



Femtosecond X-Ray Experiments (FXE)

Andreas Galler
Wojciech Gawelda
Christian Bressler

FXE Workshop

Budapest Dec 9-11, 2009

- 93 Participants
- XRD: S. Johnson (SLS)
M. Bargheer (Potsd.)
- XAS/XES/IXS: P. Glatzel(ESRF),
A. Soldatov (Rostov), G. Vankó
(Budapest), D. Grolimund (SLS),

■ http://www.xfel.eu/events/workshops/fxe_workshop_2009/

European XFEL **International workshop series on the science and instrumentation at the European XFEL: Femtosecond X-Ray Experiments**

9 – 11 December 2009
Hotel Benczür
Budapest, Hungary

The Instrument for Femtosecond X-Ray Experiments (FDE) will exploit the unique time structure and intensity of the European XFEL for structural dynamics studies of molecules, biological species and solid state materials. This instrument will allow new investigations of electronic and atomic structure changes that are not possible today. It will thus supplement to several fields of contemporary research including chemical and biological dynamics and solid state physics. Advanced X-Ray Spectroscopies and Scattering will be implemented with femtosecond time resolution, but also techniques that require the intense average XFEL flux are foreseen.

This meeting forms part of a series of workshops aiming to discuss scientific cases and designs of the European XFEL instruments. It features a number of invited lectures on scientific and technical aspects, followed by group sessions providing opportunities for extended discussions from broad user communities on the construction of the FDE instrument and its capabilities.

Local organizers
György Vankó, Dénes Nagy
KFKI RMKI, Budapest, Hungary

International programme committee
Matias Bargheer, University of Potsdam, Germany
Christian Bressler, European XFEL Project Team, Hamburg, Germany
Gyula Faigel, MTA SZFKI, Budapest, Hungary
Pieter Glatzel, ESRF, Grenoble, France
Steven Johnson, Swiss Light Source, Villigen, Switzerland
Martin Nielsen, University of Copenhagen, Denmark
Alexander Soldatov, Rostov University, Russian Federation
Simone Techert, MPI Göttingen, Germany



■ ■ ■ **Young scientists bursaries**
Deadline extended to 1 Nov 2009
(for details see website)

■ ■ ■ www.xfel.eu/fxe-workshop-2009
Registration deadline
01 Nov 2009

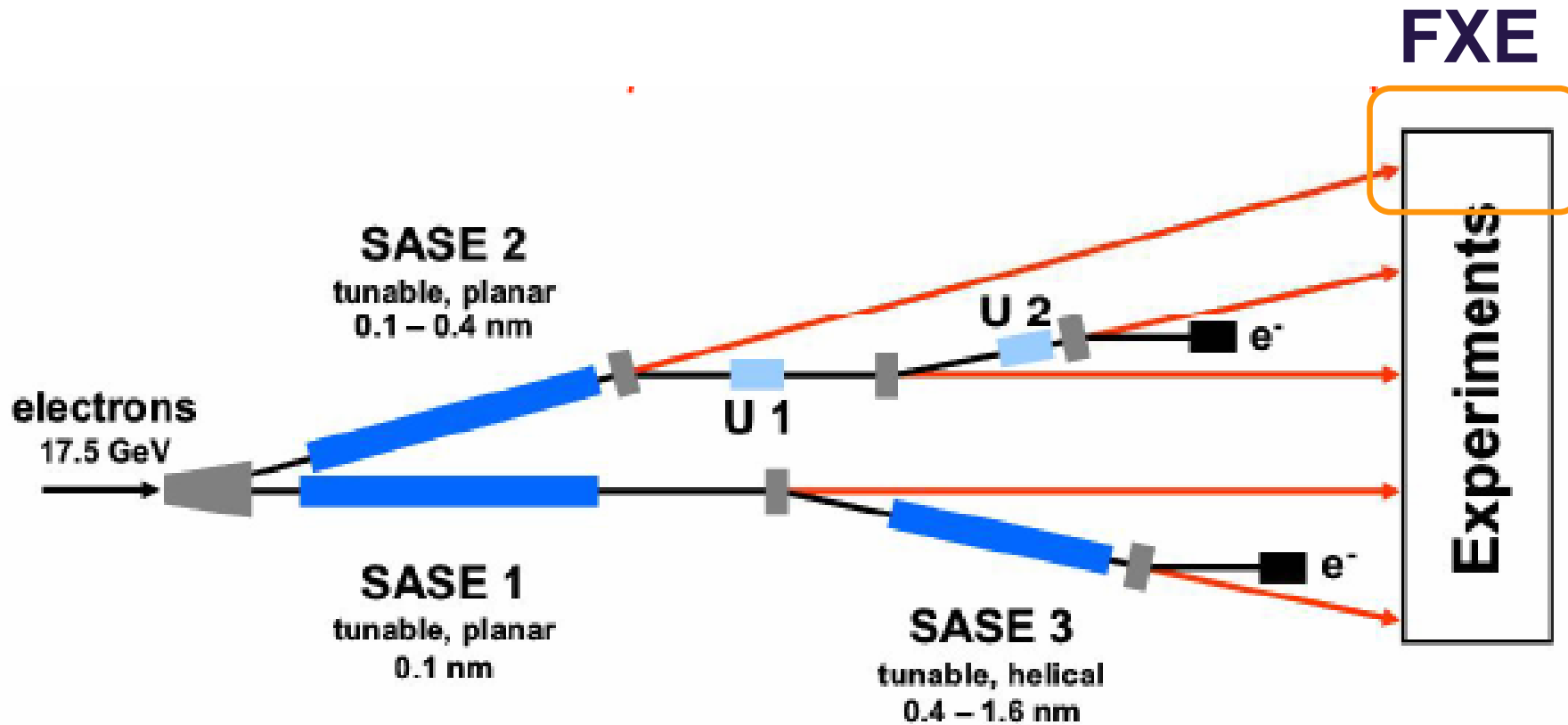
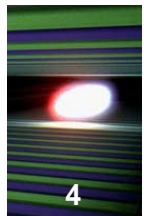
The workshop is co-funded by the European Commission through the Pre-XFEL grant. This will allow free of charge access to the workshop.

Hosting the workshop and support from institutions of the Hungarian Academy of Sciences (MTA SZFKI, KFKI RMKI, and the Hungarian Synchrotron Committee), is gratefully acknowledged.

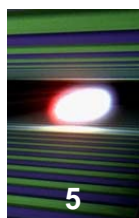
Organisational issues
Imke Gemballies
imke.gemballies@xfel.eu
European XFEL
Hamburg, Germany



- Application Areas
 - ultrafast chemical dynamics (biology)
 - solid state dynamics (phase transitions, spin conversion)
- Combine XRD with x-ray spectroscopies
 - global (local) structural information
 - electronic and spin information
 - all with fs time resolution
- Flexible incoming beam
 - 0.1 – 0.5 mm diameter (gas phase/cluster → Xtals)
 - rectangular profile (liquid jets, dispersive XANES)
- Endstation should simultaneously allow
 - XRD (LPD, AGIPD)
 - XES/XAS/IXS (1D suitable)
- and include all-optical diagnostics (pp, fs-fluor,...)

