



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

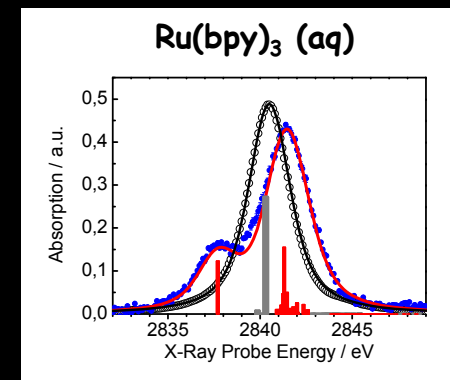
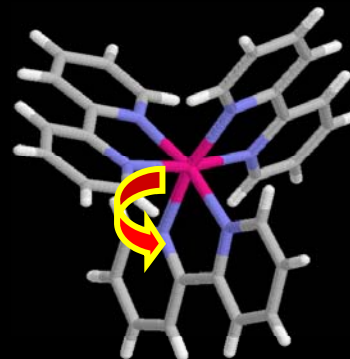
Christian Bressler



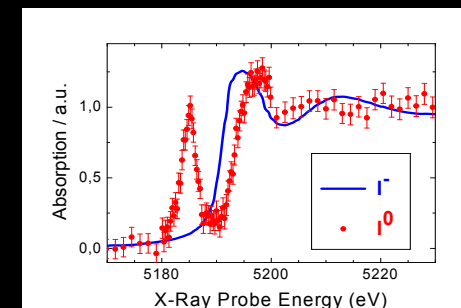
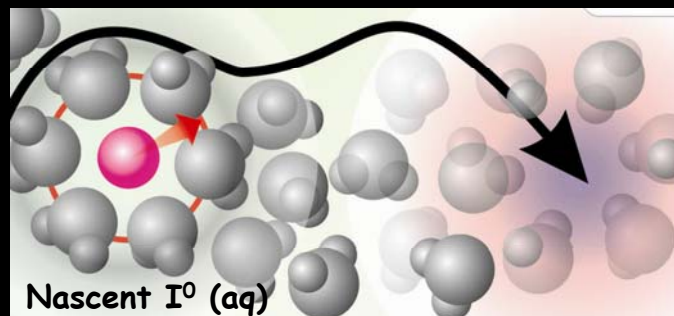
XDL Workshop "tickle and probe", Cornell University, June 21, 2011

Dynamic Studies in Photochemistry

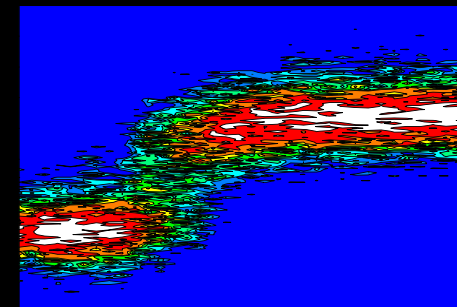
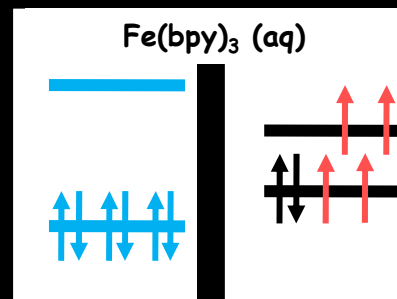
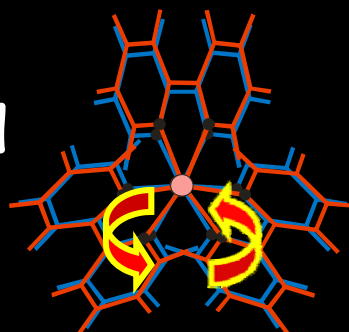
1. Intramolecular Charge Transfer



2. Towards Solvation Dynamics

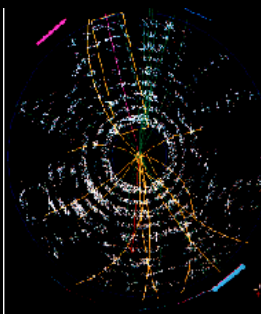


3. Light-Induced Spin Crossover

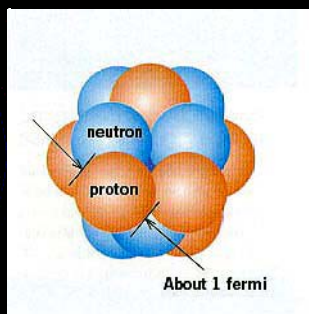


What are the fundamental timescales?

Chemistry and Biochemistry



Strings,
Cosmology

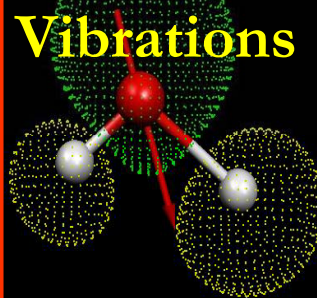


Particle
Collisions

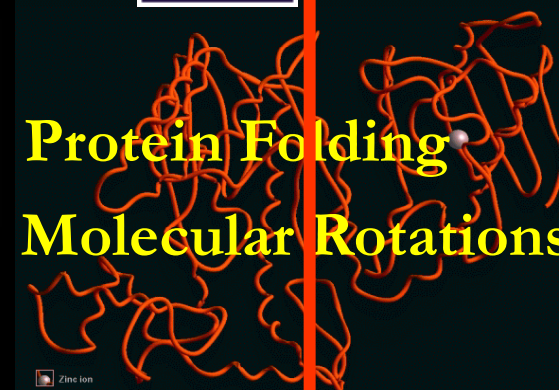
Photosynthesis

Vision

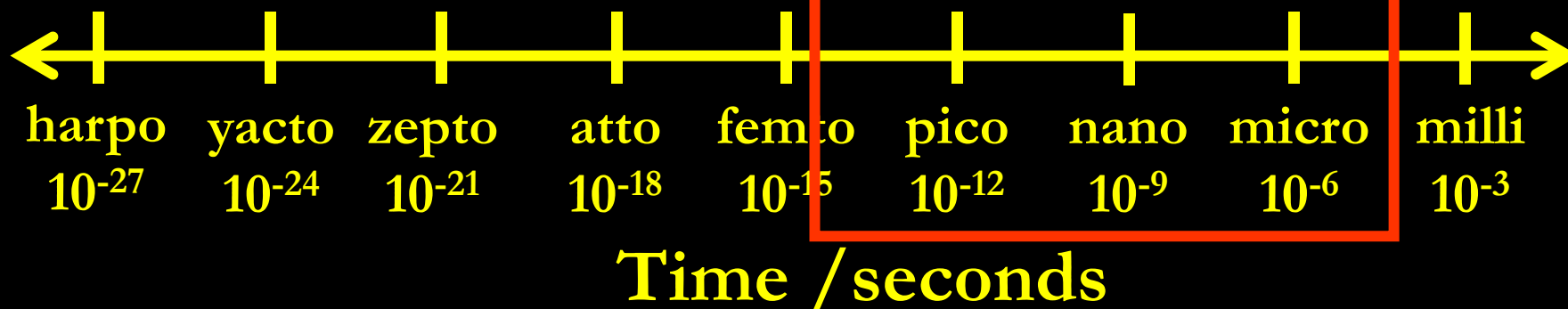
Molecular
Vibrations



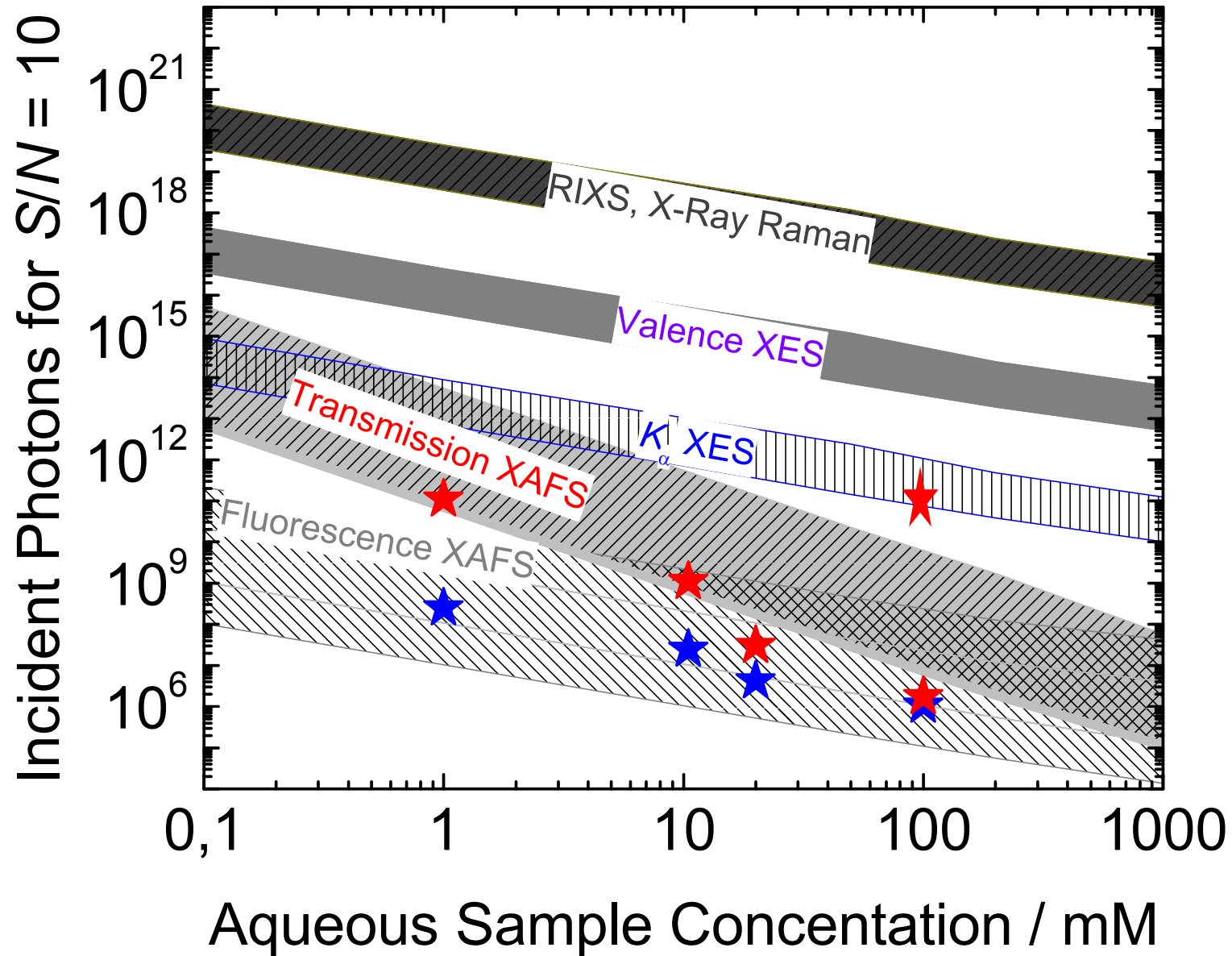
Protein Folding
Molecular Rotations



Electron dynamics

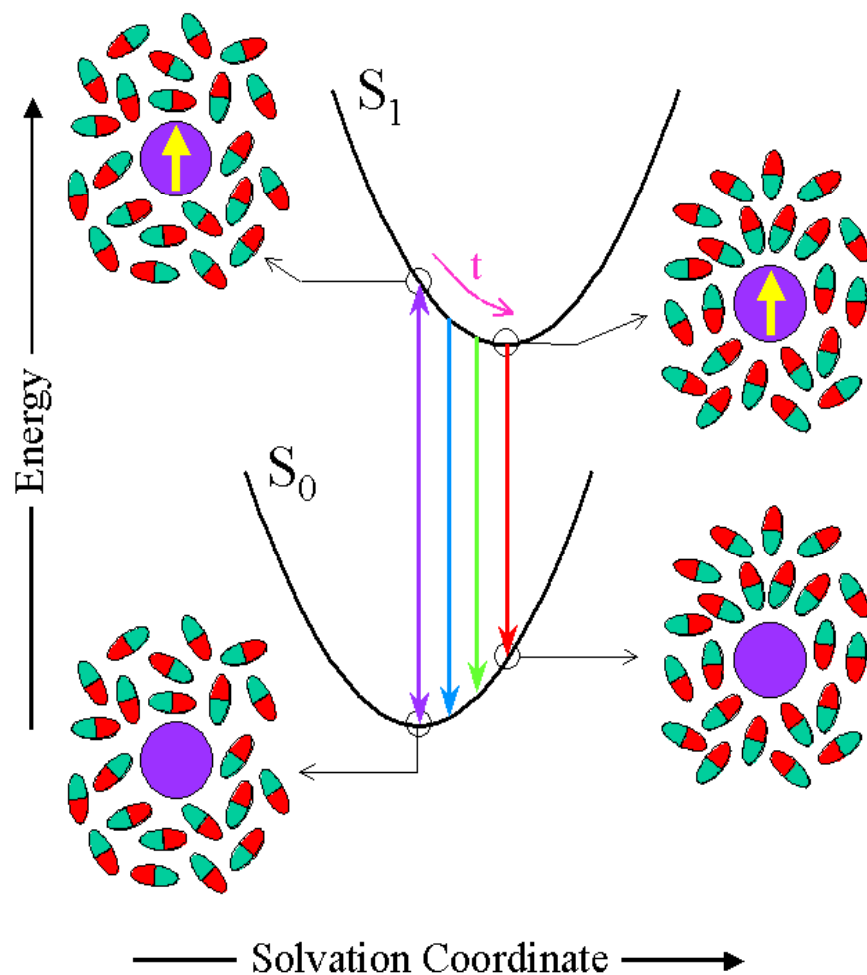


Now for the low-lying fruit (K edges)



