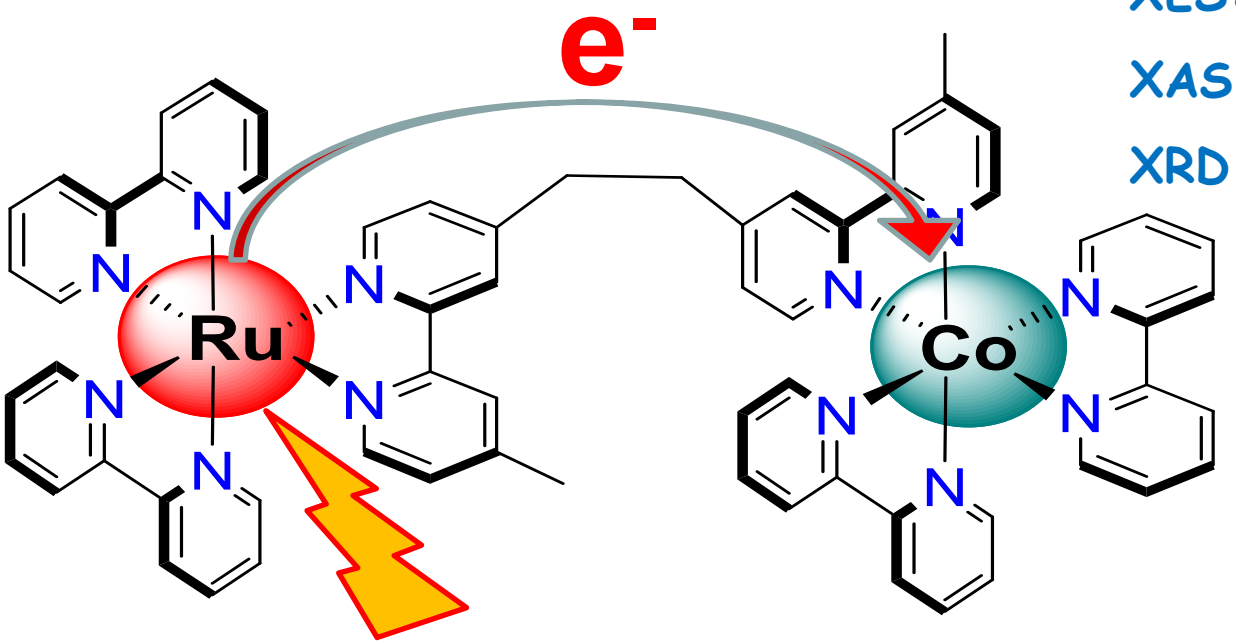




Need to include XES (spin) and even XRD (solvent)
…experiments at APS/ESRF to prepare for LCLS

Next Step: Exploit Complementary Structural Tools (LCLS project 2011):

→ Towards understanding chemical reactivity



XES: occupied DOS (spin)

XAS: empty DOS (orbitals)

XRD: geometric structures

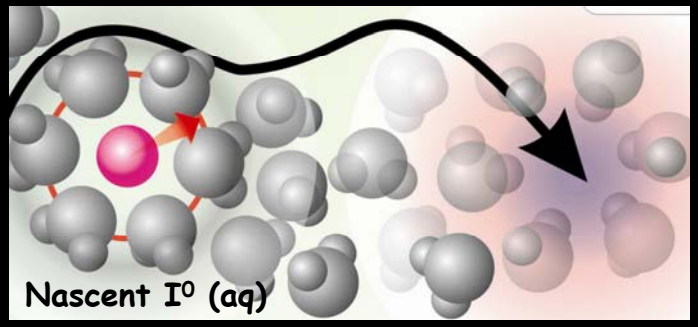
1) Ru(II) → Ru(III)	(XAS, XES, optical)
2) IVR + e-transport	(XRD, optical)
3) Co(III) → Co(II)	(XAS, XES, optical)
4) Co(II) LS→HS	(XAS, XES)

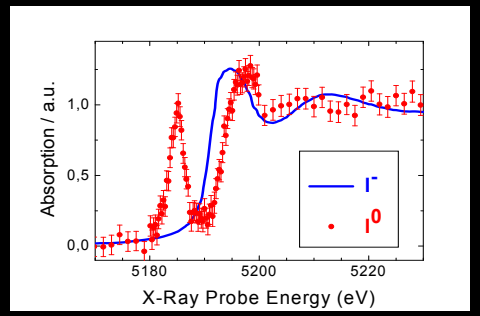
Collaboration:

M. Nielsen (Copenhagen)
V. Sundström (Lund)
G. Vanko (Budapest)
P. Glatzel (ESRF)
A. Meents (Petra3)
R. Abela (SwissFEL)

Conclusions

Towards Solvation Dynamics

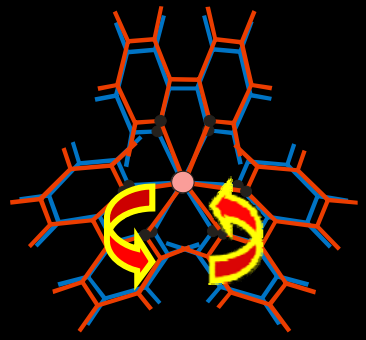


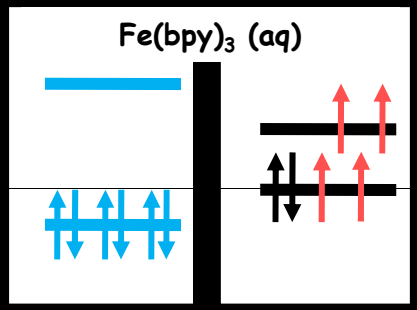


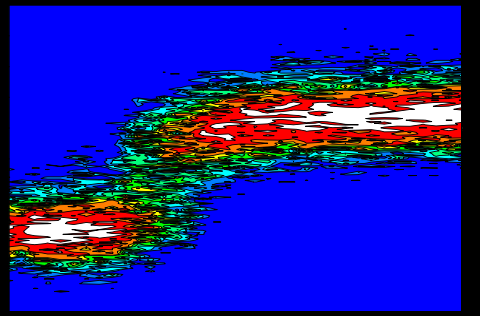
- We can follow the sequence of events from 300 fs onwards
  Even the (few) ps time scale we do not fully understand
  → Theoretical input important

- We need to know how things evolve between 0-300 fs
  → New experiments are planned (theory required)

Light-Induced Spin Crossover







- We do not understand this correlated SCO behavior!
  …but we are already looking into the elementary steps !!!

Acknowledgments

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Lund University
- Villy Sundström
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- Andreas Galler

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(XPP Oct 2010)