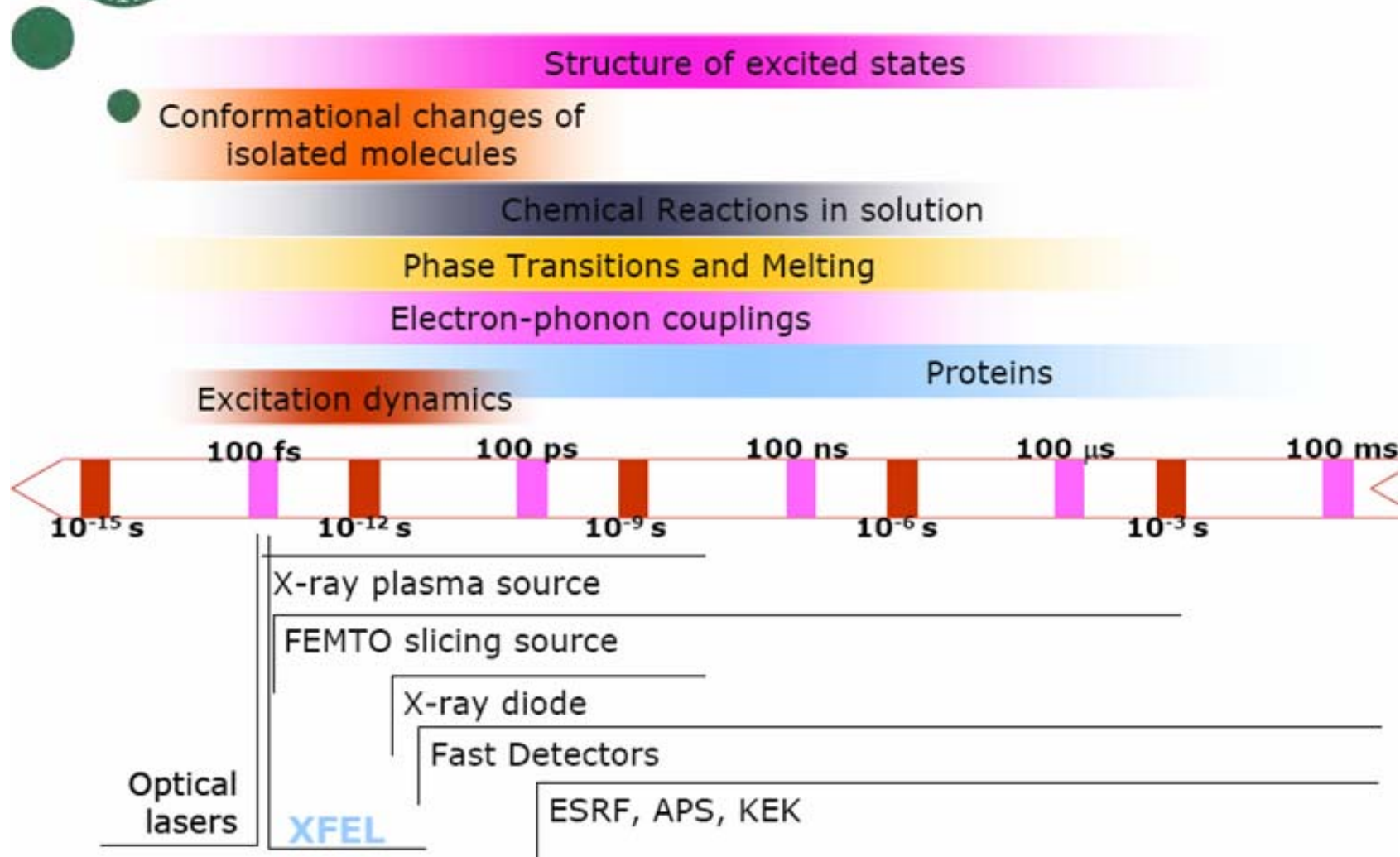


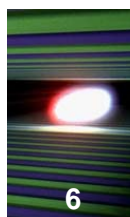
from TDR 2006



Timescales and X-ray Sources

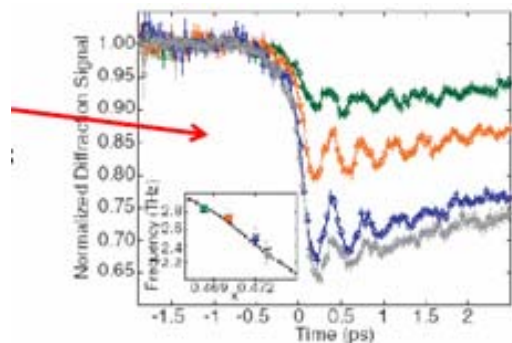
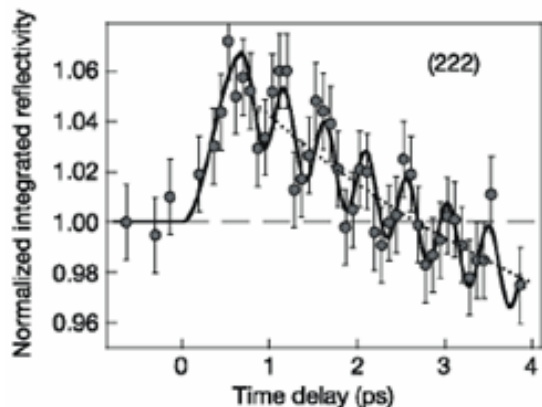
Molecular
Movies





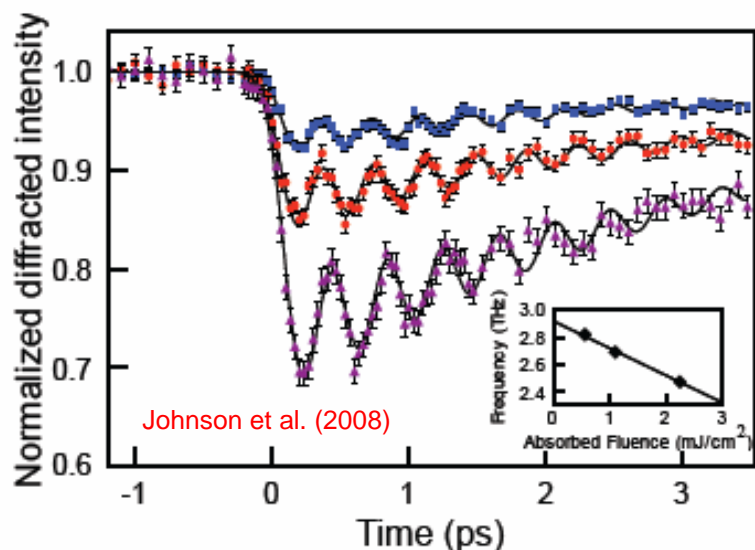
Physics:

- Coherent phonons in Bi



Fritz et al., Science 315, 633 (2007)

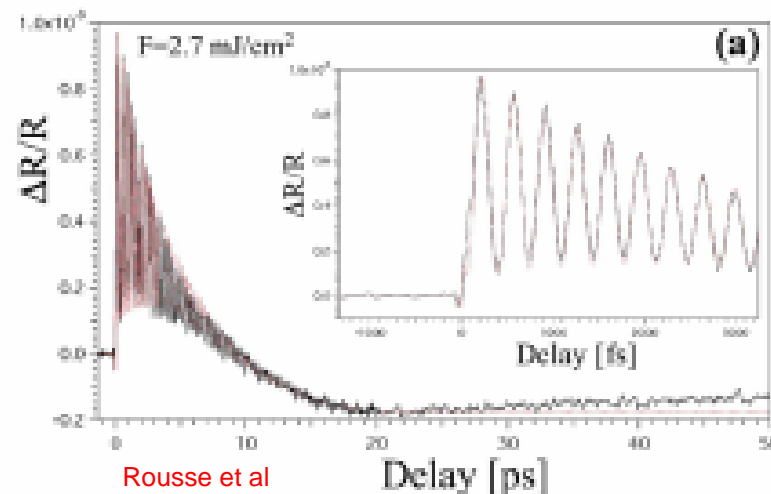
K. Sokolowski-Tinten et al.,
Nature 422, 287 (2003)



Johnson et al. (2008)

PRL 100, 027404 (2008)

PHYSICAL REV



Rousse et al

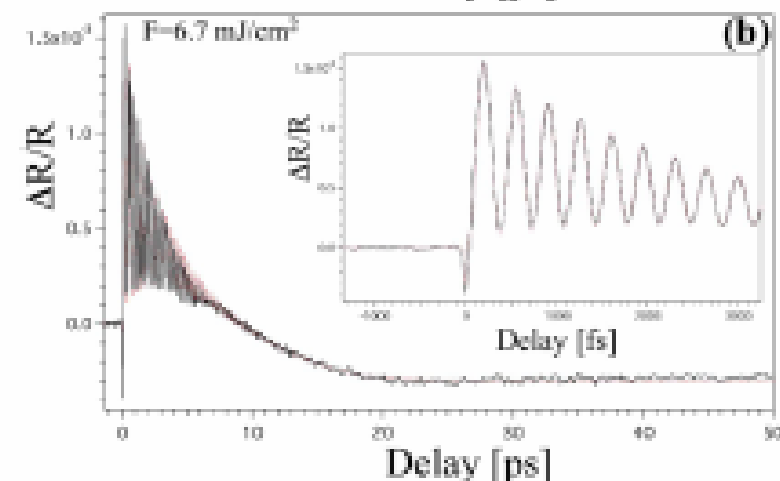
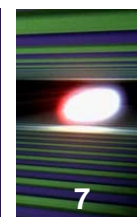
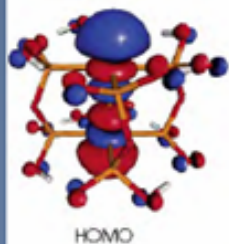
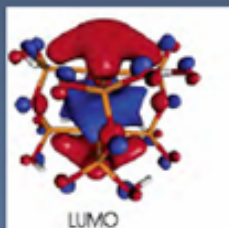
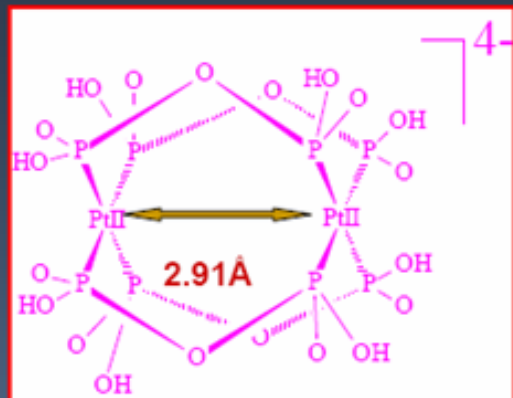


FIG. 1 (color online). Comparison between the experimental [solid (dark) line] and theoretical [dashed (red) line] behavior of the transient reflectivity: (a) excitation flux 2.7 mJ/cm² and (b) excitation flux 6.7 mJ/cm².