Towards Solvation Dynamics

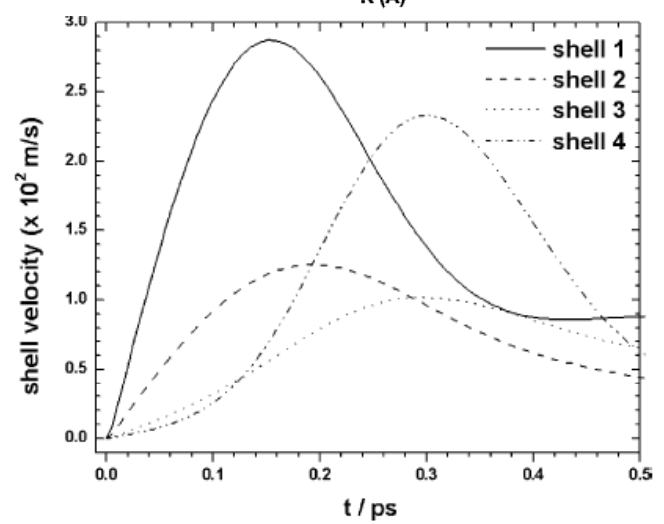
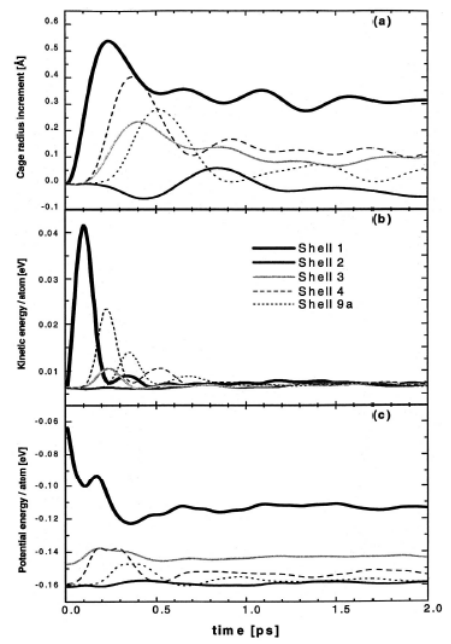
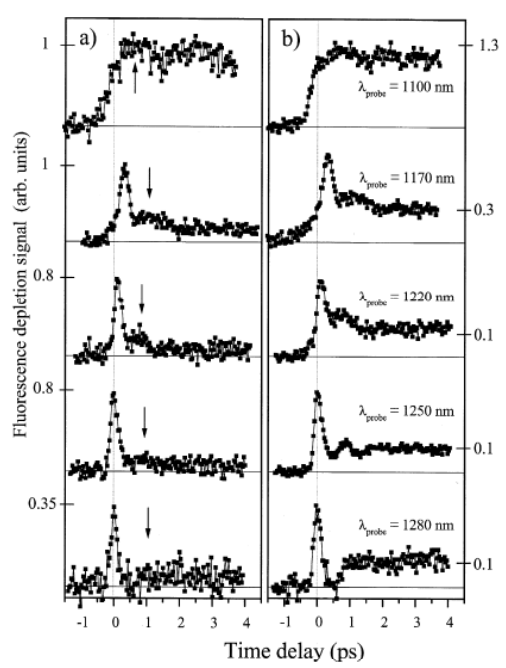
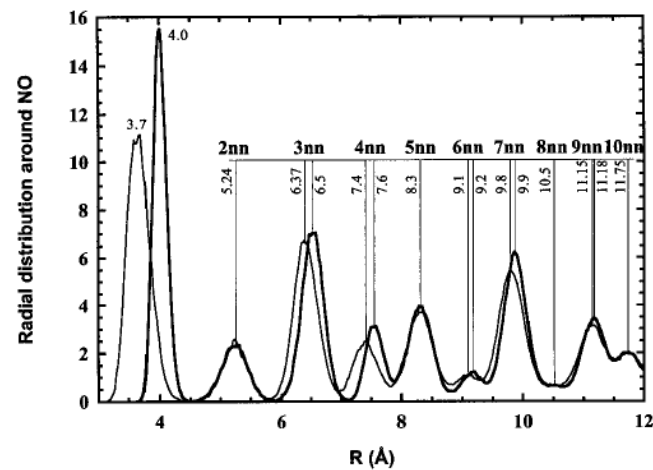
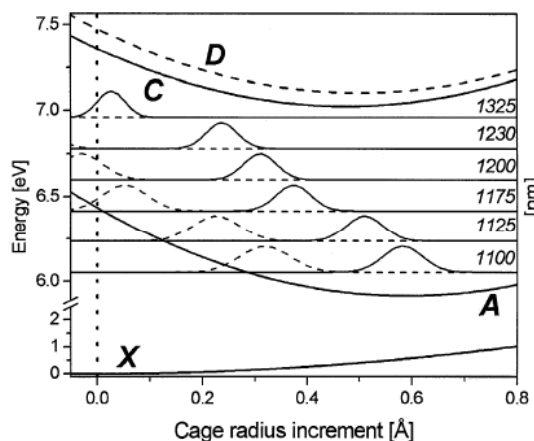
Dynamic Stokes Shift



-Distinguish IVR from guest-host interactions

-Example: NO/Rg matrix

Rydberg NO in rare gas matrices: bubble formation



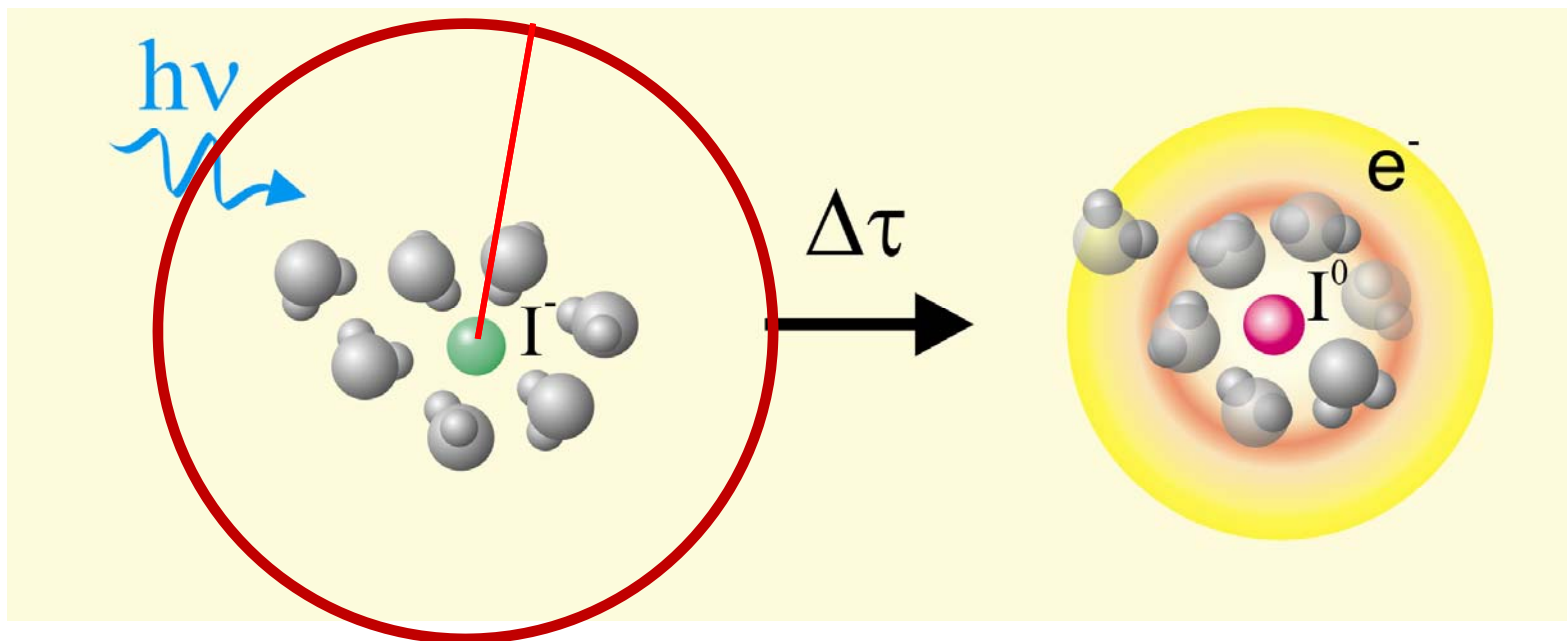
F. Vigliotti et al. / Chemical Physics Letters 362 (2002) 31–38

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: $>10 \text{ \AA/ps}$

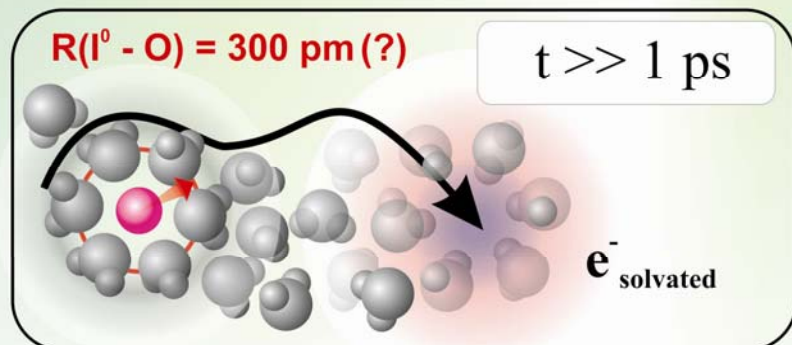
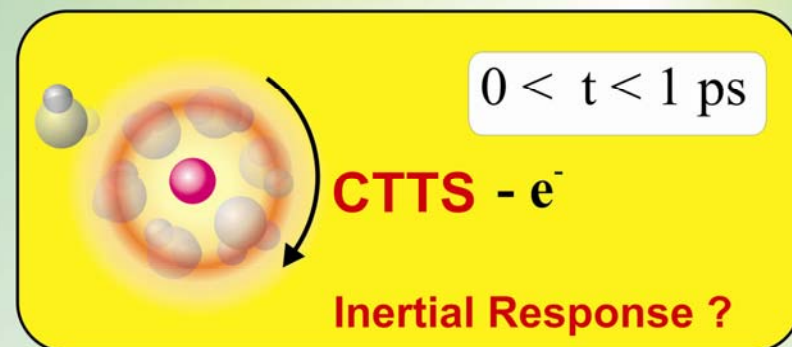
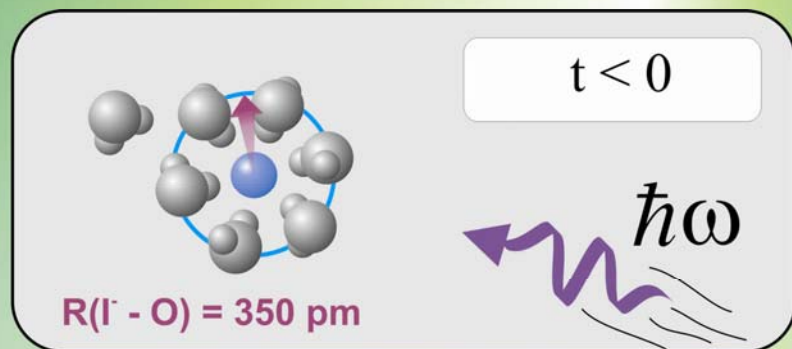


... \rightarrow ca 100-1000 Solvent Molecules involved

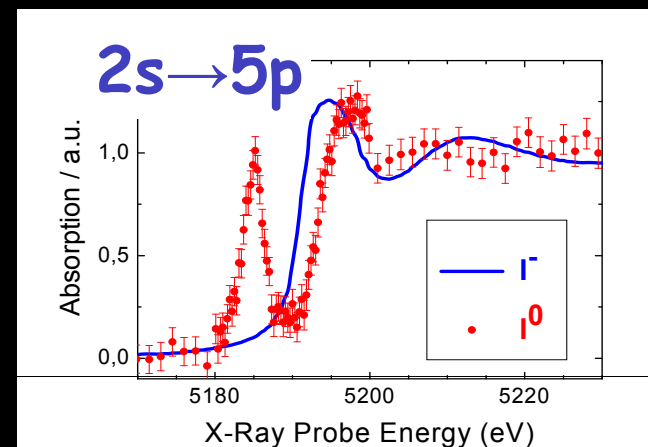
X-Ray Absorption Spectroscopy
Singles Out Reaction Center ...

Electron Detachment Reactions (via XAFS)

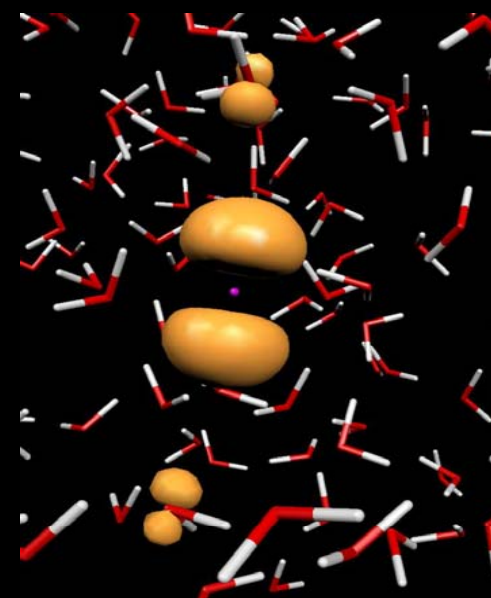
Condensed Phase Dynamics



Nascent I atoms in solution

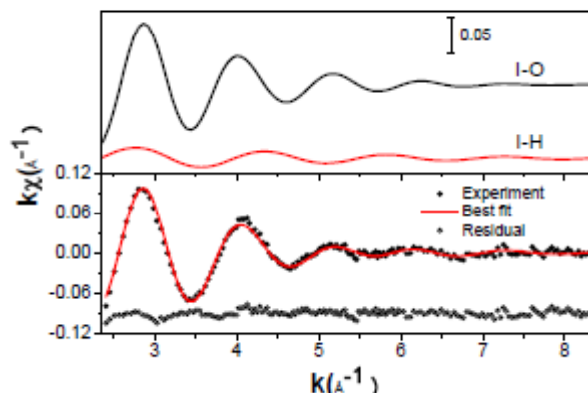


Pham *et al.*, JACS (2007)



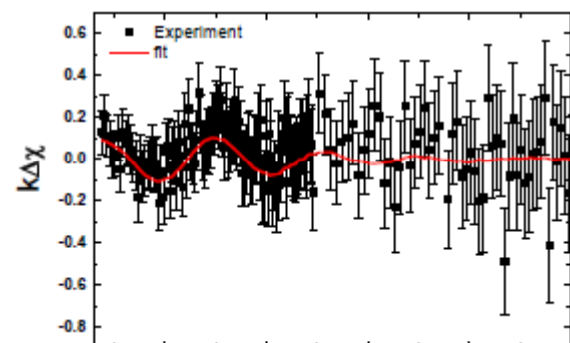
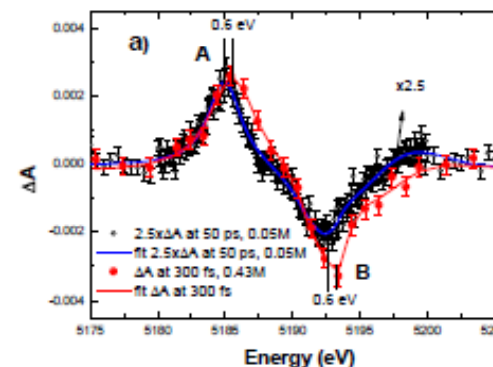
I. Tavernelli (EPFL)

EXAFS and XANES of nascent iodine radicals



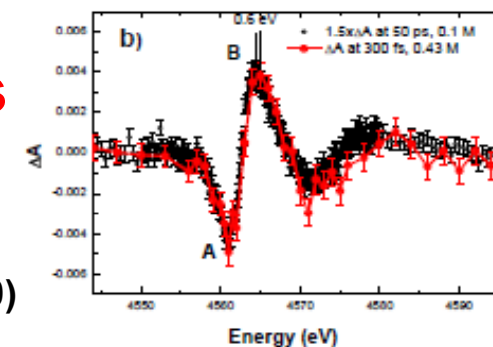
static

300 fs
50 ps



50 ps

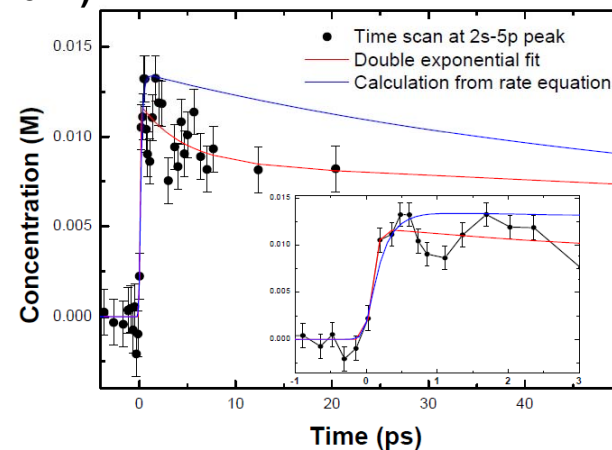
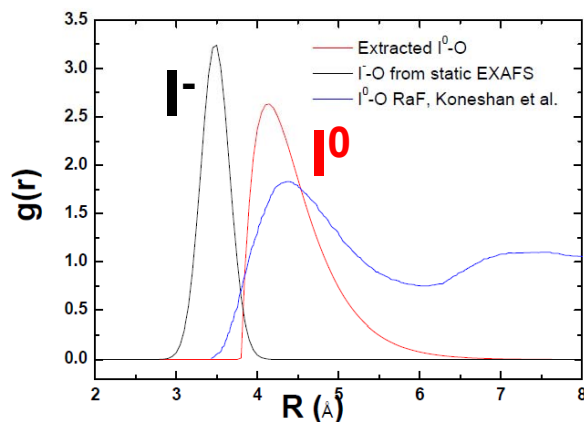
300 fs
50 ps



