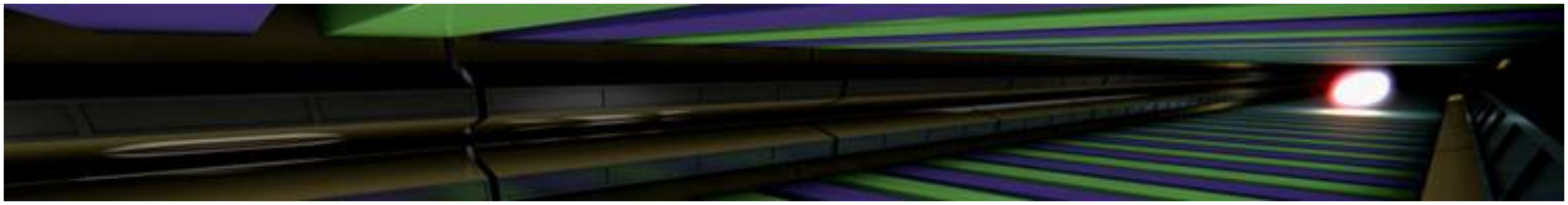


Femtosecond X-Ray Experiments (FXE)

Andreas Galler
Wojciech Gawelda
Christian Bressler

…input from the FXE workshop participants

FXE Workshop

Budapest Dec 9-11, 2009

- 93 Participants
- XRD: S. Johnson (SLS)

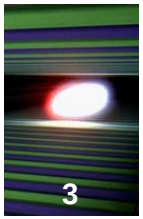
M. Bargheer (Potsd.)

- XAS/XES/IXS: P. Glatzel(ESRF),

A. Soldatov (Rostov), G. Vankó (Budapest), D. Grolimund (SLS),

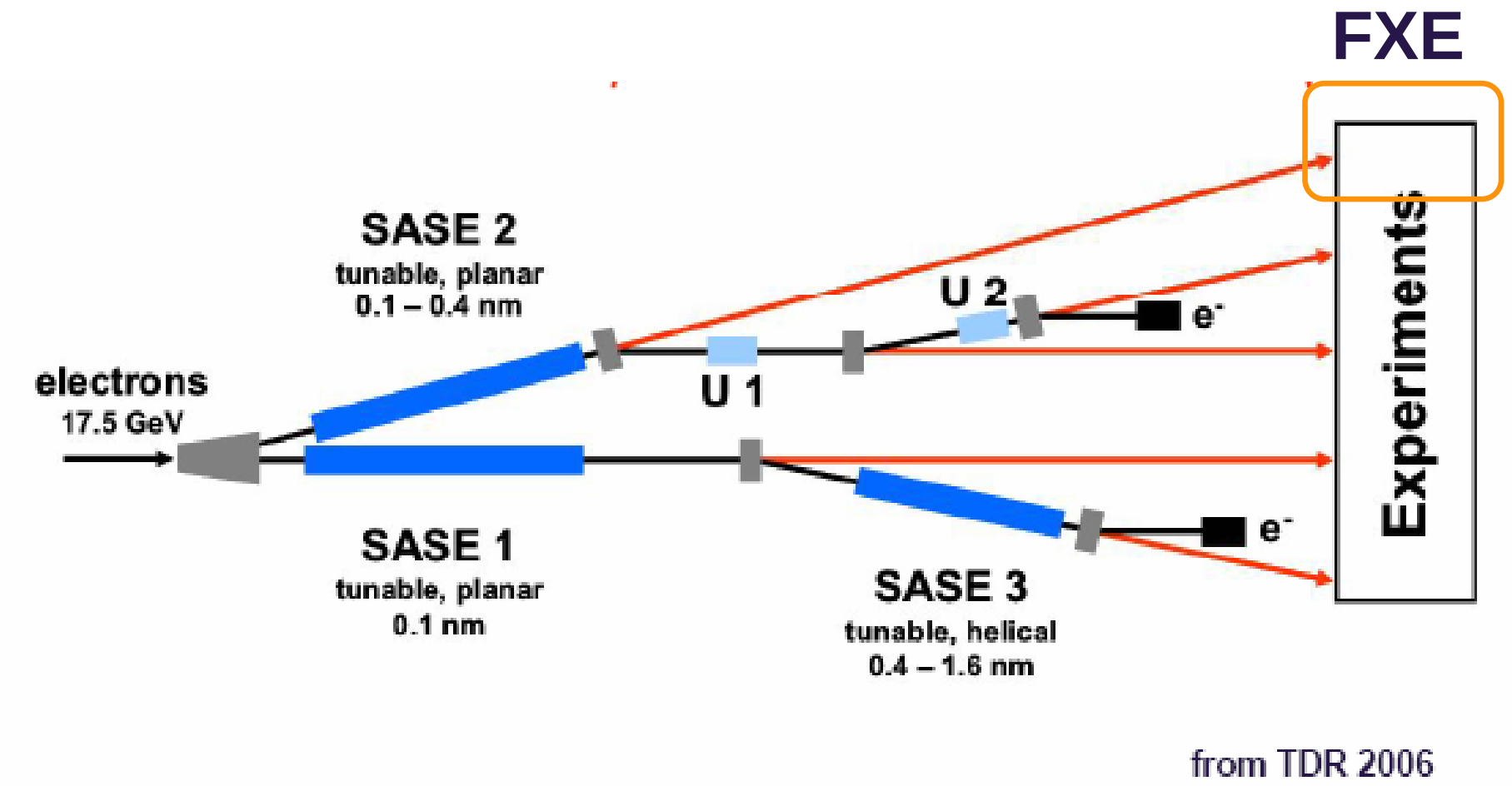
- http://www.xfel.eu/events/workshops/fxe_workshop_2009/