$[Pt_2 (P_2O_5H_2)_4]$ 'PtPop'

50 μ s lifetime at 17K



Contraction of Pt-Pt on excitation:

Diffraction

Solid State

Kim et al 2002, 17K: **0.29(8)Å**

Ozawa et al 2003 54K: **0.23(4) Å**

Solution (aqueous)

Christensen et al 2009 RT: **0.24(6)Å**

EXAFS

Solution (ethanol)

van der Veen et al 2009 RT: **0.31(5) Å**

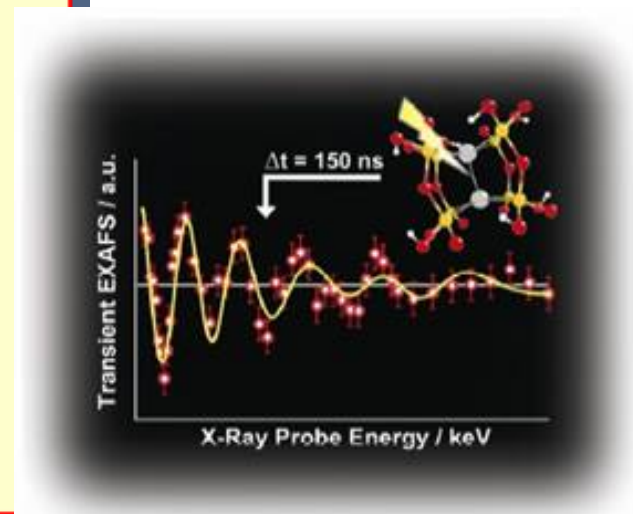
Spectroscopy

Solid State

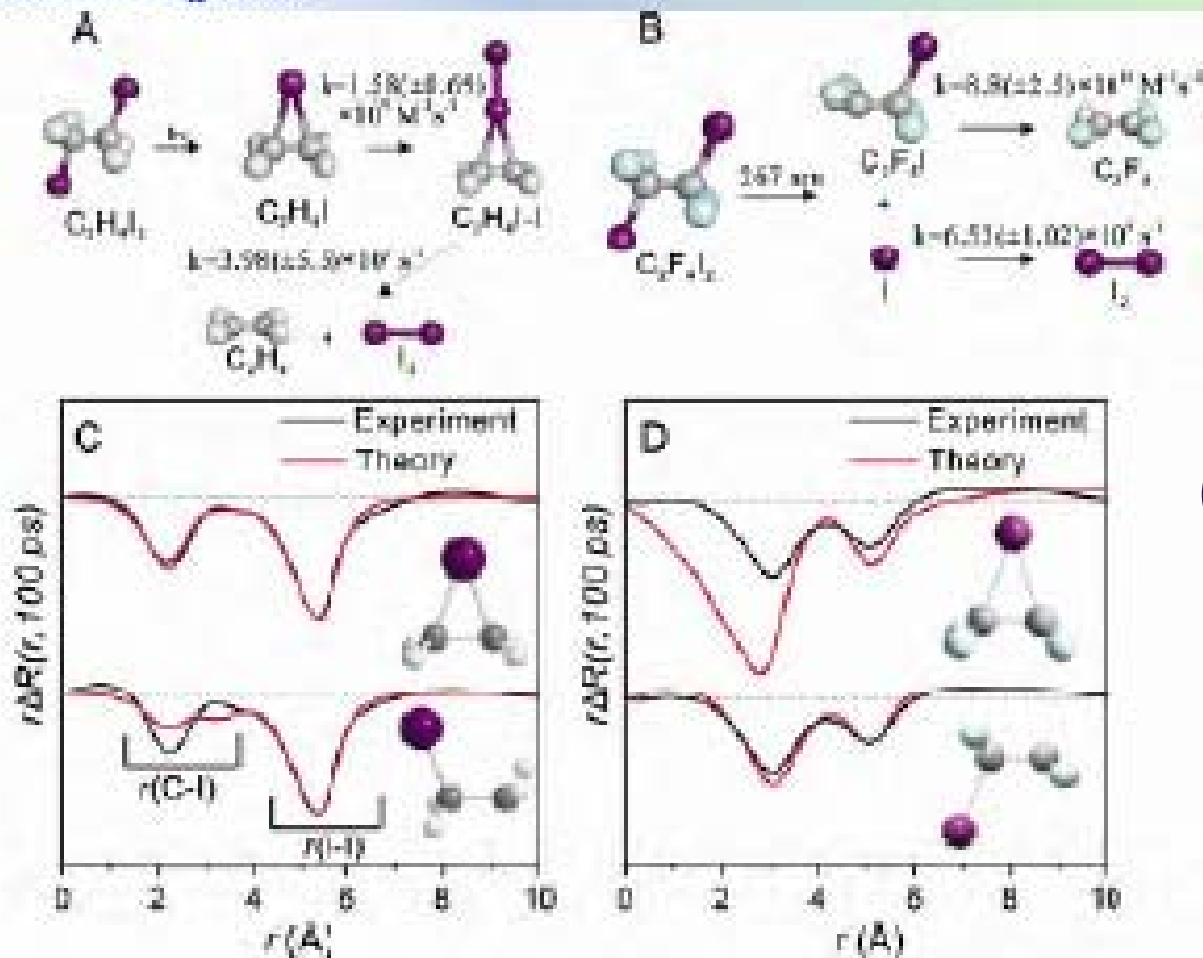
Rice and Gray 1983: **0.21 Å**

Solution (acetonitrile)

Leung et al 1999: **0.225 Å**



Center for Time-Resolved Diffraction



Science, 309, 1223-1227 (2005)

JACS, 130, 5834-5835 (2008)

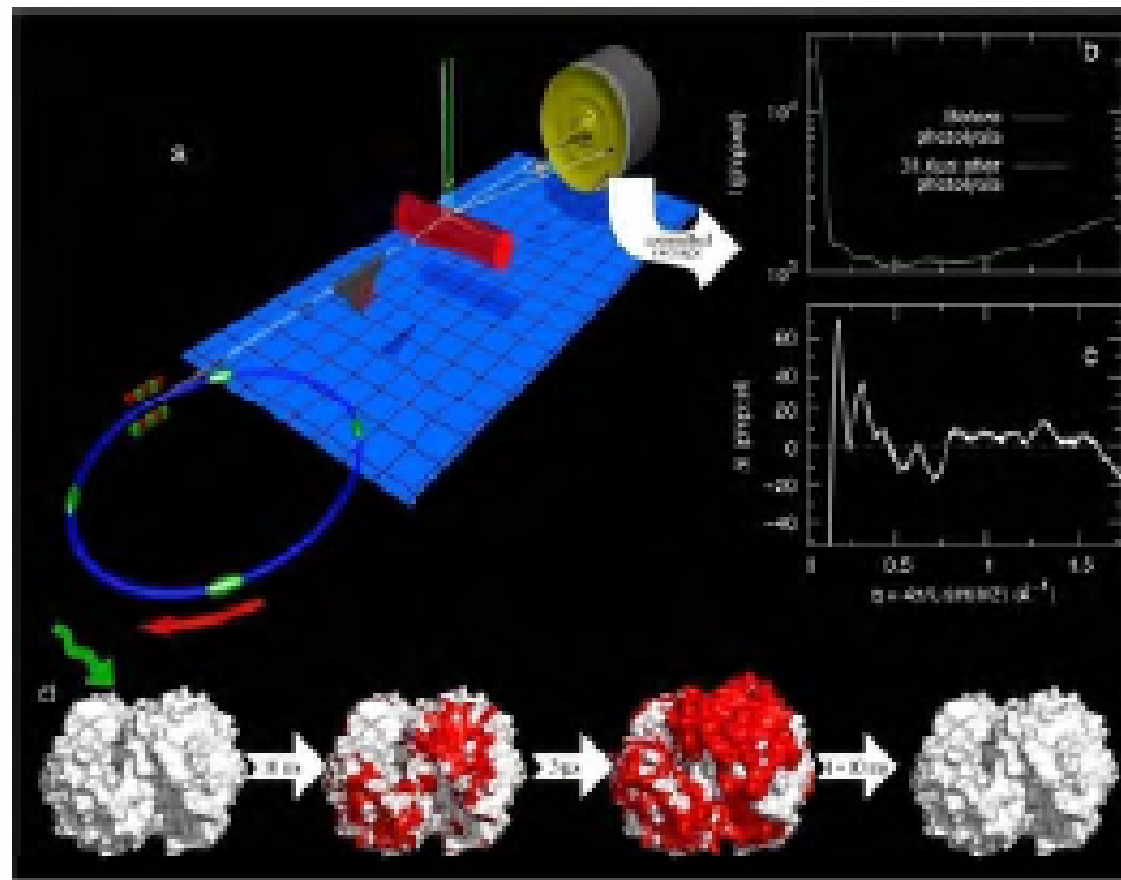
KAIST H. Ihee

Liquid
Phase

Gas
Phase

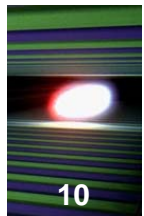
Center for Time-Resolved Diffraction

Time-Resolved WAXS (TR-WAXS)



Nature Methods, 5, 881-887 (2008) (COVER in the October Issue)

KAIST H. Ihee



"Boundary conditions" for XFEL experiments



Referring to C. Bresslers "boundary-conditions" synopsis

$\Delta E/E \sim 0.1\%$ OK

Experiments are easiest, which can be done

- without any monochromator
- with commercial XRD detector pixel sizes (although 2D detectors still need to address the burst mode), or commercial curved Xtals for XES
- moderate spot sizes ($> 0.1 \text{ mm}$)

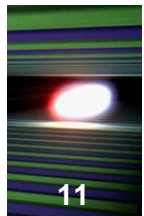
Low demands on angular resolution, 1 mm^2 pixels OK

Experiments that can deal with burst mode operation are very attractive.