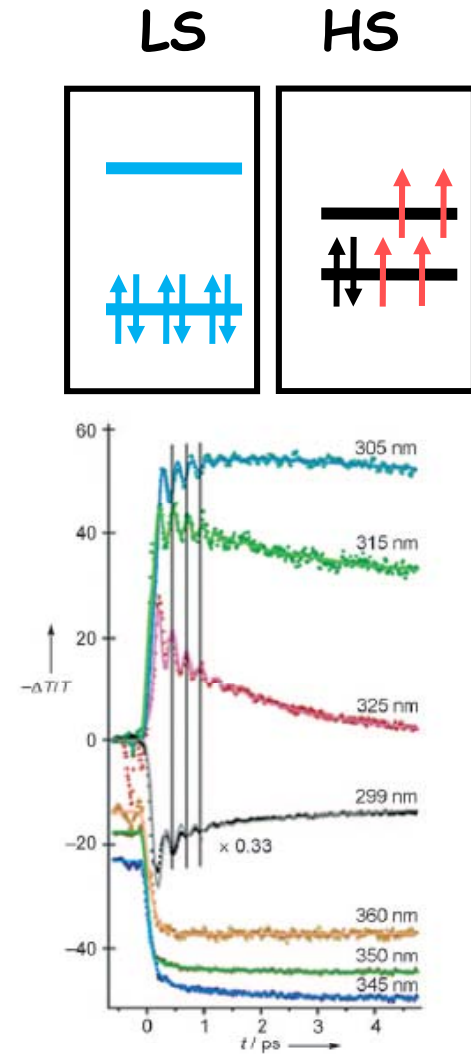
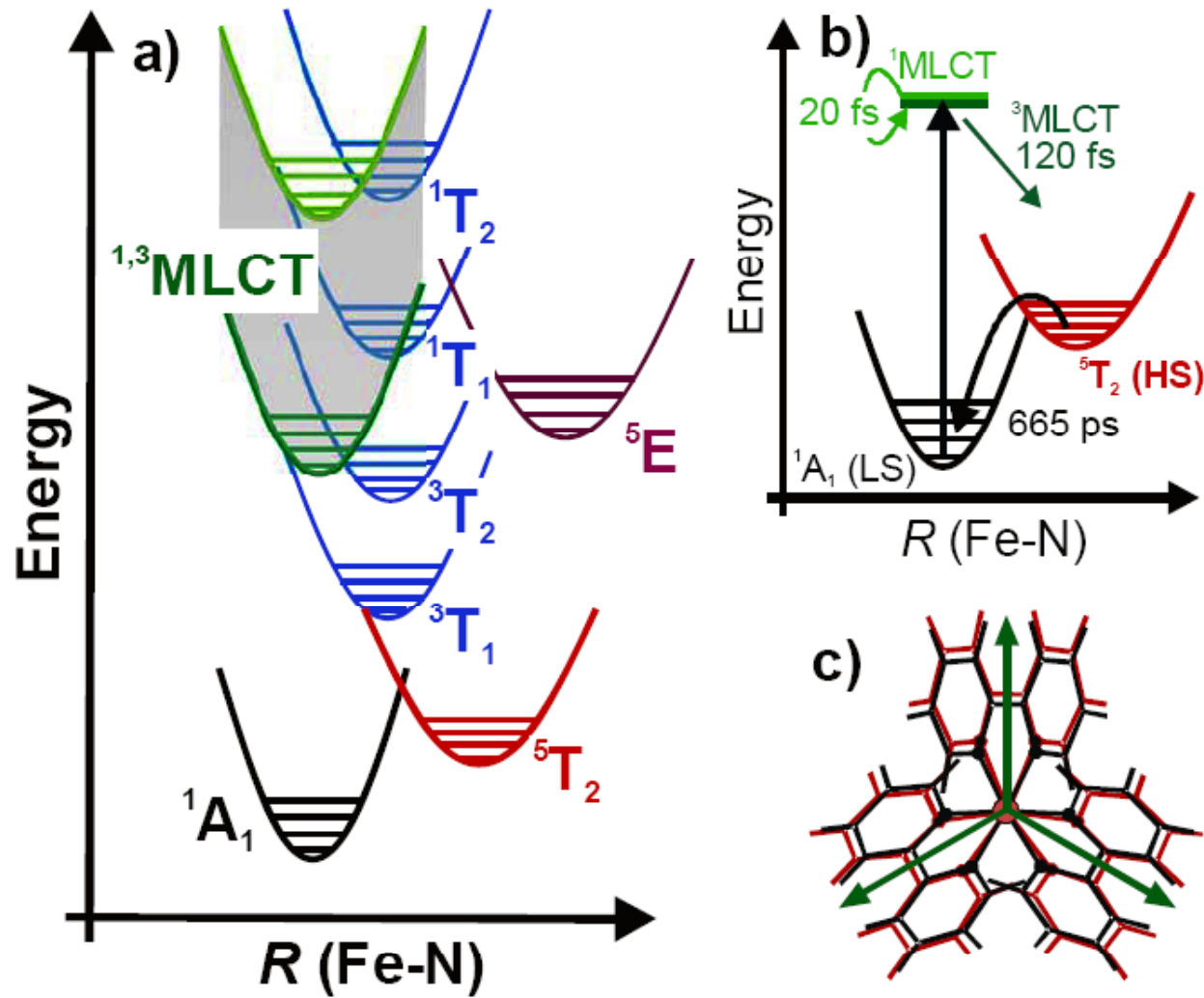
V.-T. Pham *et al.* Chem. Phys. (2010)

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

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

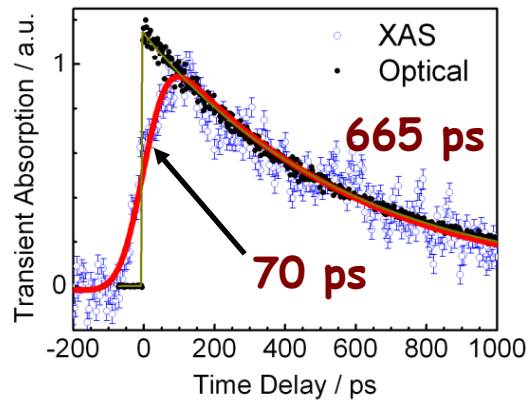
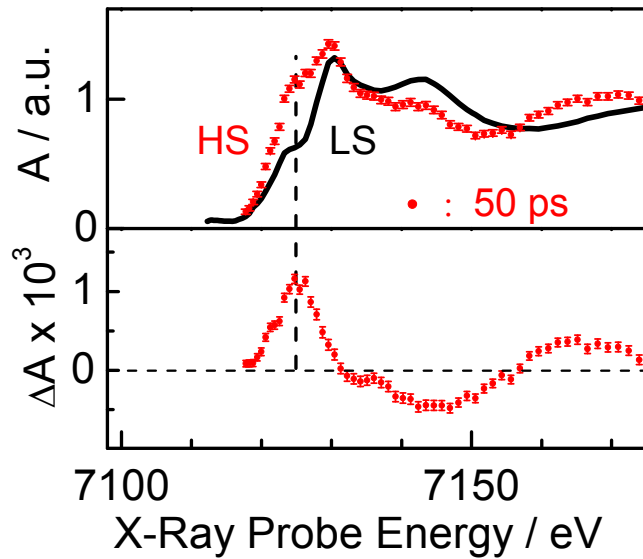


Now to something completely different....

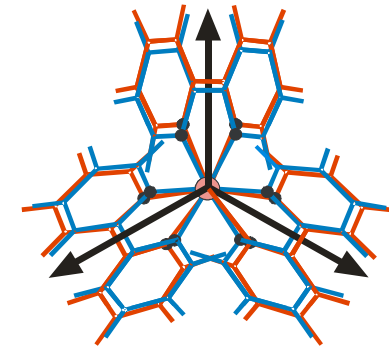
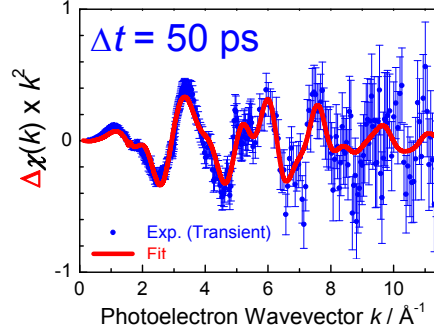
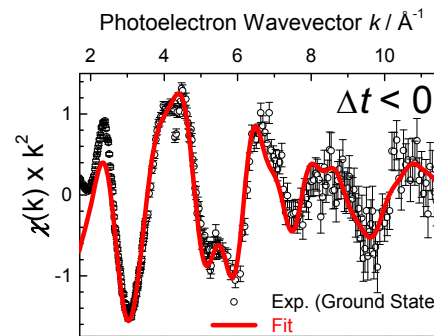
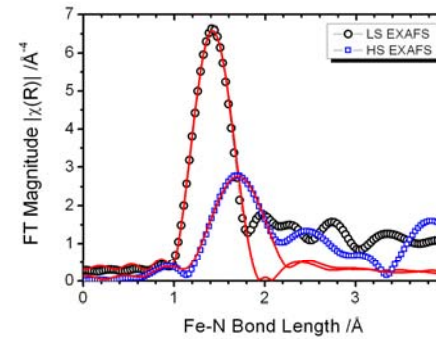


C. Consani *et al.*
Angew Chem (2009)

Towards Transient Structures via TR-XAFS

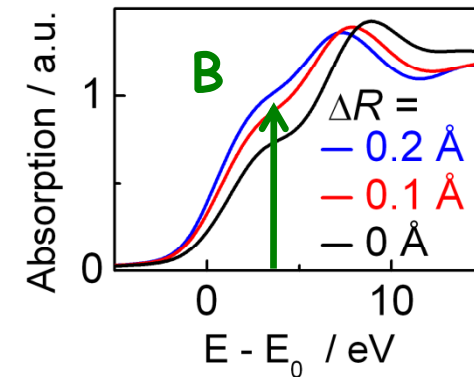


W. Gawelda et al.
Phys. Rev. Lett. (2007)



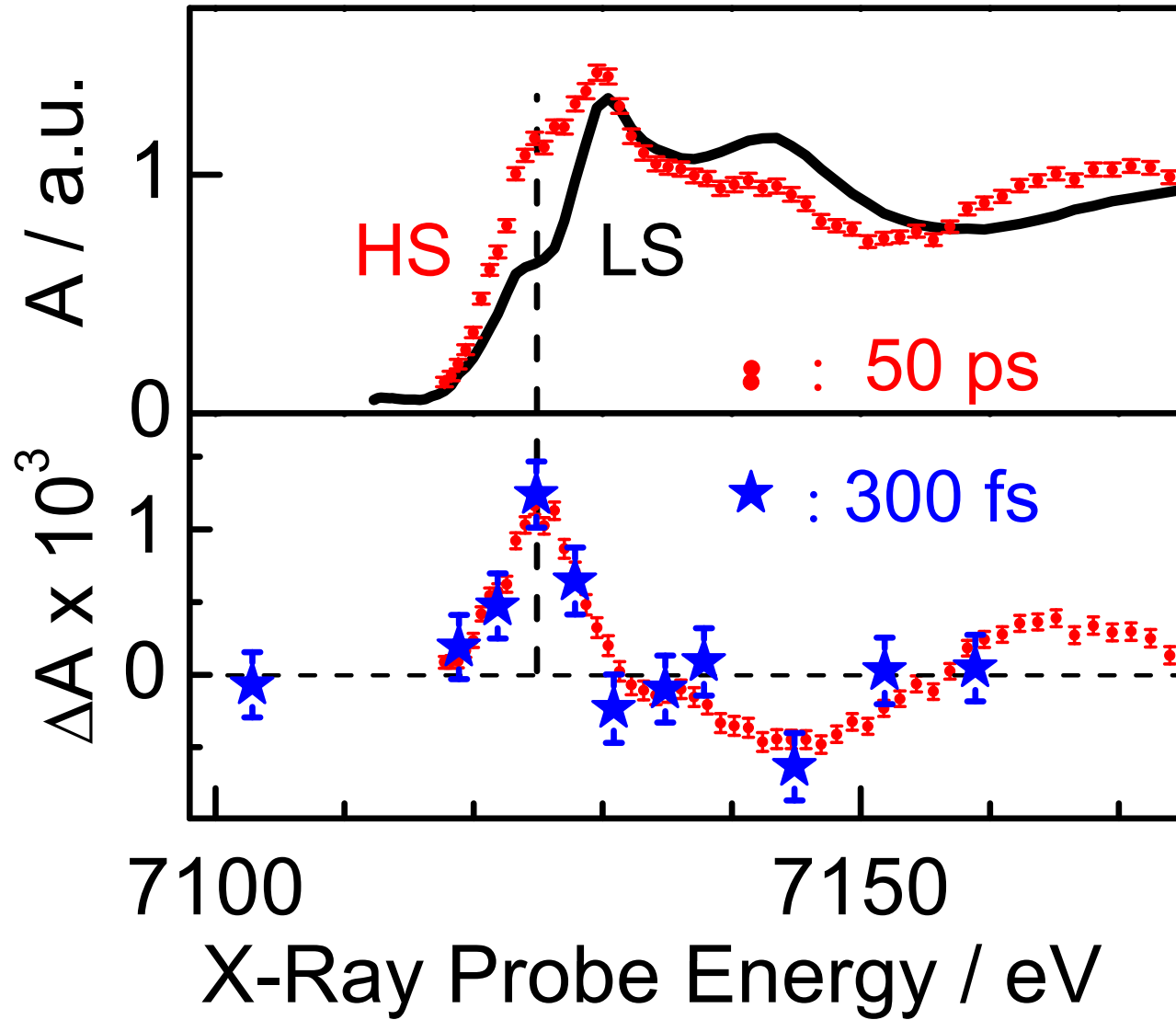
$$\Delta R_{\text{Fe-N}} = 0.2 \pm 0.008 \text{ \AA}$$

M. Benfatto (INFN Rome)



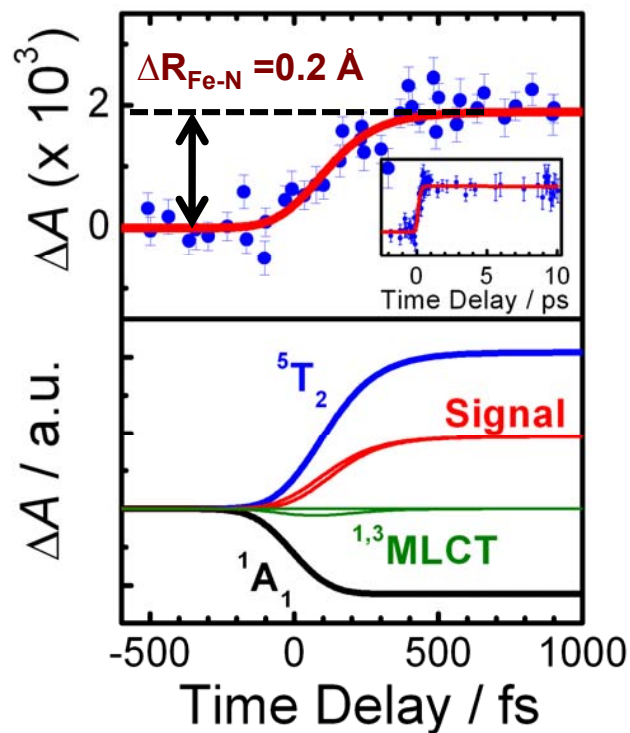
W. Gawelda et al.
J. Chem. Phys. (2009)

ps and fs XANES (Synchrotron)



C. Bressler et al., Science (2009)

Identifying intermediate states...