Overview



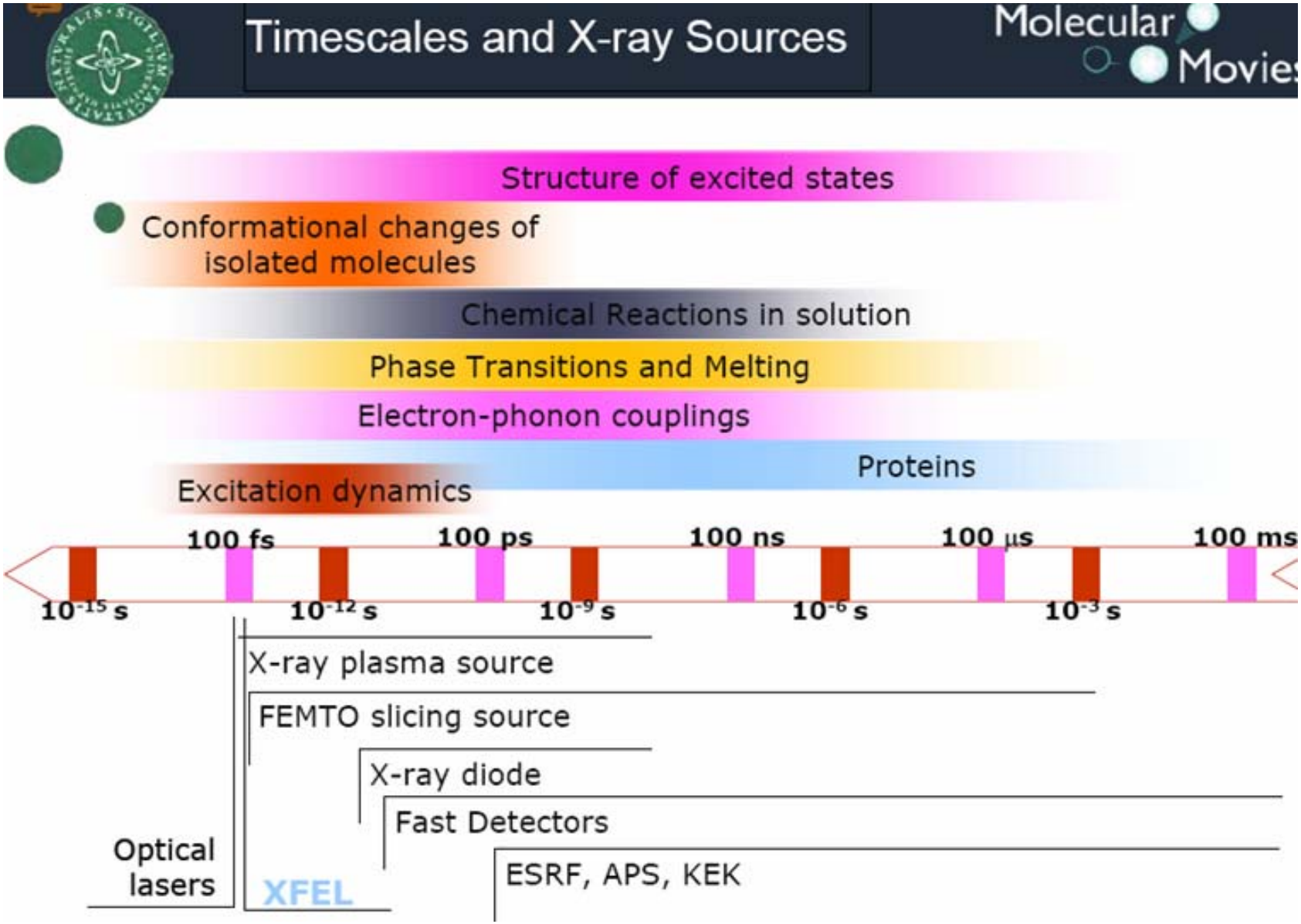
- Application Areas
  - ultrafast chemical dynamics (biology)
  - solid state dynamics (phase transitions, spin conversion)
- Combine XRD with x-ray spectroscopies
  - global (local) structural information
  - electronic and spin information
  - all with fs time resolution
- Flexible incoming beam
  - 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,…)