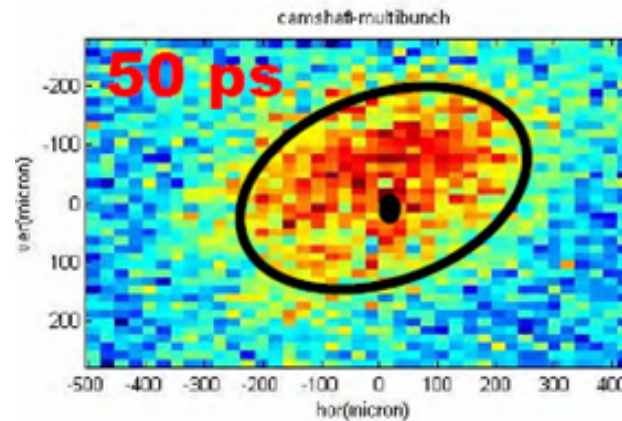
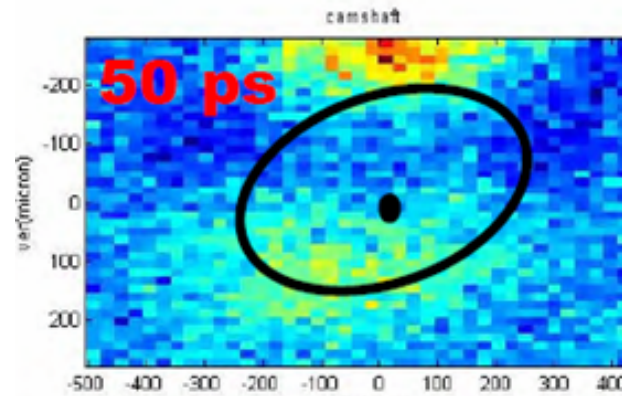
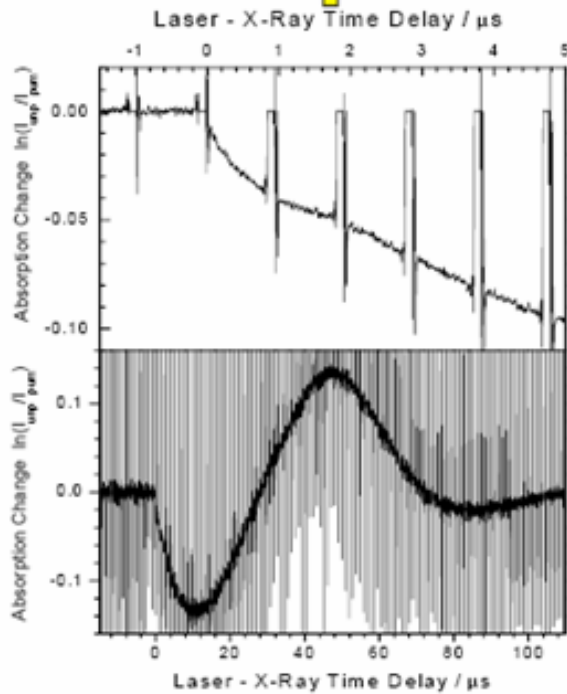
$\sim 0.5 \text{ mm}^2$ OK

Some significant challenges in this respect!

-Mainly to do with heating of sample and 5 MHz refresh

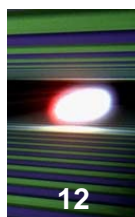


Lateral Pump-Probe

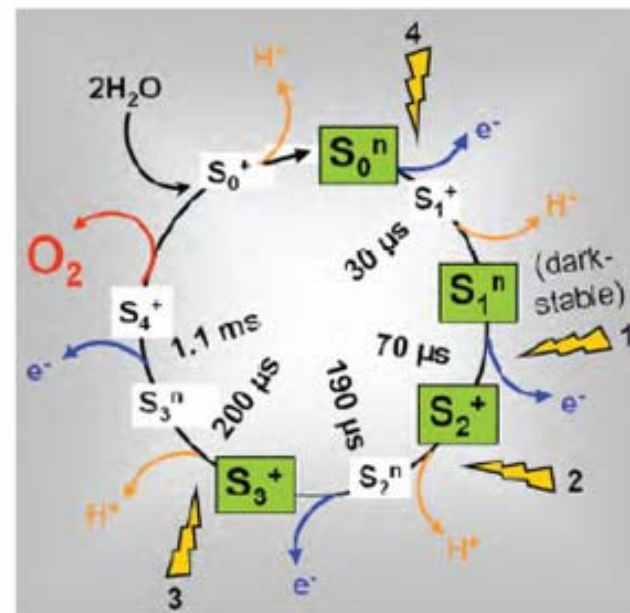
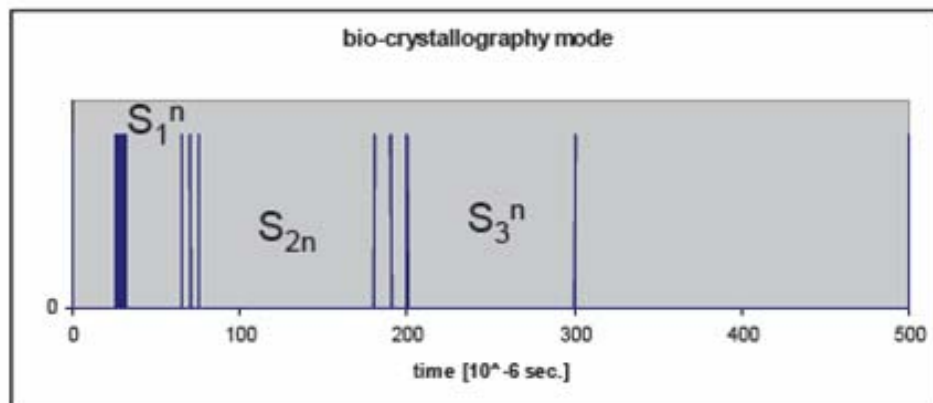
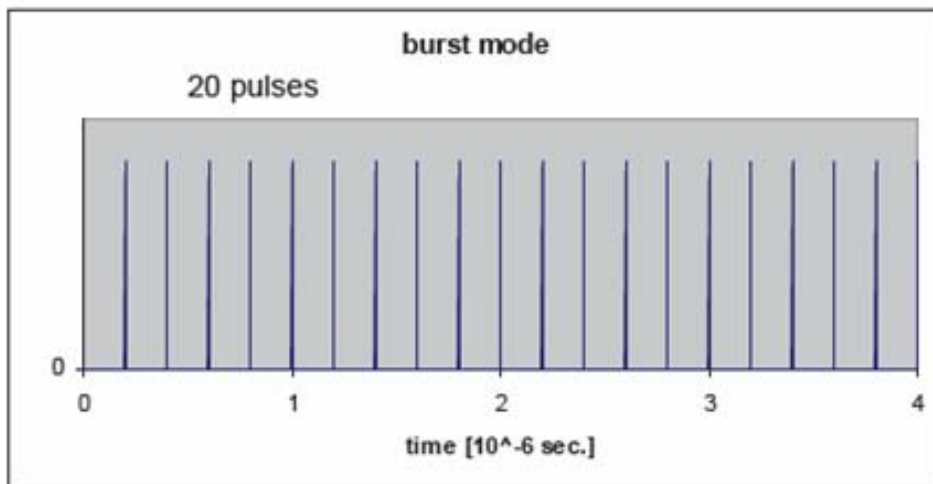


XAFS can correct for sample fluctuations...

Gawelda et al.: to be published (2010)



Bunch train structure for biological crystallography



Tolerable dose for organic / biological molecules

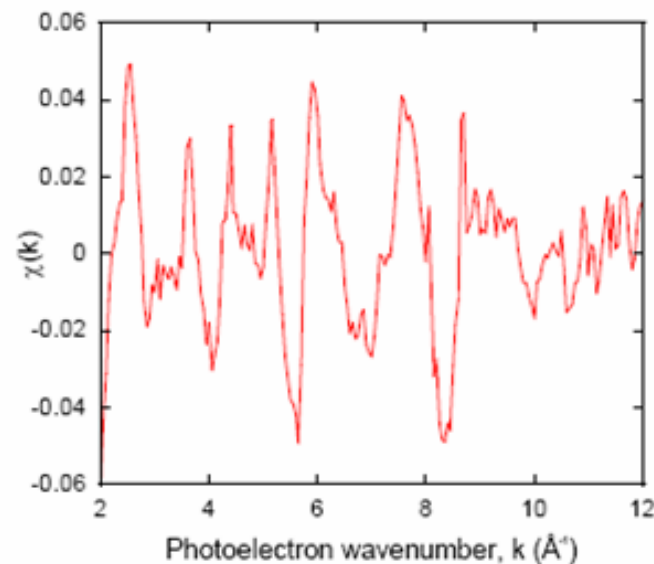
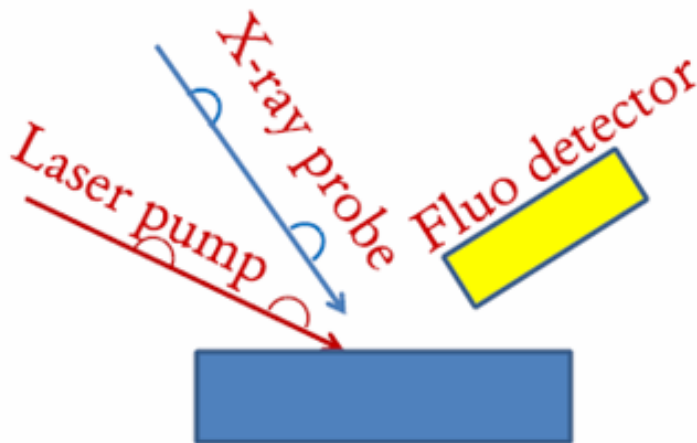
- > Dose limit in macromolecular crystallography at 100 K: 20 - 30 MGy
- > Dynamics in proteins need $T > 260$ K – otherwise ‘frozen states’
- > Dose limit at 300 K: ~ 0.3 MGy, at 260 K ~ 0.8 MGy

XFEL scenario:

- > Beam size: $200 \times 200 \mu\text{m}^2$.
- > Energy: 12 keV
- > Crystal of $200 \times 200 \times 200 \mu\text{m}^3$ and a solvent content of 65%.
- > Energy deposited in the crystal per pulse:
- > Dose per pulse: 0.012 MGy
- > Crystal can withstand about 25 – 30 pulses

Probing excited states of Ge: CdTe

- Pump – probe scheme to
 - Excite Ge dopants (Ti: sapphire fs laser)
 - Probe structure with fs XAFS