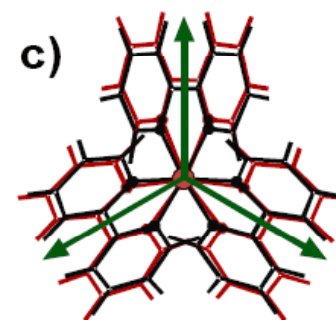
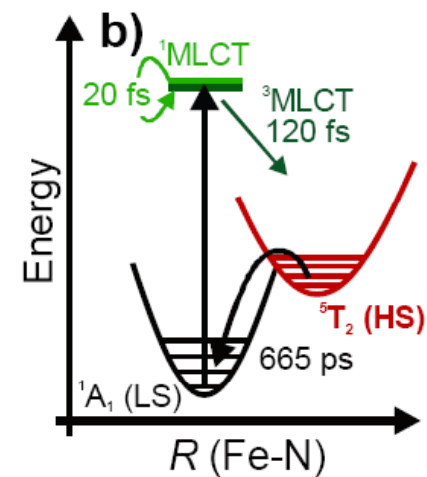
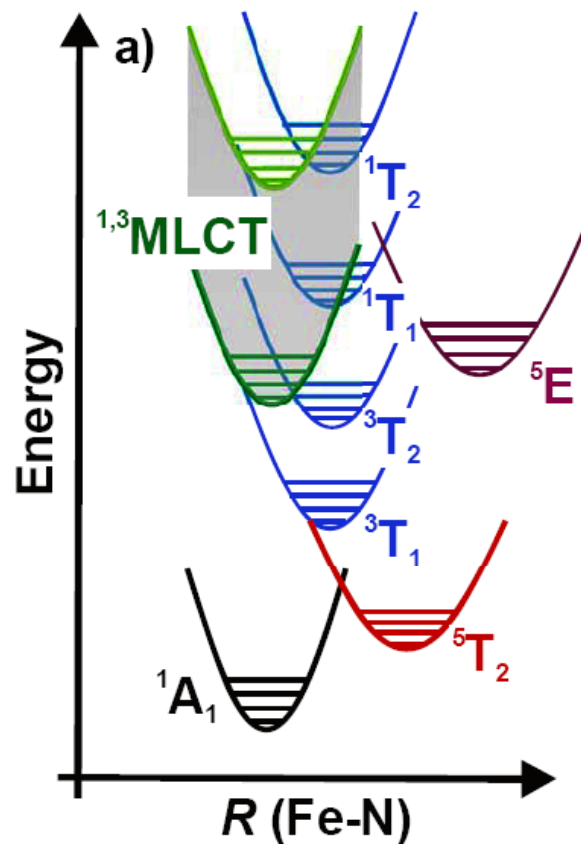


250 fs (instrument response):

140(30) fs hard x-ray pulse

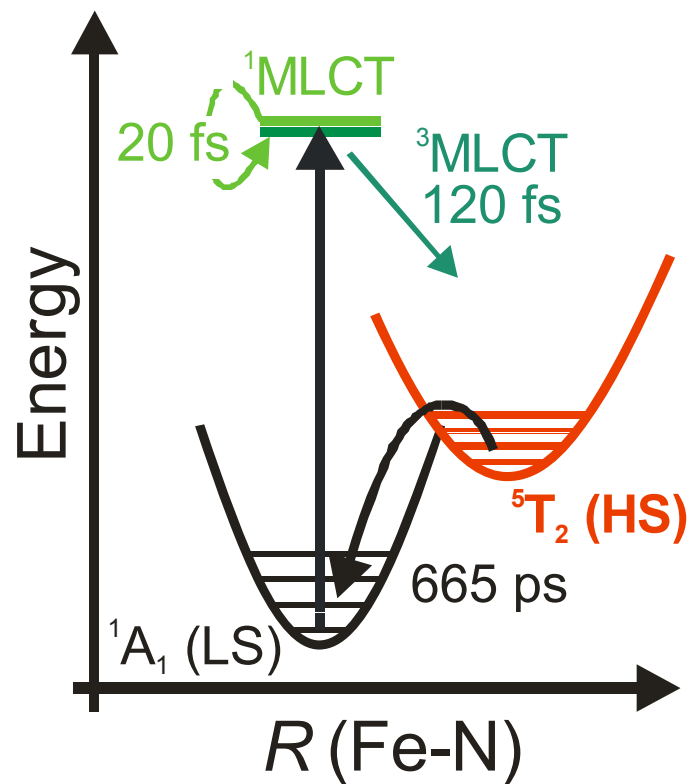
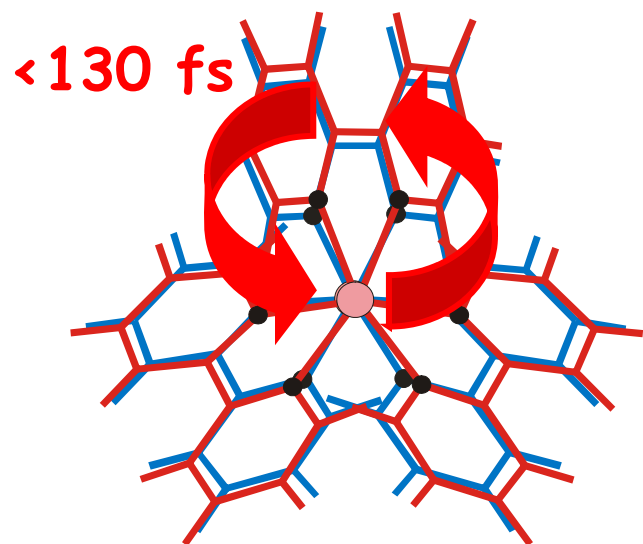
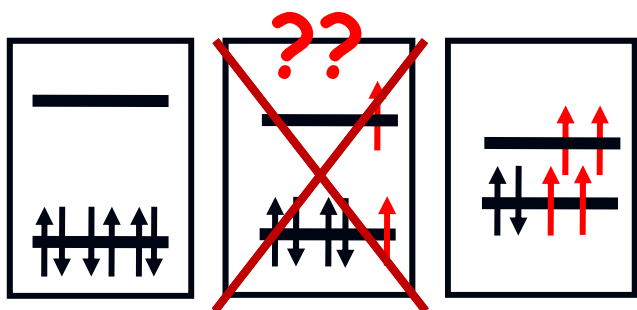
115(10) fs laser pulse

<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* !!

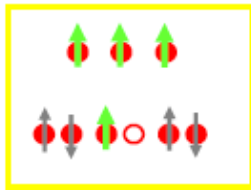
Spin sensitivity



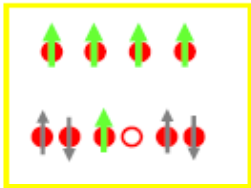
Chemical sensitivity of $K\beta$ Emission



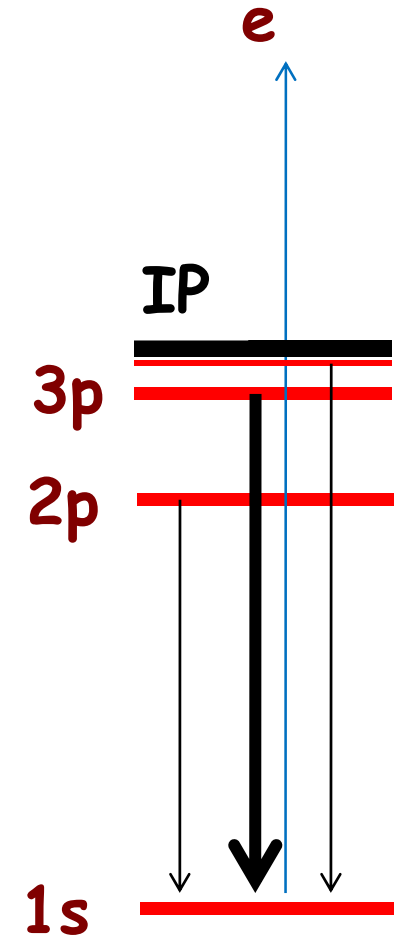
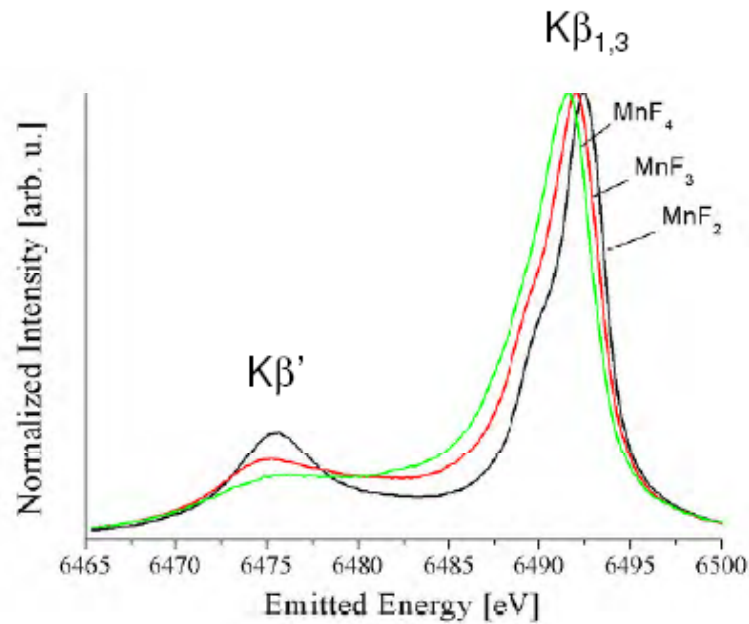
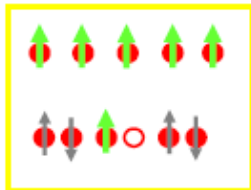
MnF_4 : $S=3/2$



MnF_3 : $S=2$



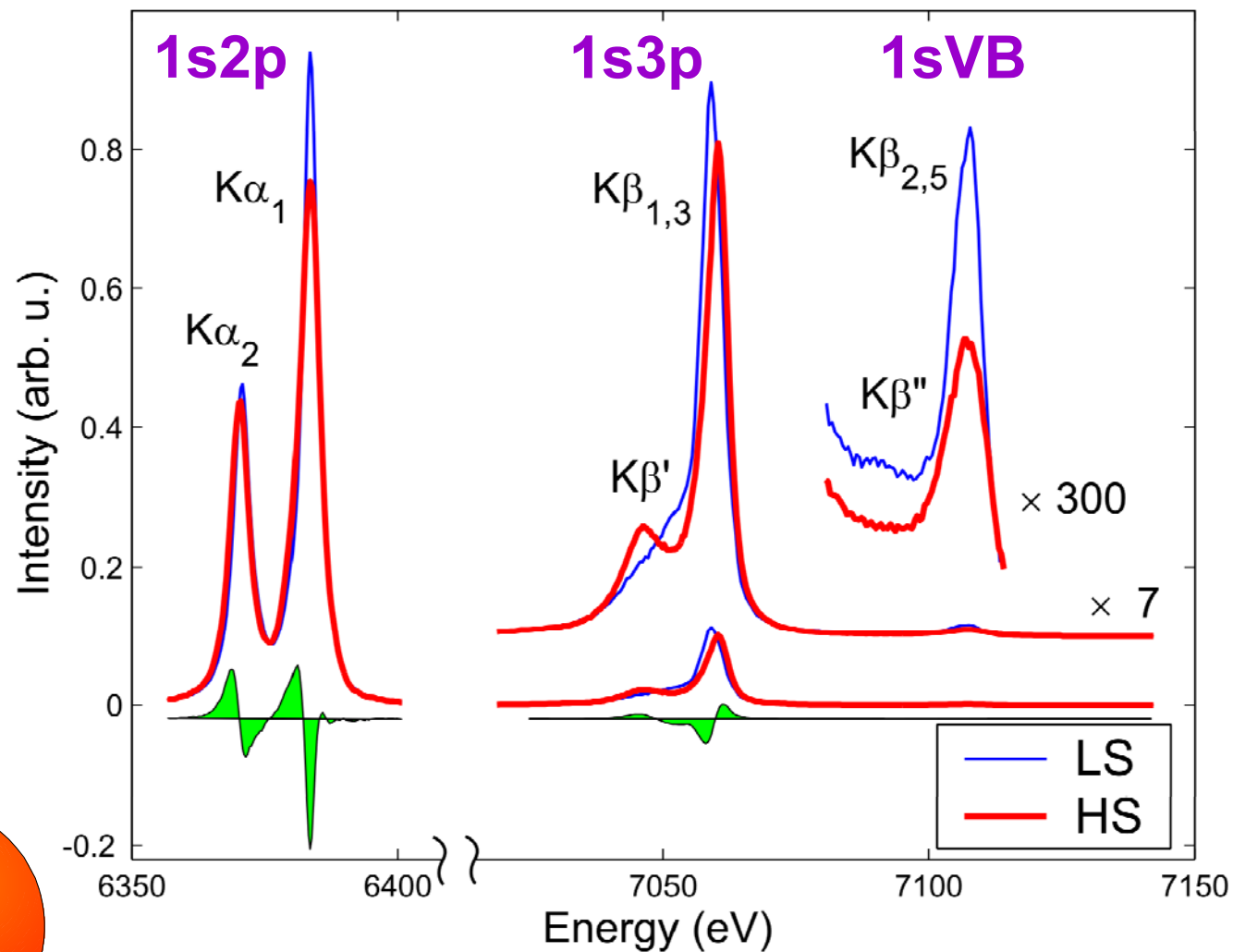
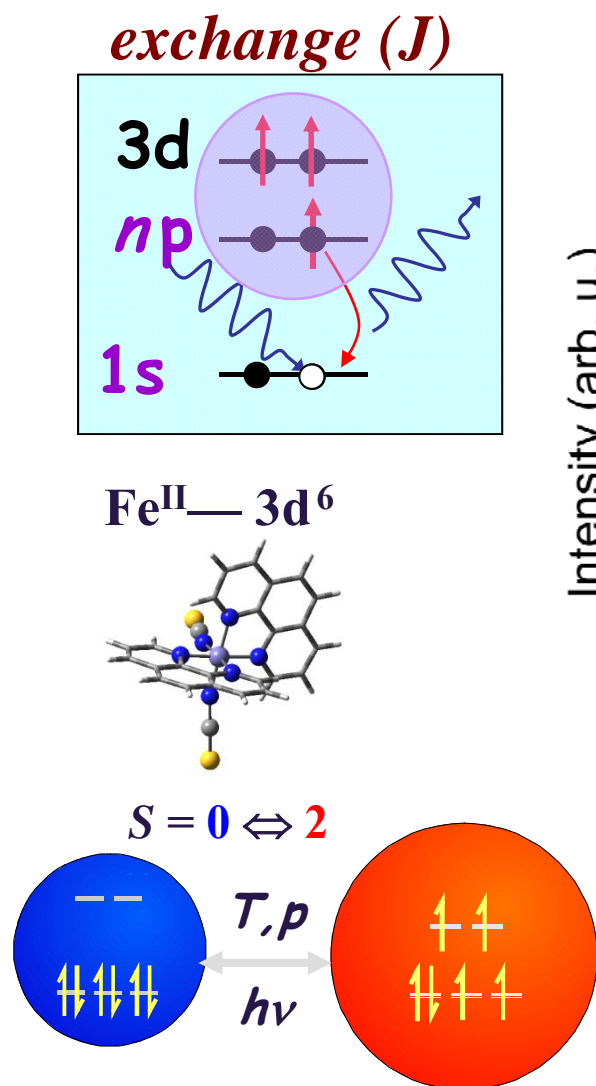
MnF_2 : $S=5/2$



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

*Courtesy: Pieter Glatzel
(ESRF)*

1s XES of a spin transition molecule



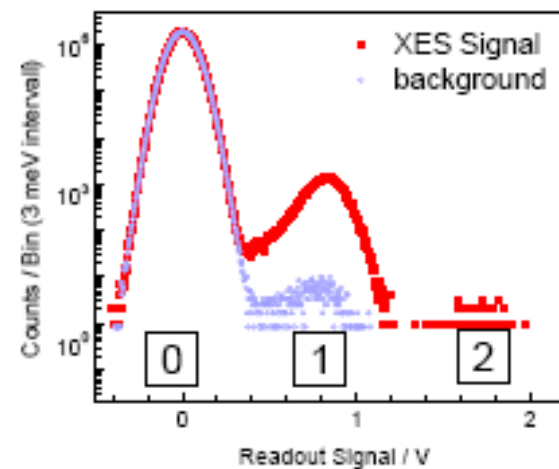
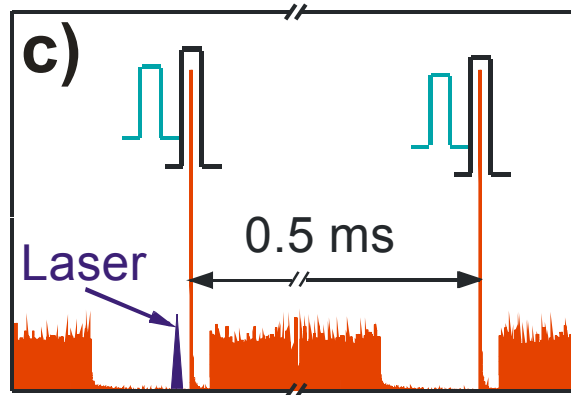
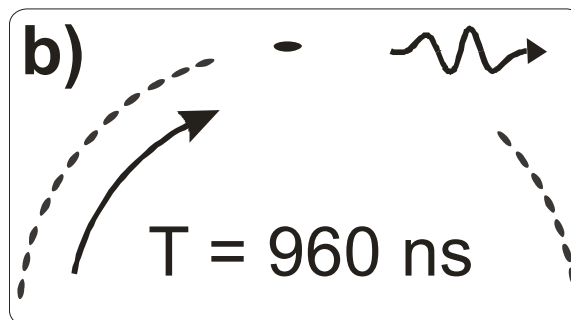
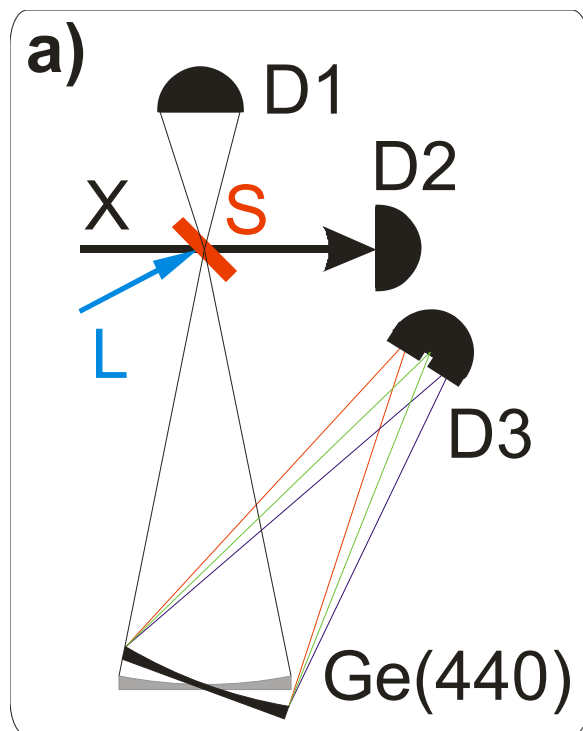
G. Vankó *et al.*, *J. Phys. Chem. B* 110 (2006) 11647

Towards ultrafast X-ray *Emission* Spectroscopy

$10^3 - 10^6$ ph/pulse (100 ps)

10-12 ph/pulse (200 fs)

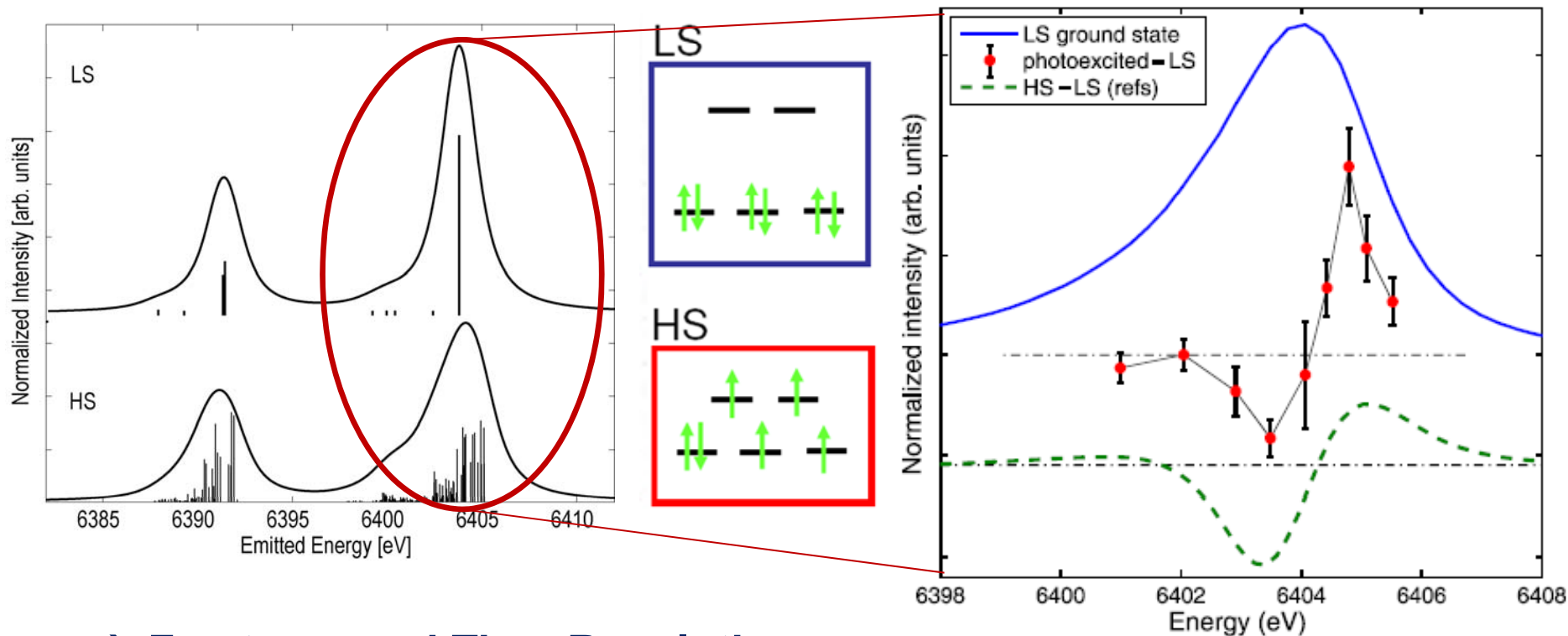
10^{-3} ph/pulse (100 ps XES)



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

Direct spin probing: first TR-XES (ps)

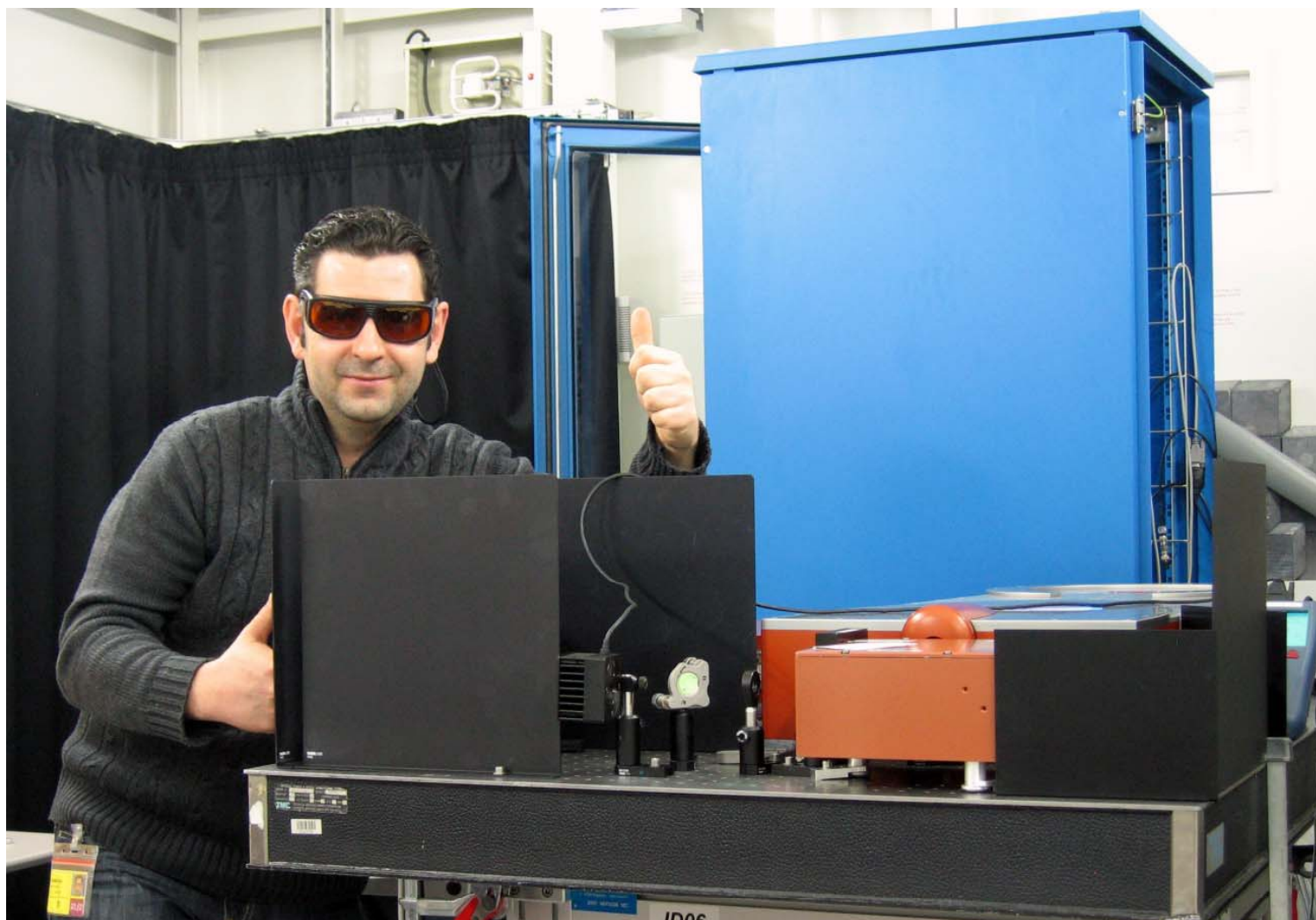
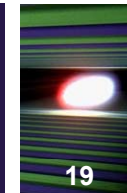
60 ps delay between laser and x-ray pulse



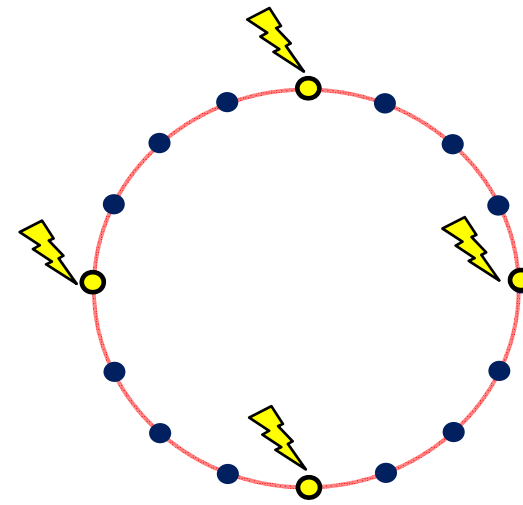
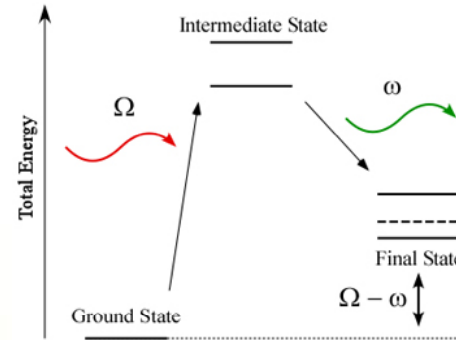
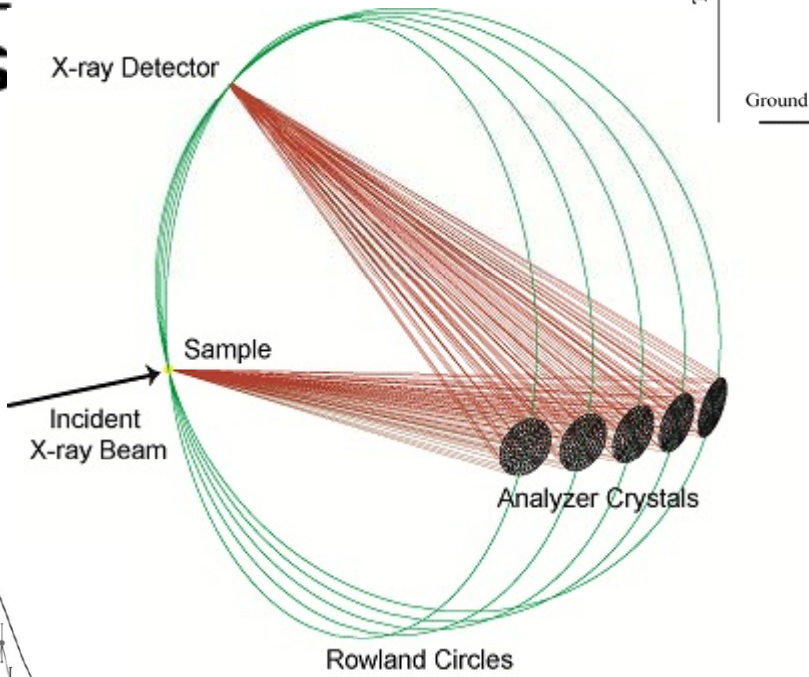
- Femtosecond Time Resolution
- Ideally suited for single wavelength XFEL experiments
- MHz repetition rates !!!!

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

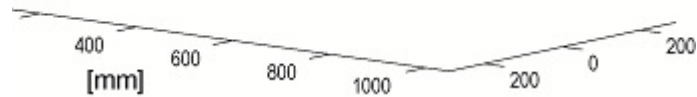
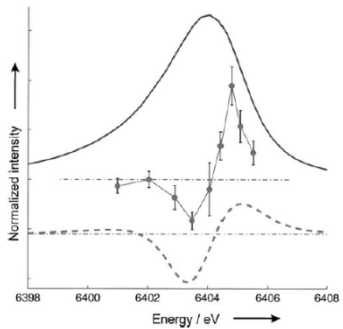
Ready to Pump-Probe at MHz rep-rates!!