XAFS spectrum
 10^{17} Ge cm⁻³ in CdTe
Recorded at ESRF / GILDA
with 10^{14} total photons
→ Feasible with not too many
pulses of EU-XFEL

VOROBEVA *et al.*

PHYSICAL REVIEW B 80, 134301 (2009)

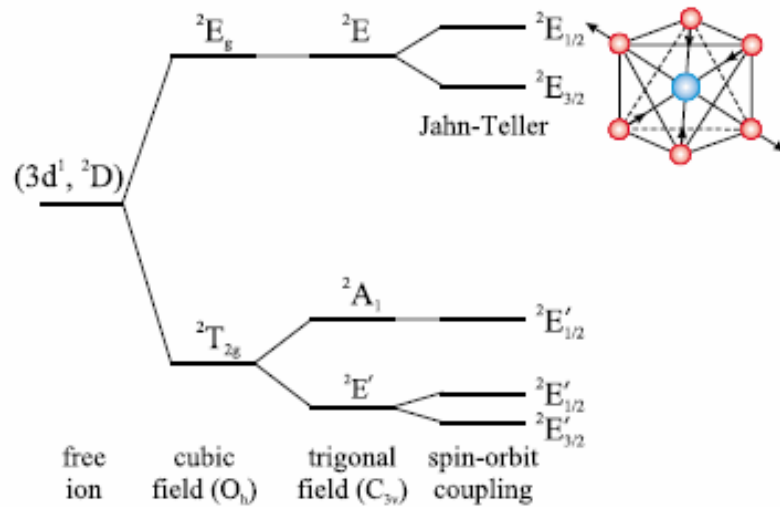
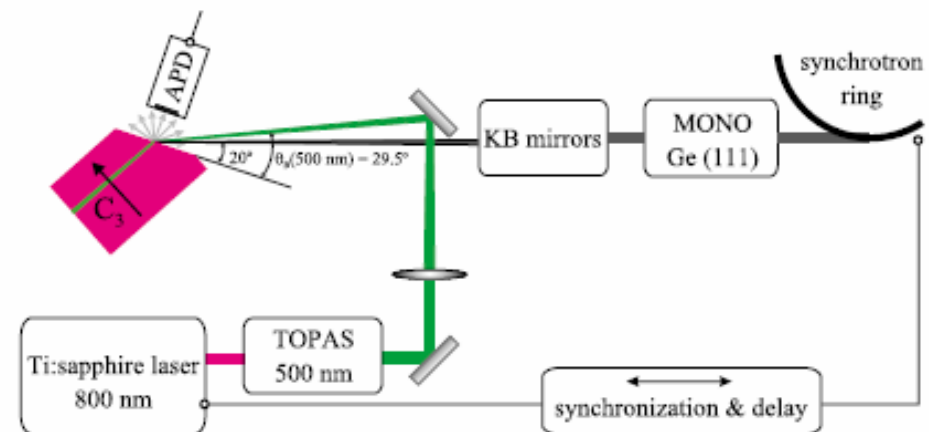
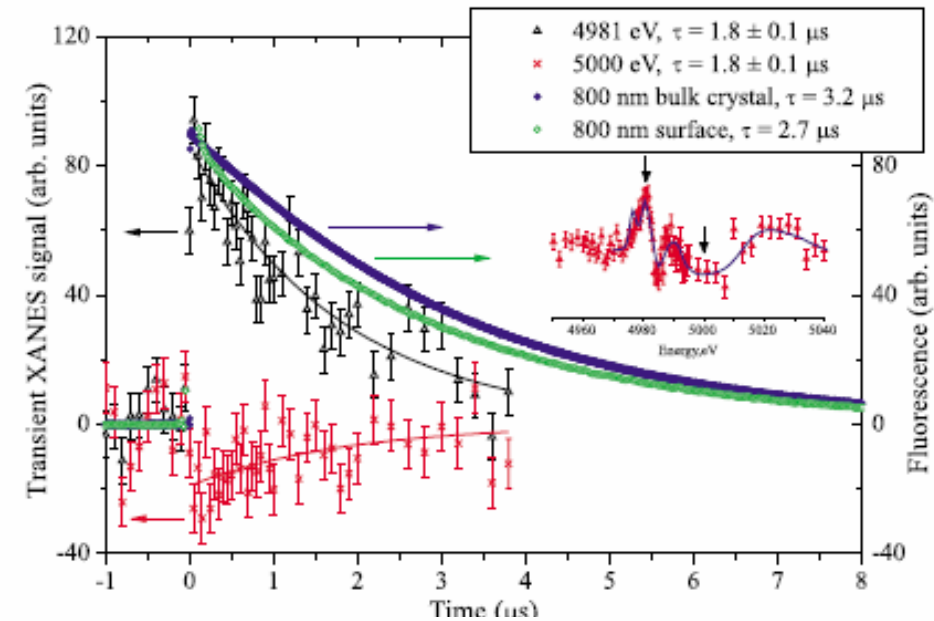


FIG. 1. (Color online) Electronic structure of the Ti^{3+} ions in the Al_2O_3 crystal.

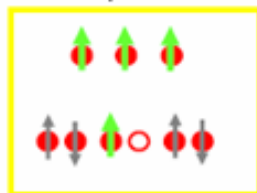




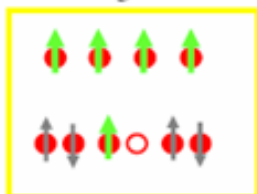
Chemical sensitivity of K β Emission



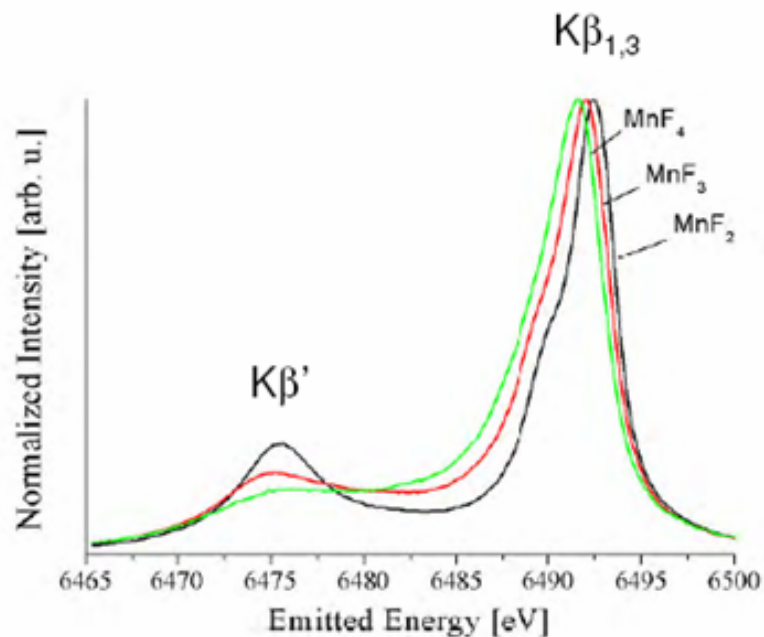
MnF₄: S=3/2



MnF₃: S=2

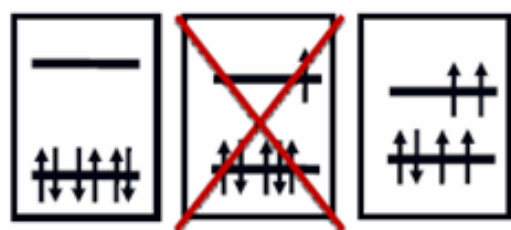


MnF₂: S=5/2

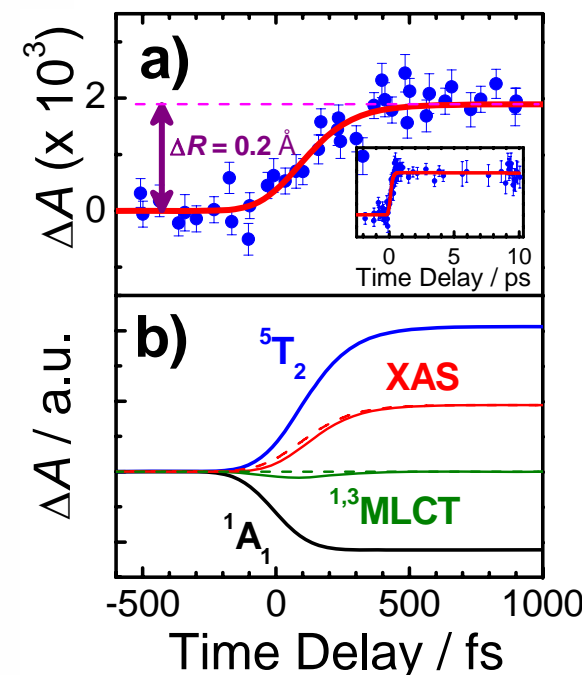
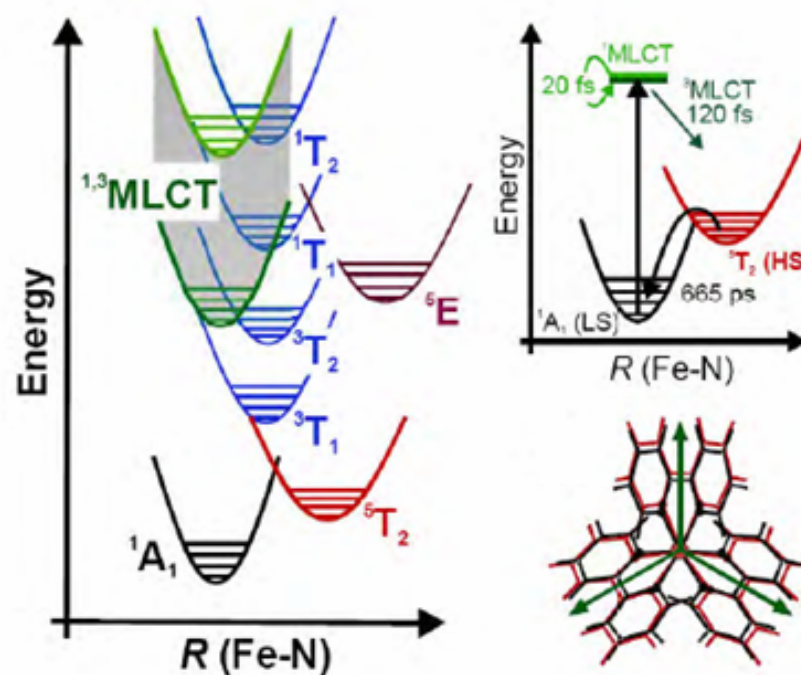
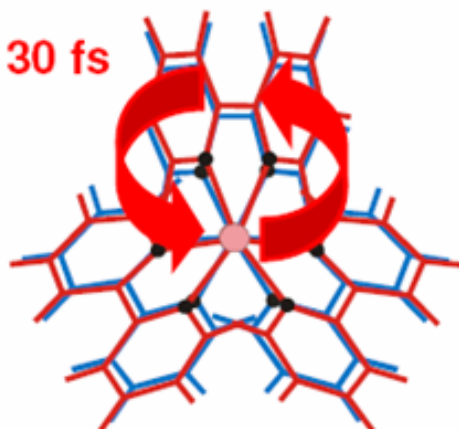