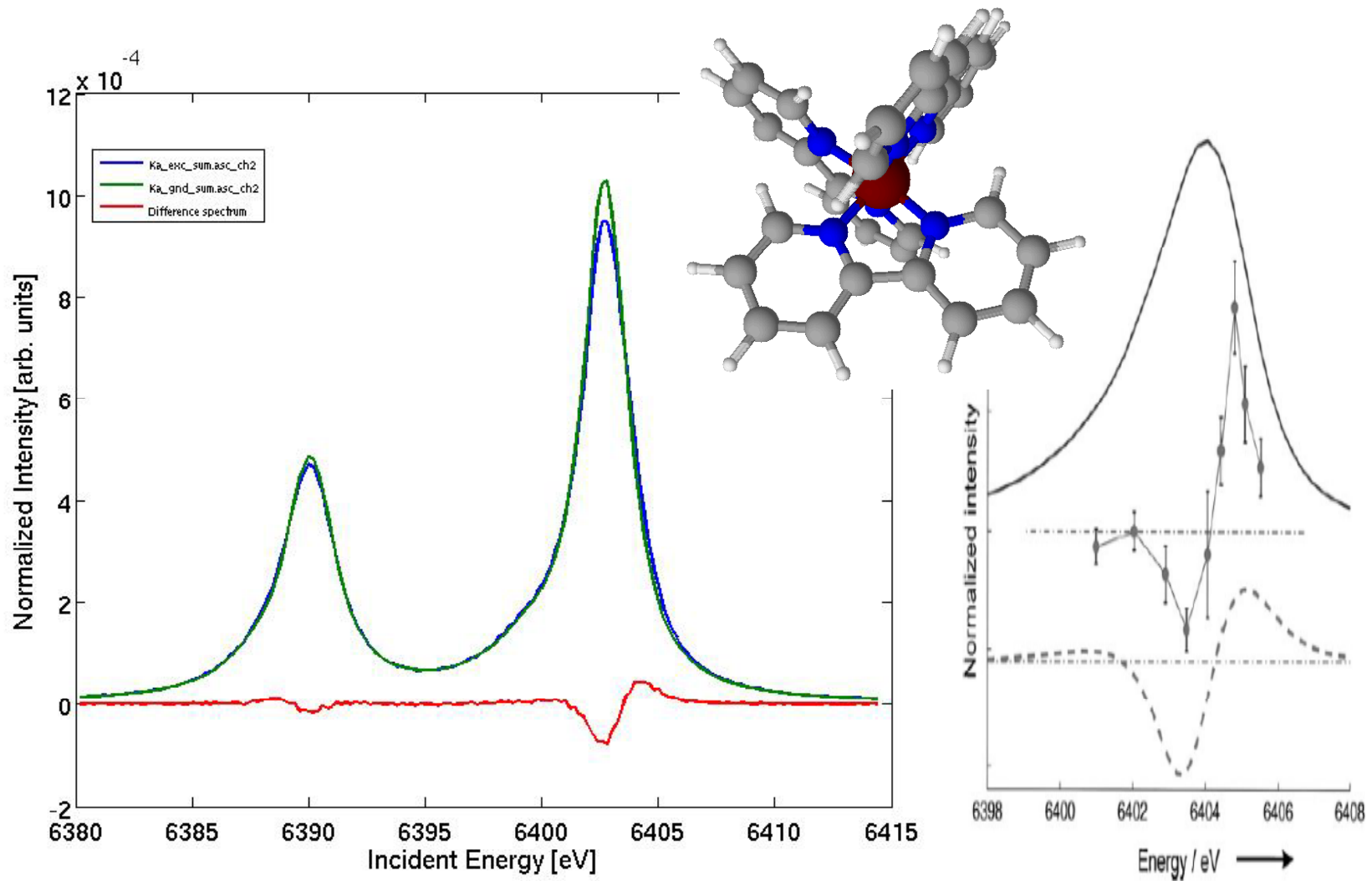
ID26 – X-ray Emission/Absorption Spectroscopy



1.4 MHz



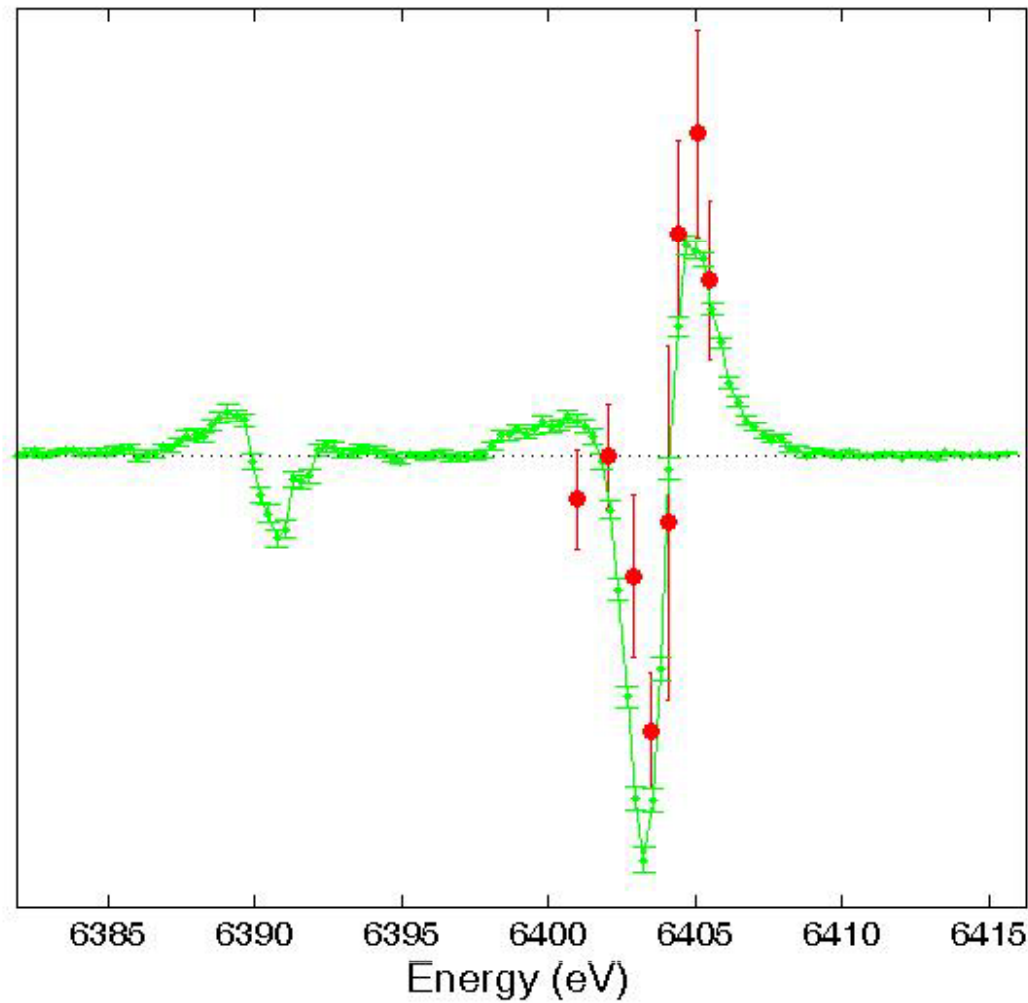
ID26/ESRF (March 2011)



APS, sector 7 (March 2011)



Picosecond K alpha XES at APS



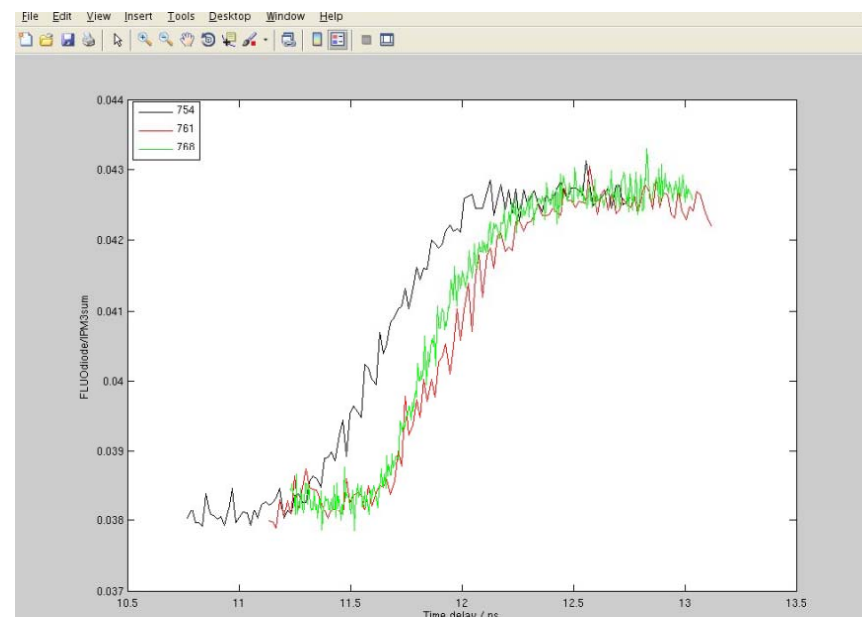
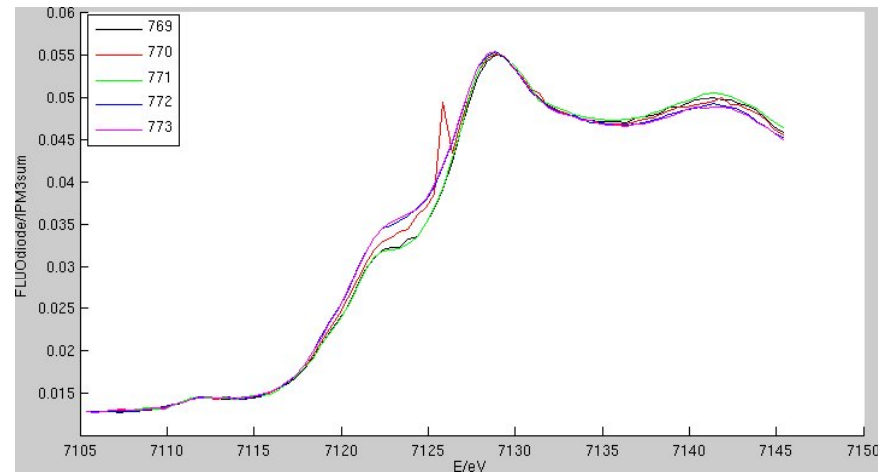
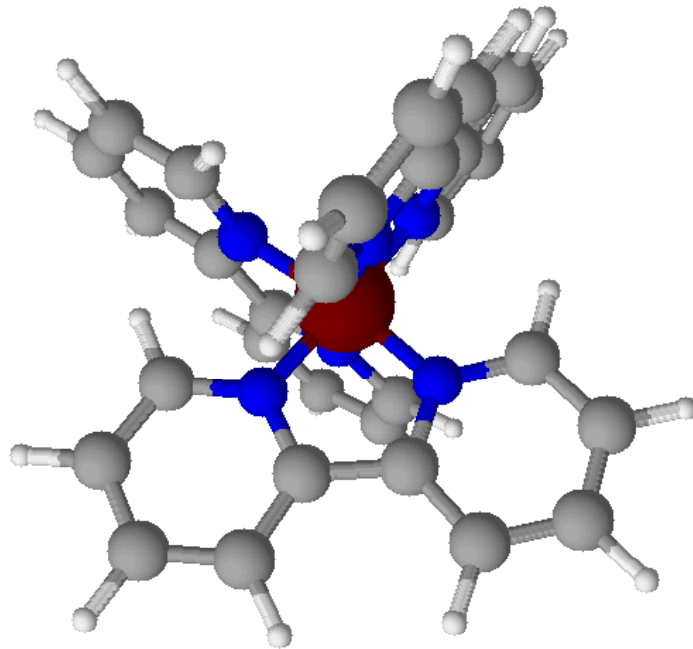
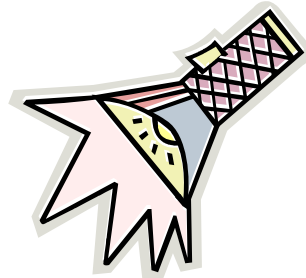
1 kHz pp studies at
SLS
(Angew. Chem. 2010)

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)



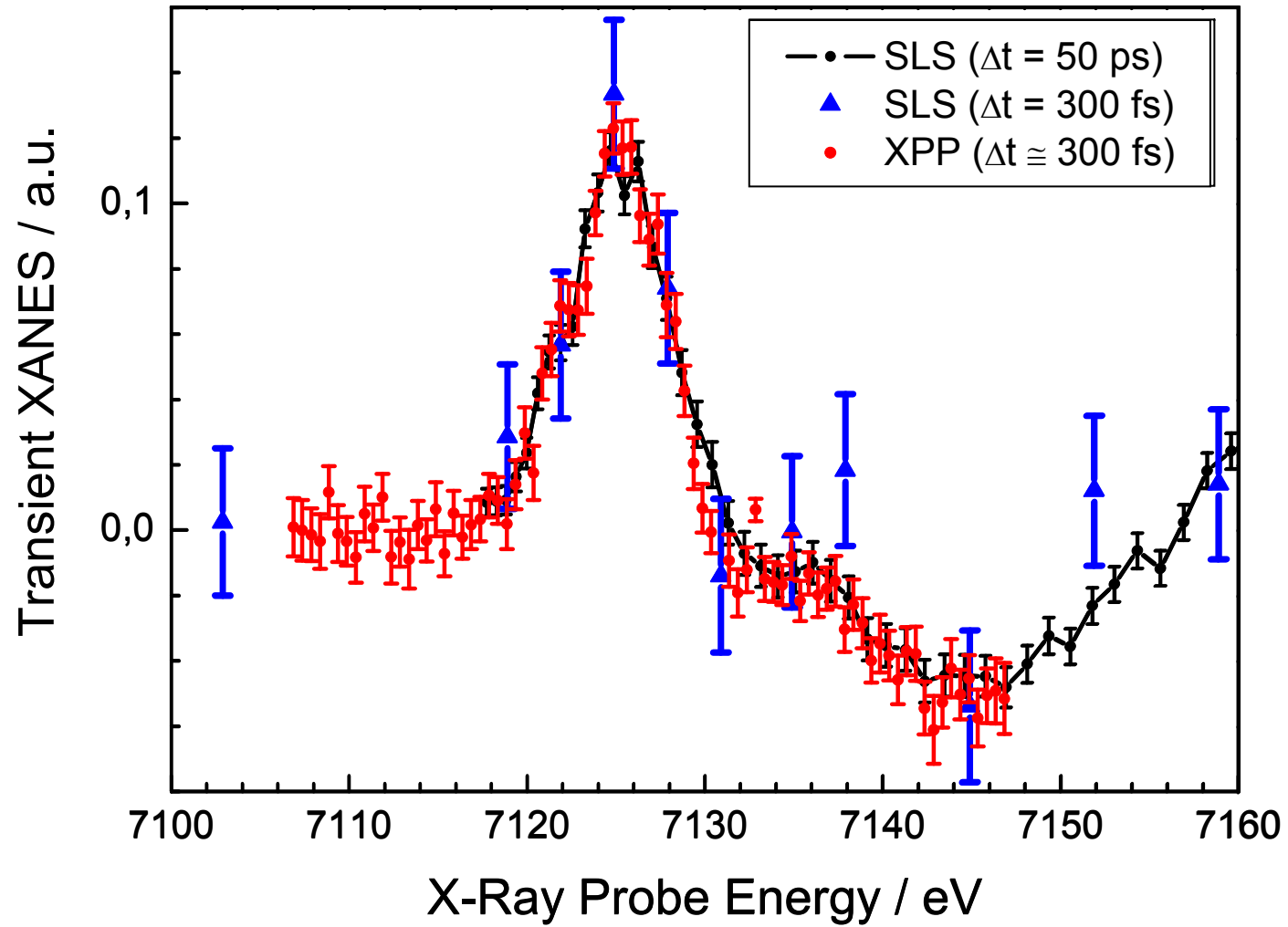
One single „File“ (10 min scan) at LCLS

The screenshot displays the HDFView application interface. The left sidebar shows a tree view of the data structure for file 'xppcom10-r0768.h5'. The main window contains two data tables. The first table, titled 'CalibCycle:0000', lists parameters for 39 cycles. The second table, titled 'data', lists channel and sum values for 30 cycles. A third table in the top right shows 'channel' and 'sum' values for 30 cycles. A plot in the bottom right corner shows 'FLUORESCENCE' vs 'Time delay / ps' with three data series (754, 761, 766).