Wang et al. Phys. Rev. B 56, 4553 (1997)

Combined optical and x-ray probing delivers a complete picture of the spin crossover process!



<130 fs

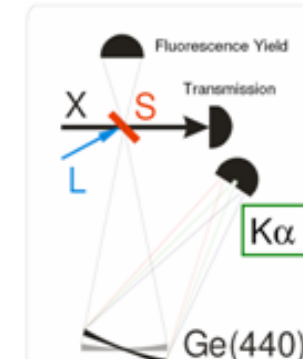


Ultrafast spin conversion: within **electron back-transfer** time from bpy to metal!
 No **intermediate states** involved...
 No **MLCT signature** detected....

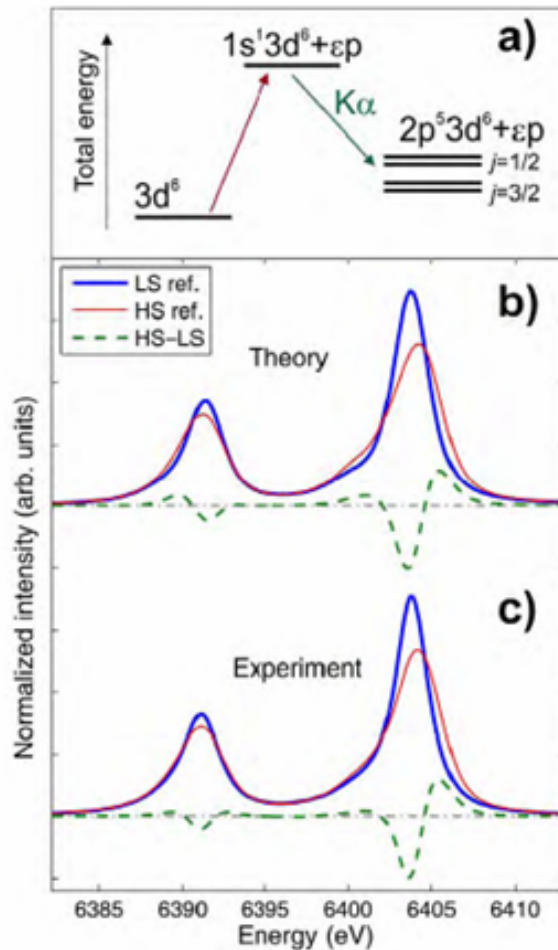
C. Bressler *et al.* Science (2009)

A. Cannizzo *et al.* Coord. Chem. Rev (accepted)

Non-resonant $K\alpha$ spectroscopy

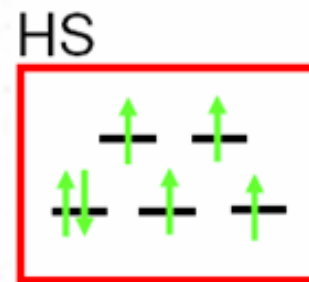
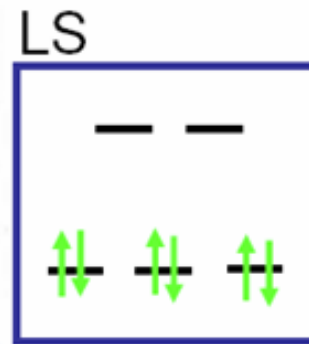


Crystal field multiplet model

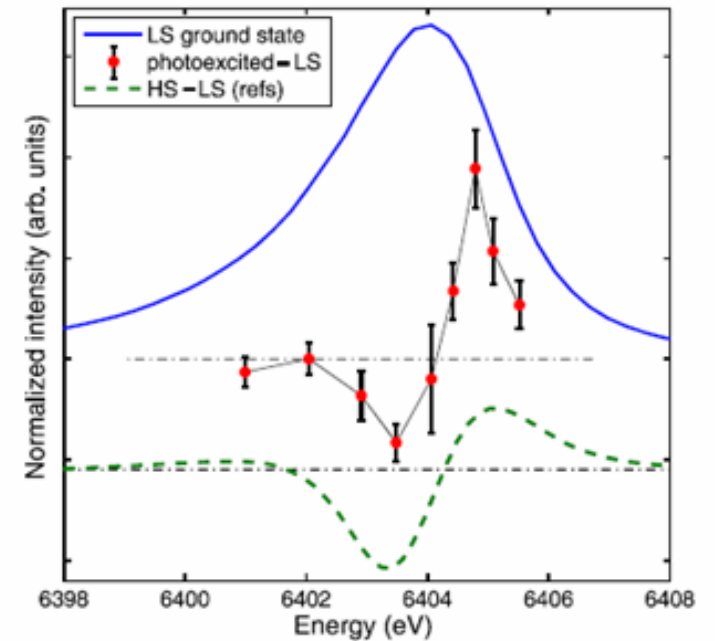


$10Dq = 1 \text{ eV}$
 $10Dq = 3 \text{ eV}$

$[\text{Fe}(\text{phen})_2(\text{NCS})_2]$
 $[\text{Fe}(\text{bpy})_3]\text{Cl}_2$

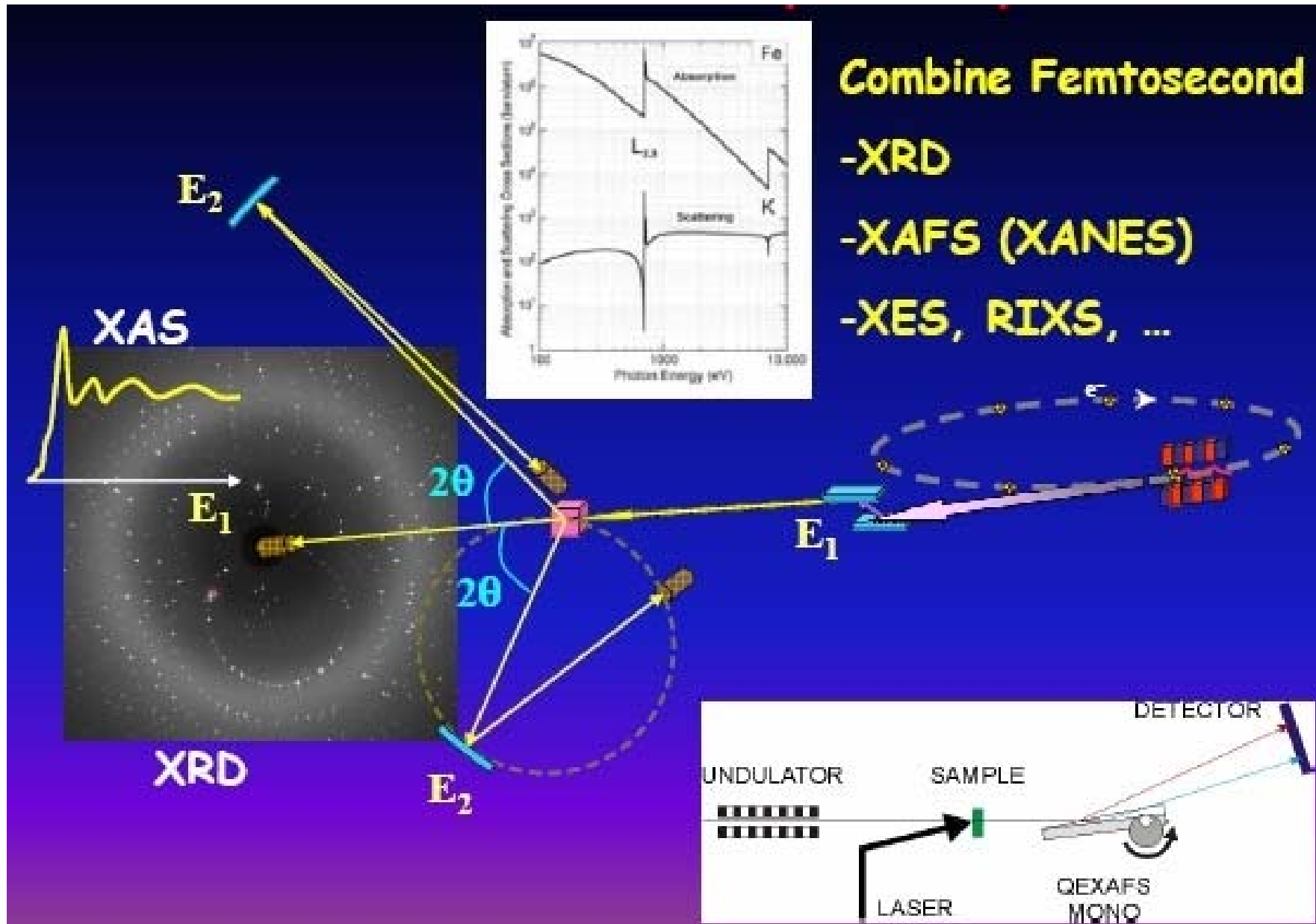


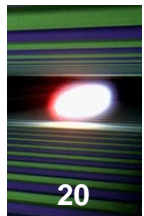
60 ps delay between laser and x-ray pulse



Direct measurement of change of Fe spin state.