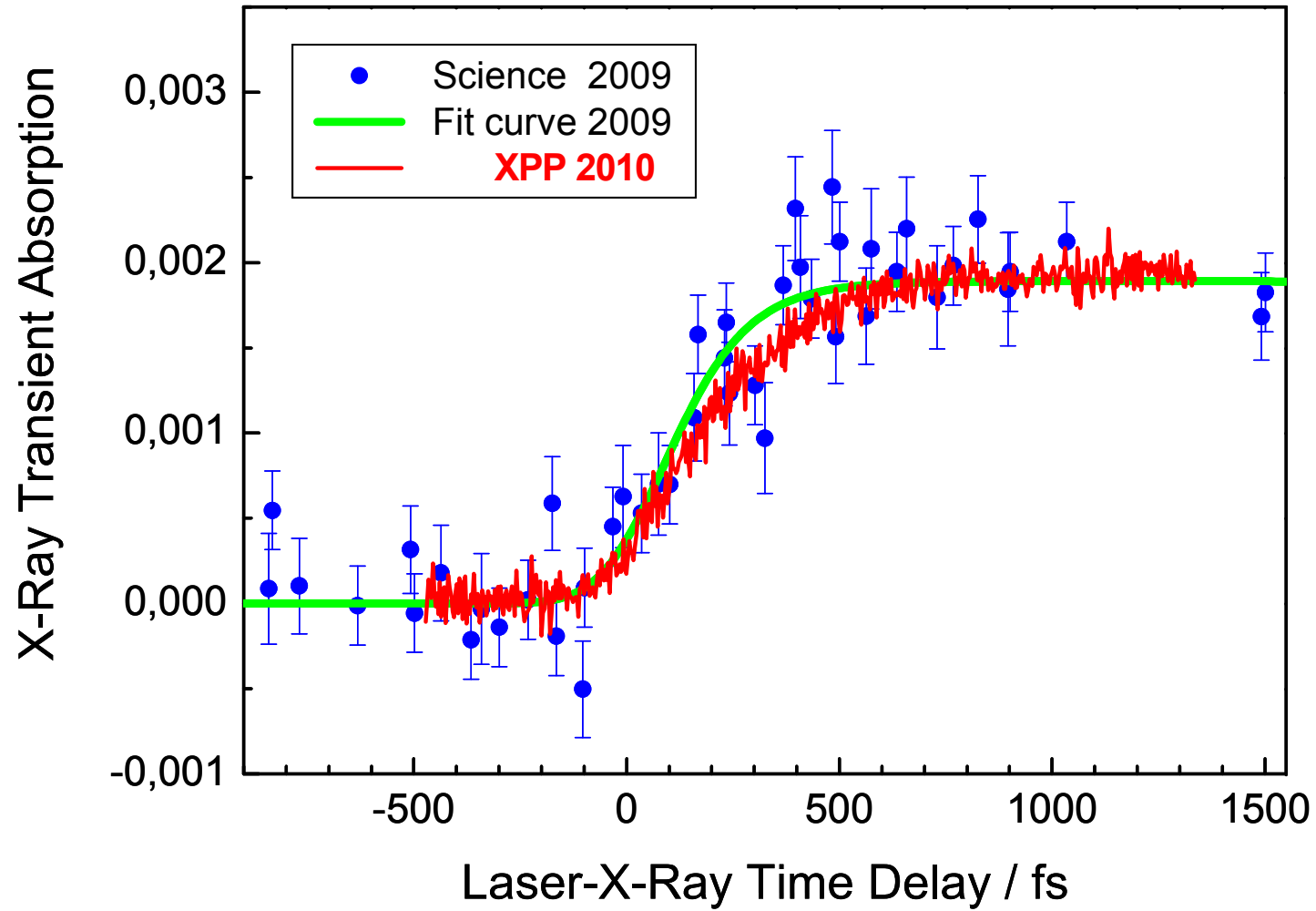
triggerCount	config0	config1	config2	channel0	channel1	channel2	channel3	checksum	channel0Vo	channel1Vo	channel2Vo	channel3Vo	
0	1	9252	0	31250	65533	65535	64256	0	3.2998993	3.3	3.3	3.2355962	
1	2	9252	0	31250	65529	65535	65533	64237	0	3.2996979	3.3	3.2998993	3.2346394
2	3	9252	0	31250	65535	65535	65517	64244	0	3.3	3.3	3.2990937	3.234992
3	4	9252	0	31250	65490	65535	65525	64249	0	3.297734	3.3	3.2994964	3.2352438
4	5	9252	0	31250	65531	65535	65530	64236	0	3.2997985	3.3	3.2997482	3.234589
5	6	9252	0	31250	65521	65532	65511	64234	0	3.299295	3.299849	3.2987914	3.2344885
6	7	9252	0	31250	65528	65535	65535	64251	0	3.2996476	3.3	3.3	3.2353444
7	8	9252	0	31250	65535	65535	65535	64251	0	3.3	3.3	3.3	3.2353444
8	9	9252	0	31250	65510	65535	65529	64233	0	3.298741	3.3	3.2996979	3.2344382
9	10	9252	0	31250	65535	65533	65535	64239	0	3.3	3.2998993	3.3	3.2347403
10	11	9252	0	31250	65535	65535	65535	64236	0	3.3	3.3	3.3	3.234589
11	12	9252	0	31250	65535	65535	65522	64252	0	3.3	3.3	3.2993455	3.2353947
12	13	9252	0	31250	65535	65535	65535	64241	0	3.3	3.3	3.3	3.2346409
13	14	9252	0	31250	65535	65535	65535	64237	0	3.3	3.3	3.3	3.2346394
14	15	9252	0	31250	65535	65524	65527	64232	0	3.3	3.299446	3.2995973	3.2343876
15	16	9252	0	31250	65535	65535	65535	64251	0	3.3	3.3	3.3	3.2353444
16	17	9252	0	31250	65531	65535	65533	64234	0	3.2997985	3.3	3.2998993	3.2344885
17	18	9252	0	31250	65500	65533	65519	64217	0	3.2982376	3.2998993	3.2991943	3.2336323
18	19	9252	0	31250	65535	65535	65535	64242	0	3.3	3.3	3.3	3.2348912
19	20	9252	0	31250	65532	65535	65535	64252	0	3.299849	3.3	3.3	3.2353947
20	21	9252	0	31250	65514	65523	65521	64233	0	3.2989426	3.2989426	3.2989426	3.2348912
21	22	9252	0	31250	65509	65533	65531	64236	0	3.2986908	3.3	3.3	3.2348912
22	23	9252	0	31250	65535	65535	65535	64236	0	3.3	3.3	3.3	3.2348912
23	24	9252	0	31250	65535	65535	65535	64255	0	3.3	3.3	3.3	3.2348912
24	25	9252	0	31250	65535	65535	65535	64250	0	3.3	3.3	3.3	3.2348912
25	26	9252	0	31250	65535	65533	65535	64241	0	3.3	3.3	3.3	3.2348912
26	27	9252	0	31250	65535	65535	65535	64234	0	3.3	3.3	3.3	3.2348912
27	28	9252	0	31250	65535	65535	65535	64074	0	3.3	3.3	3.3	3.2348912
28	29	9252	0	31250	65514	65539	65511	64240	0	3.2989426	3.2989426	3.2989426	3.2348912
29	30	9252	0	31250	65491	65529	65525	64235	0	3.2977843	3.3	3.3	3.2348912
30	31	9252	0	31250	65500	65528	65508	64229	0	3.2982376	3.3	3.3	3.2348912
31	32	9252	0	31250	65533	65535	65530	64251	0	3.2998993	3.3	3.3	3.2348912
32	33	9252	0	31250	65535	65535	65535	64238	0	3.3	3.3	3.3	3.2348912
33	34	9252	0	31250	65515	65531	65532	64222	0	3.2989929	3.3	3.3	3.2348912
34	35	9252	0	31250	65535	65535	65535	64236	0	3.3	3.3	3.3	3.2348912
35	36	9252	0	31250	65535	65535	65535	64255	0	3.3	3.3	3.3	3.2348912
36	37	9252	0	31250	65530	65535	65523	64243	0	3.2997482	3.3	3.3	3.2348912
37	38	9252	0	31250	65524	65535	65535	64236	0	3.299446	3.3	3.3	3.2348912
38	39	9252	0	31250	65535	65535	65535	64248	0	3.3	3.3	3.3	3.2348912

channel	sum	xpos		
0	7.1525574E-7	-9.9897385E-5	0.0641047...	
1	2.0217896E-4	-9.9897385E-5	0.0653636...	
2	-9.9897385E-5	-9.9897385E-5	0.0655145...	
3	0.0021660328	-9.9897385E-5	0.0671260...	
4	1.01566315E-4	-9.9897385E-5	0.0654645...	
5	6.0510635E-4	5.1021576E-5	0.06717634...	
6	2.5248528E-4	-9.9897385E-5	0.0646083...	
7	-9.9897385E-5	-9.9897385E-5	0.06425595...	
8	0.0011589527	-9.9897385E-5	0.06872311...	
9	-9.9897385E-5	7.1525574E-7	0.06496072...	
10	-9.9897385E-5	-9.9897385E-5	0.06501126...	
11	-9.9897385E-5	-9.9897385E-5	0.0648601...	
12	-9.9897385E-5	-9.9897385E-5	0.06475949...	
13	-9.9897385E-5	-9.9897385E-5	0.06496096...	
14	-9.9897385E-5	4.5394897E-4	0.06616826...	
15	-9.9897385E-5	-9.9897385E-5	0.06425595...	
16	1.01566315E-4	-9.9897385E-5	0.06541395...	
17	0.0016624928	7.1525574E-7	0.0686366...	
18	-9.9897385E-5	-9.9897385E-5	0.06470919...	
19	5.1021576E-5	-9.9897385E-5	0.0643665...	
20	9.57489E-4	5.042653E-4	6.05	0.0675287...
21	0.001209259	7.1525574E-7	1.	0.0666224...
22	-9.9897385E-5	-9.9897385E-5	0.06501126...	
23	-9.9897385E-5	-9.9897385E-5	0.06405449...	
24	-9.9897385E-5	-9.9897385E-5	0.06430626...	
25	-9.9897385E-5	7.1525574E-7	0.0648601...	
26	-9.9897385E-5	-9.9897385E-5	0.0651118...	
27	-9.9897385E-5	-9.9897385E-5	0.0731687...	
28	9.57489E-4	2.0217896E-4	0.0.	0.0673778...
29	0.002157265	2.0217896E-4	0.	0.06808281...
30	0.0016624928	3.533633E-4	0.	0.06893873...

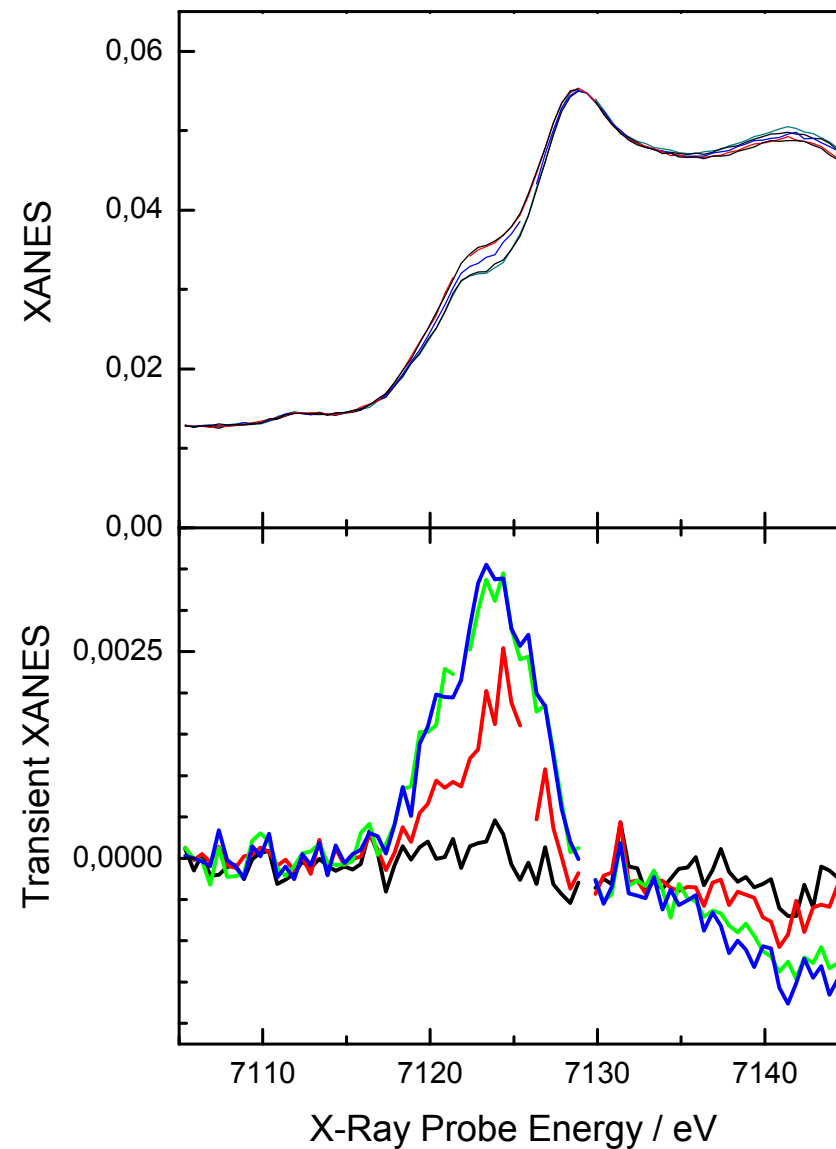
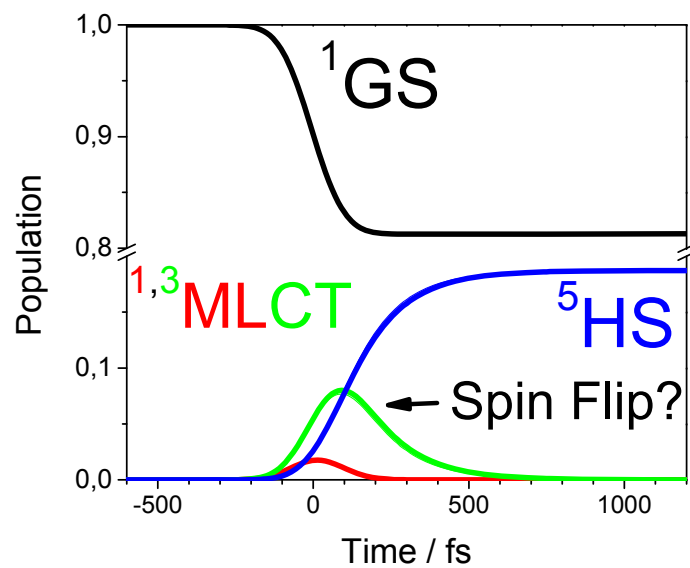
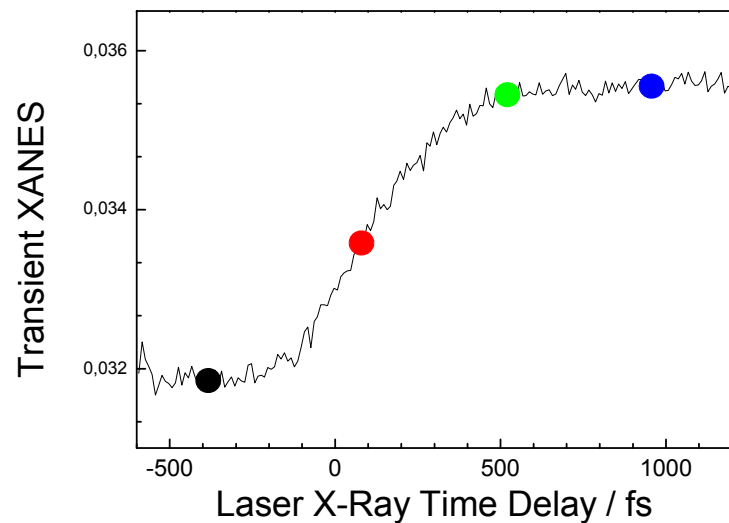
Oct 2010: XPP commissioning