G. Vankó, ... Ch. Bressler, submitted





- Beam Divergence:
 - no problem for XAS/XES/IXS
 - not clear at this stage for XRD („no problem“)

- Detectors:
 - XRD seems happy with LPD (?)
 - XES/IXS will find a solution within 5 years (DA currently)

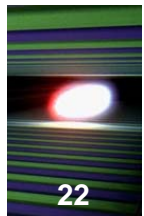
- Infrastructure (Chambers, etc):
 - Vacuum/ambient pressure will become important
 - (homework)



- XRD
 - 0.1 % bw fine for diffuse scattering (liquid, gas phase)
 - 1-3 % desired for Xtallography

- XAS/XES/IXS
 - 0.1 % mostly fine (XAS, XES)
 - 0.01 % desired for RIXS

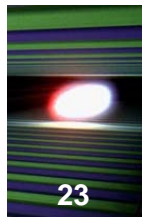
- XANES
 - 1 % sufficient. Include dispersive mode (close to exp)?



- Incident Beam:
 - focussed (0.1 mm or smaller) *gas phase and clusters*
 - unfocussed (ca. 0.6 mm) *Xtallography, XRD*
 - line focus (ca. 0.1 x 10 mm²) *spectroscopies*
 - dispersive (1 % bw) *XANES*

- Burst Mode
 - full burst (1500 pulses) *gas phase, $t < 200$ ns*
 - log fill (< 30 pulses) *Xtallography, $t > 200$ ns*

- Diagnostics
 - intensity monitor upstream (1 %)
 - intensity monitor in hutch (< 1 %?)



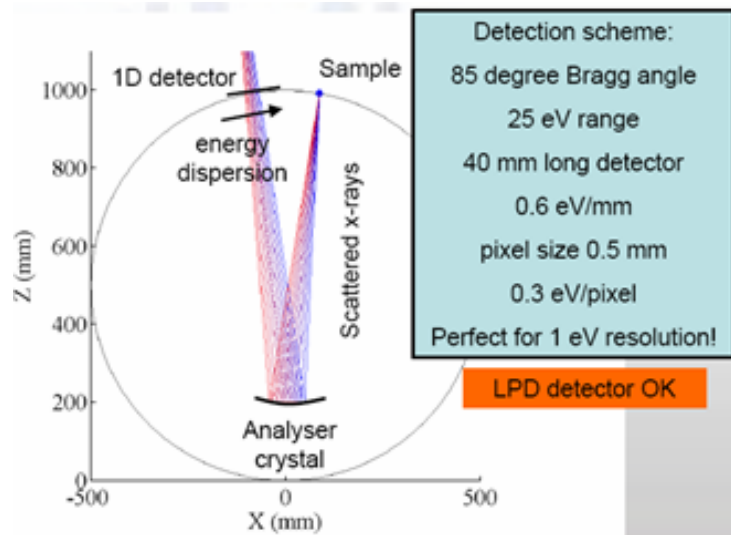
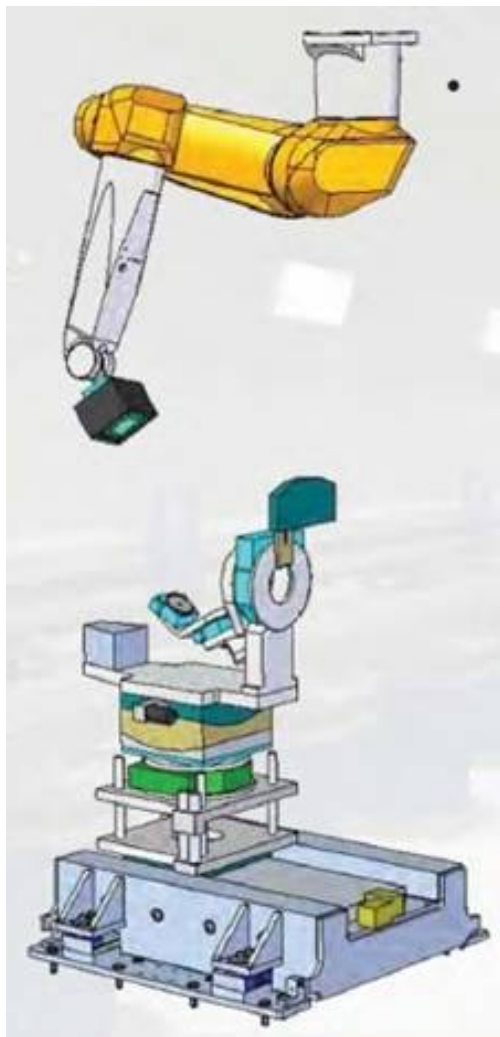
- Timing issues
 - femtosecond desired (10 ? 50? 100?)

- Sample excitation
 - laser preferred (so far, no x-ray pump x-ray/laser probe)
 - wavelengths (of course: THz to UV/VUV...)
 - laser pulse intensity (mJ perfectly fine, even less)

- Additional Monitors (Experiments)
 - *in situ* optical pump-probe
 - *in situ* femtosecond fluorescence (!)

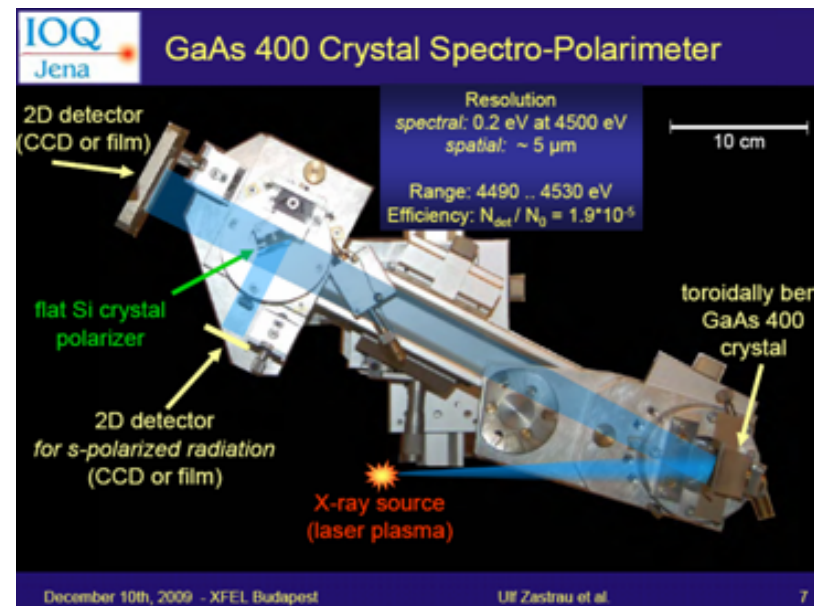
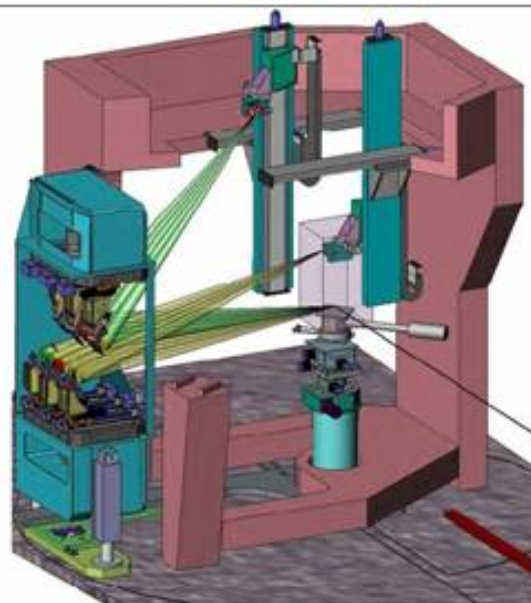
- Sample Chambers (mainly gas phase, others prefer He/air)

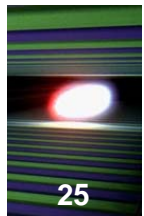
- LCLS XPP will deliver input...