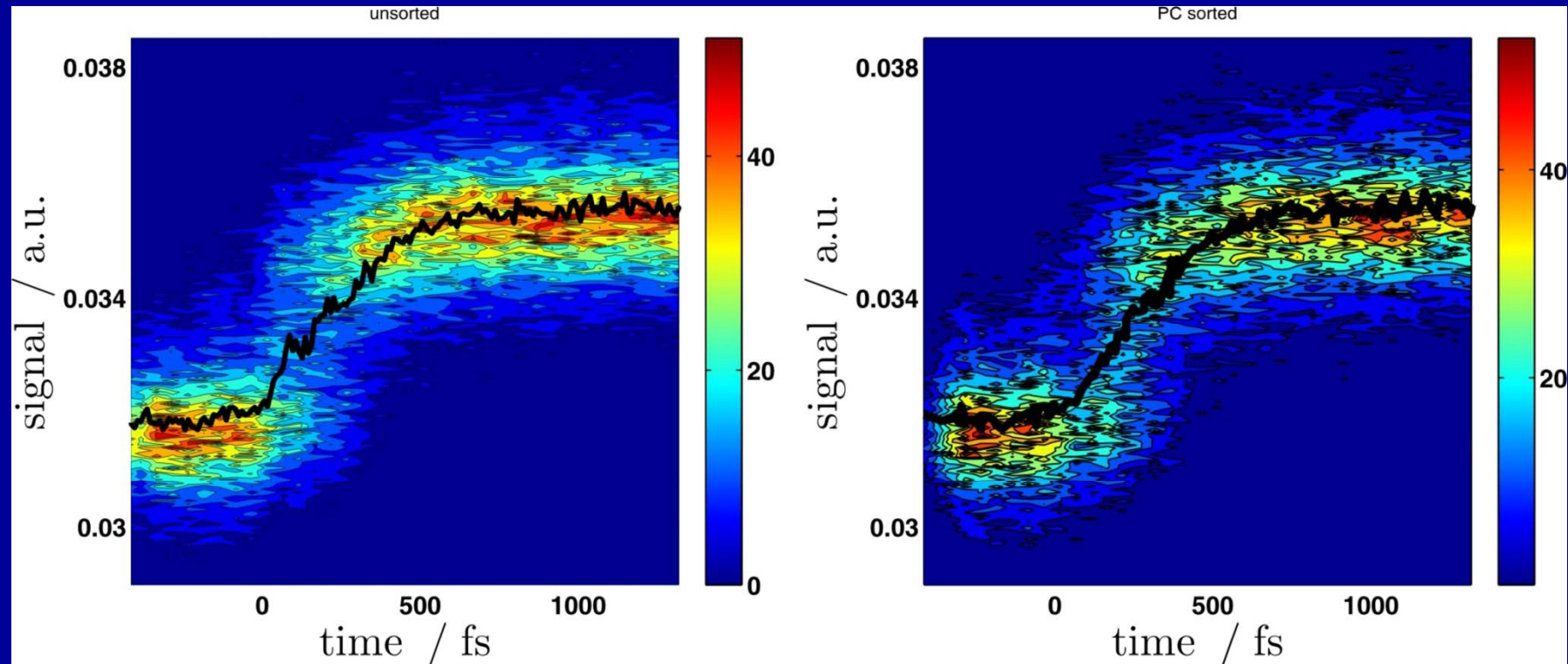
Real-Time Traces



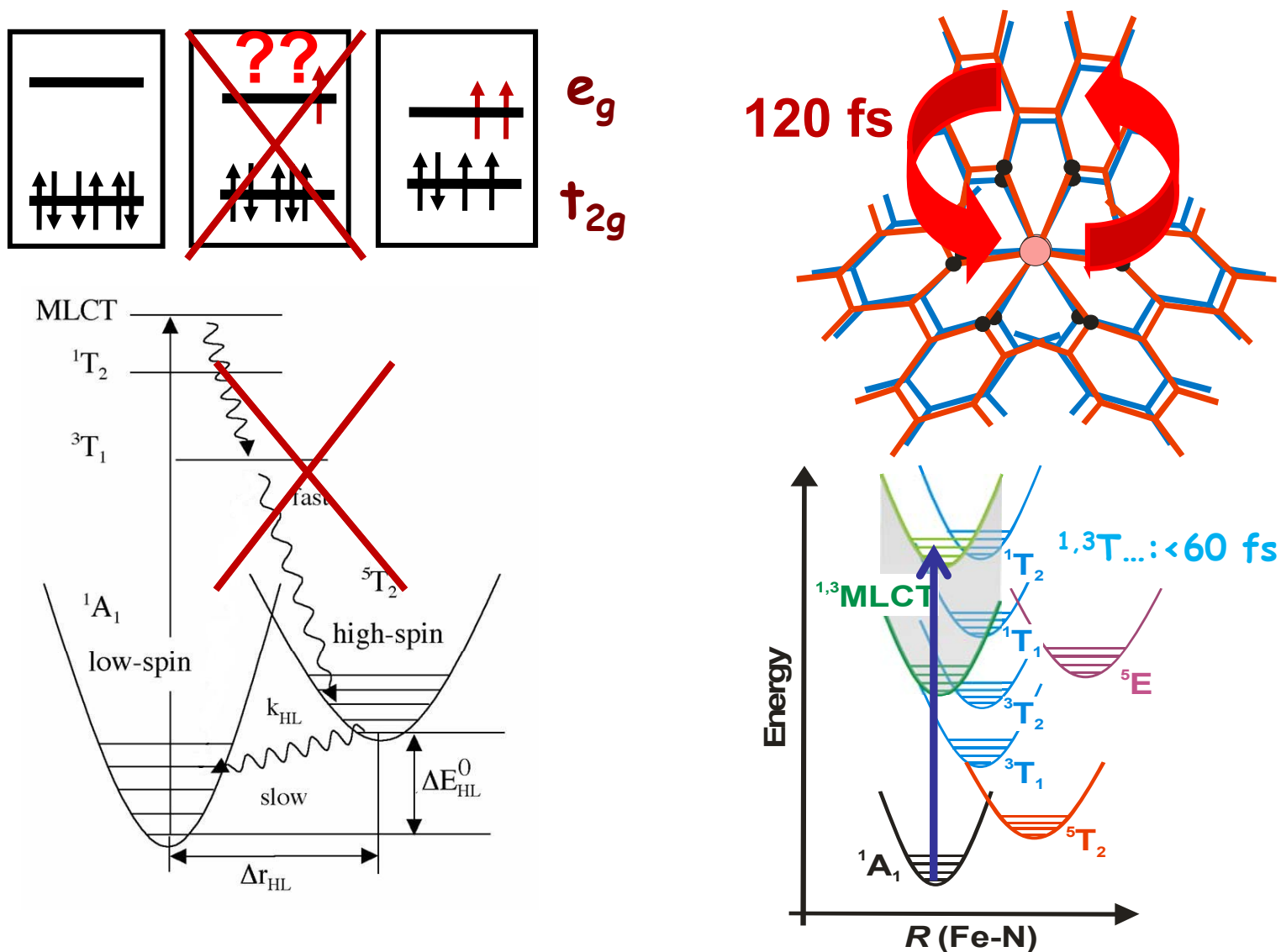
Transient Spectra around Time Zero



Looking into the raw data...



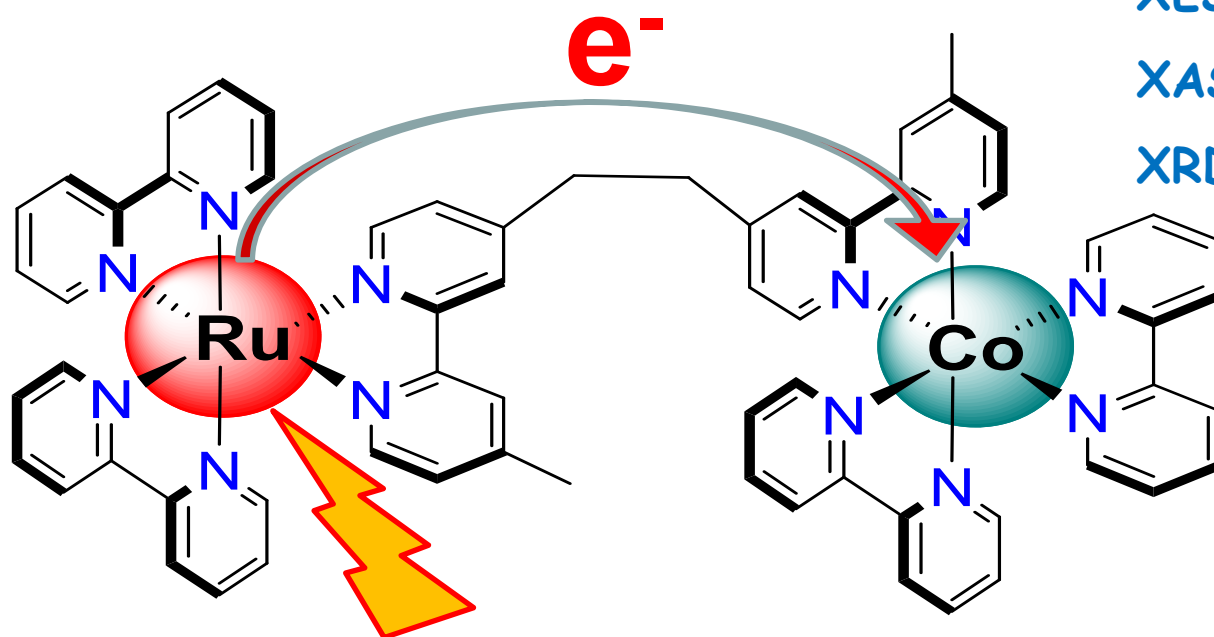
Summary of combined optical/XAS studies



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

Collaboration:

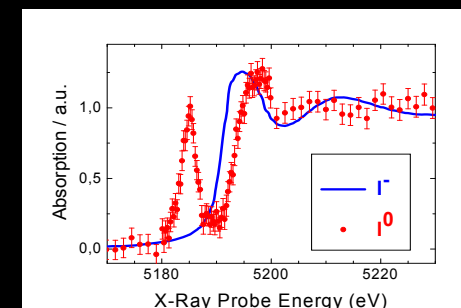
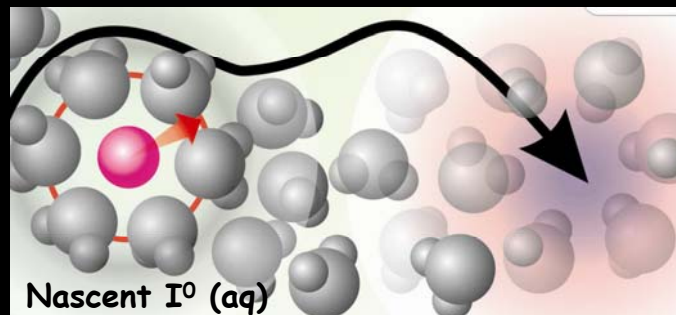
- M. Nielsen (Copenhagen)
- V. Sundström (Lund)
- G. Vanko (Budapest)
- P. Glatzel (ESRF)
- A. Meents (Petra3)
- R. Abela (SwissFEL)

- 1) Ru(II) \rightarrow Ru(III)
- 2) IVR + e^- -transport
- 3) Co(III) \rightarrow Co(II)
- 4) Co(II) LS \rightarrow HS

- (XAS, XES, optical)
- (XRD, optical)
- (XAS, XES, optical)
- (XAS, XES)

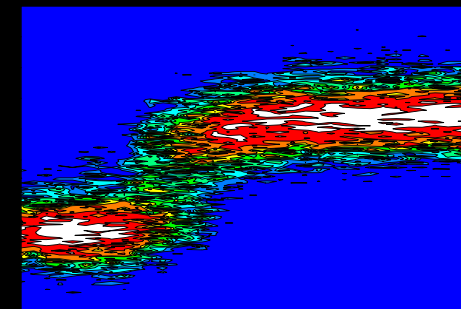
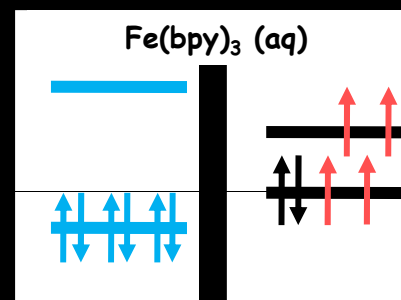
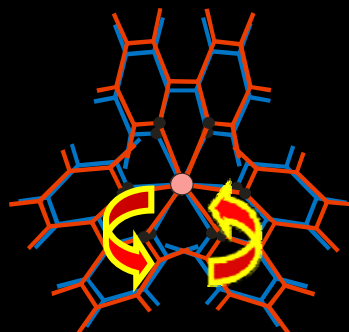
Conclusions

Towards Solvation Dynamics

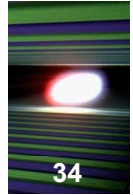


- We can follow the sequence of events from 300 fs onwards
Even the (few) ps time scale we do not fully understand
→ Theoretical input important
- We need to know how things evolve between 0-300 fs
→ New experiments are planned (theory required)

Light-Induced Spin Crossover



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



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- Martin Meedom Nielsen
- Kristoffer Haldrup

Lund University

- Villy Sundström
- Sophie Canton
- Jens Uhlig
- Grigory Smolentsev

SwissFEL

- Rafael Abela

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- Pieter Glatzel
- Erik Gallo

LCLS (SLAC)

- David Fritz, Marco Cammarata

Argonne National Lab (APS)

- Steven Southworth
- Anne-Marie March (MHz laser)
- Gilles Doumy
- Elliot Kanter
- Dipanwita Ray
- Robert Dunford
- Linda Young

KFKI Budapest

- György Vankó

European XFEL Facility

- Wojciech Gawelda
- Andreas Galler

K. Gaffney, L. X. Chen, H. Ihee
(XPP Oct 2010)