Combination of two spectrometers

■ XANES received a quite large demand, thus a 1 % dispersive setup would be mostly appreciated





The End

Multi-step spin-crossover Photo-switching

M. Lorenz et al, Phys. Rev. Lett (2009)
N. Moisan et al, C.R. Chimie (2008)

time span of spin switching

Step 1.
picosecond non-thermal molecular transformation (fs-ps),
under constant volume.
See also femtosecond optical spectroscopy

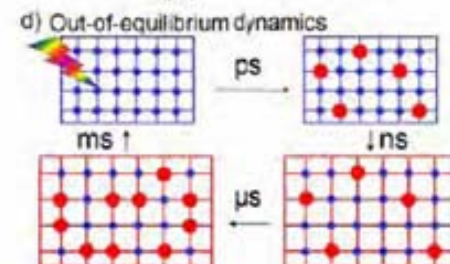
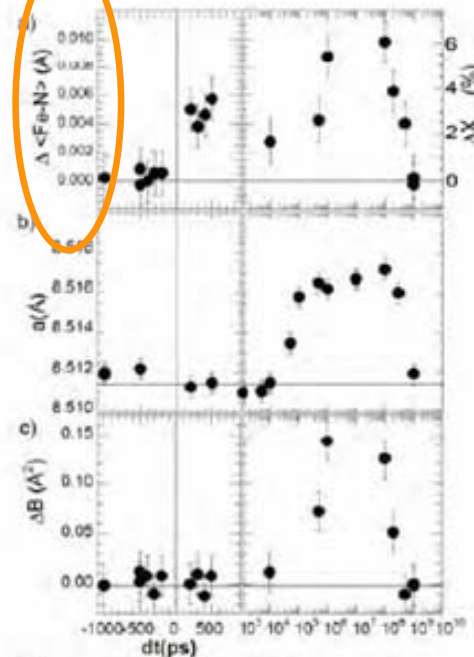
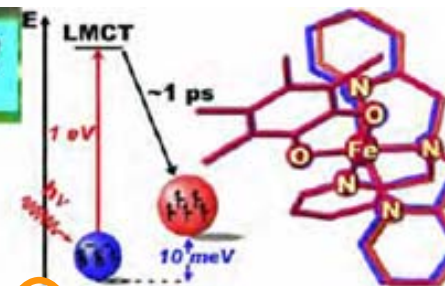
Step 2.
elastic stress induced by propagating sound waves
volume expansion (10ns-10 μ s)

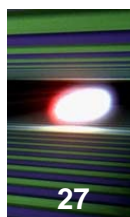
Step 3.
slower diffusive heating processes through the lattice (μ s-
ms), delayed thermal population of HS state

Out of equilibrium thermodynamics:

-Early stage: $E=Nh\nu$
N Photoconverted molecules i.e. =5% fraction

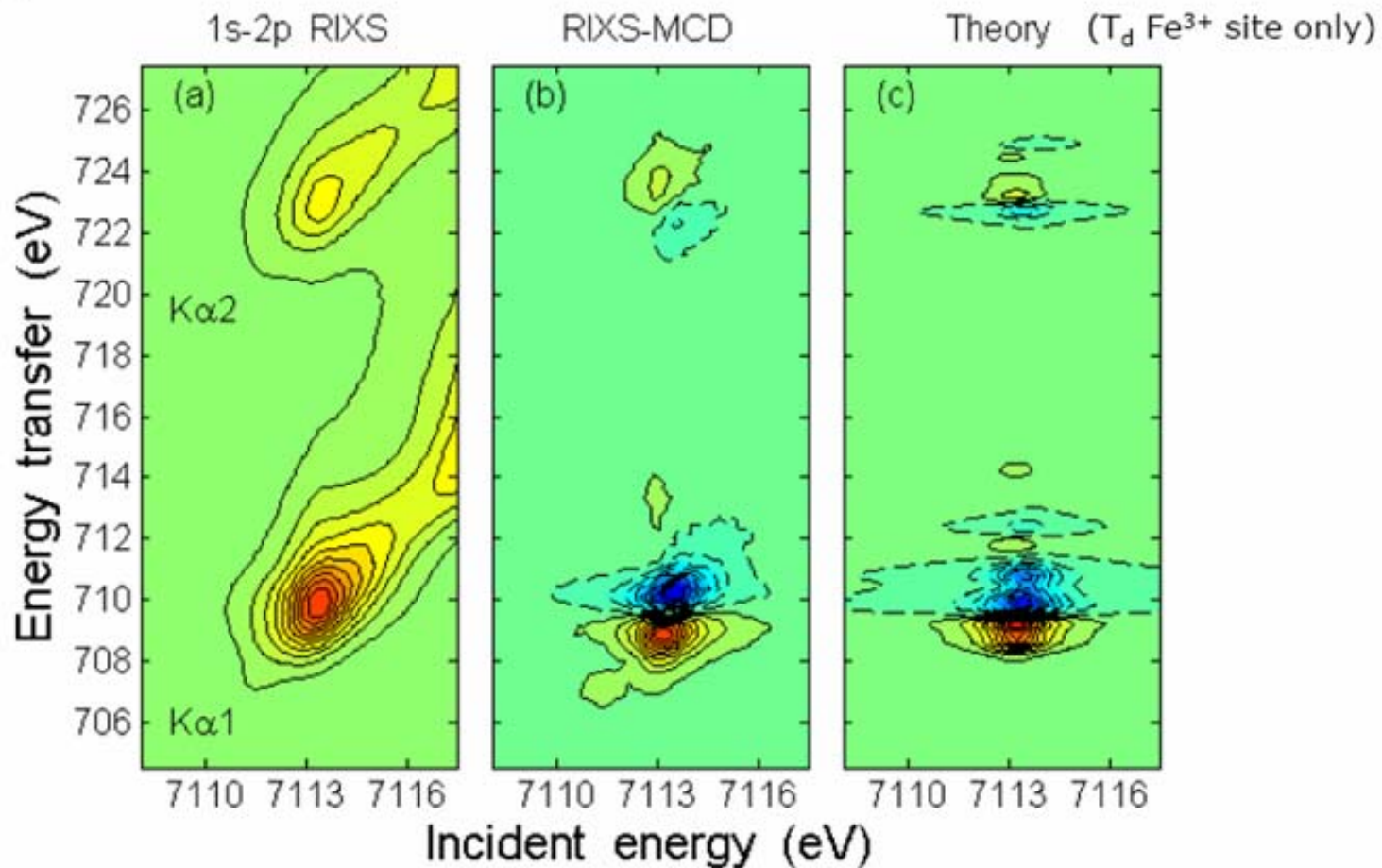
-Late stage temperature increase:
additional 5% thermal spin switching





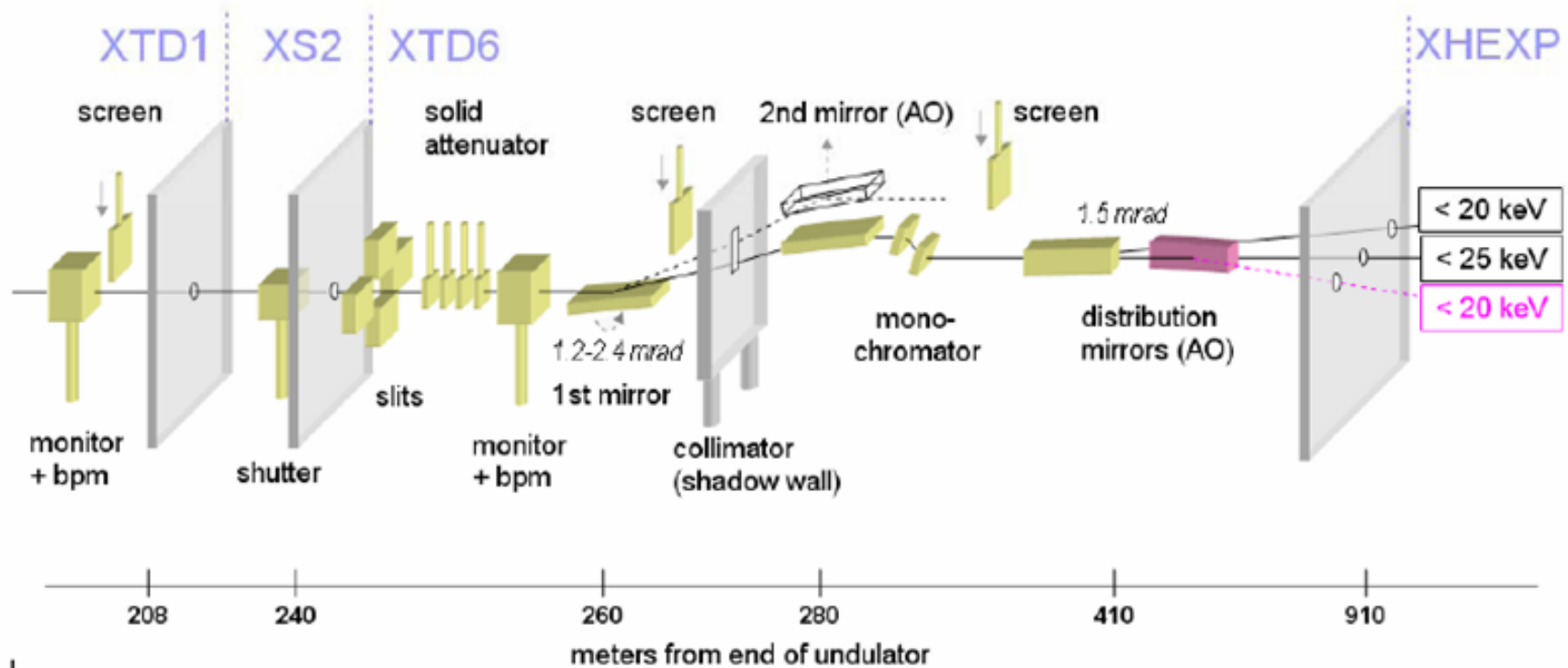
ESRF
ID26

1s2p RIXS-MCD: Fe_3O_4



M.Sikora, A. Juhin, T.-C. Weng, C. Detlefs, P. Saintavrit, F. de Groot, P. Glatzel

SASE 2 beamline



- Burst Mode is not yet fully appreciated (or thought through)
- Intensity monitor: down to $10e-5$
 - need to evaluate necessity for $< 1\%$, may be solvable inside exp. hutch