FXE Instrument



from TDR 2006

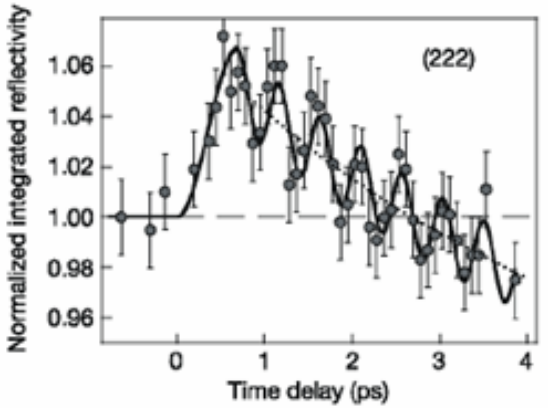
Chemistry and Biology (R.Feidenhansl)



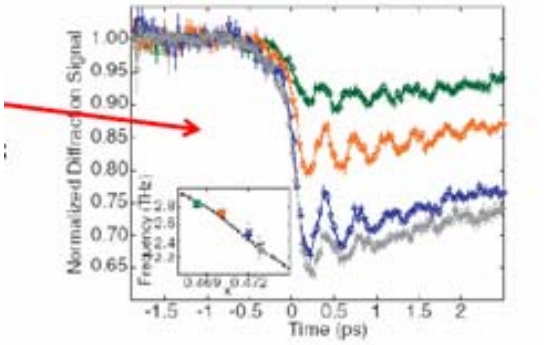
XRD vs All-Optical Tools

Physics:

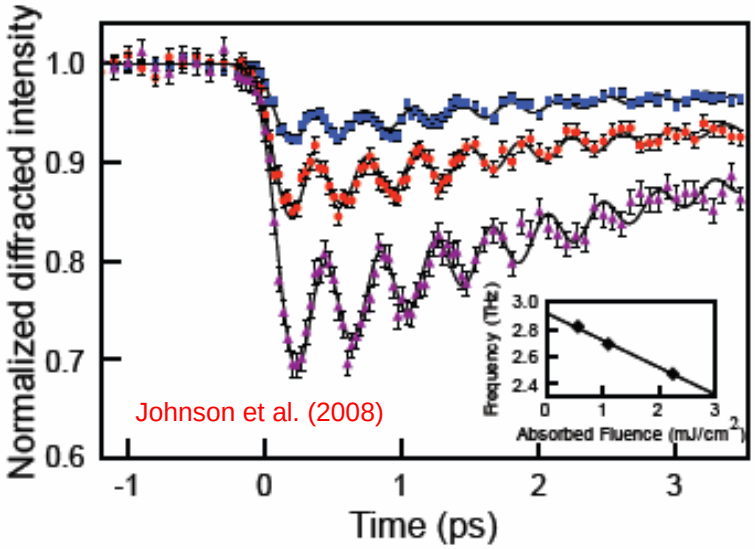
- Coherent phonons in Bi



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



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



PRL 100, 027404 (2008) PHYSICAL REV

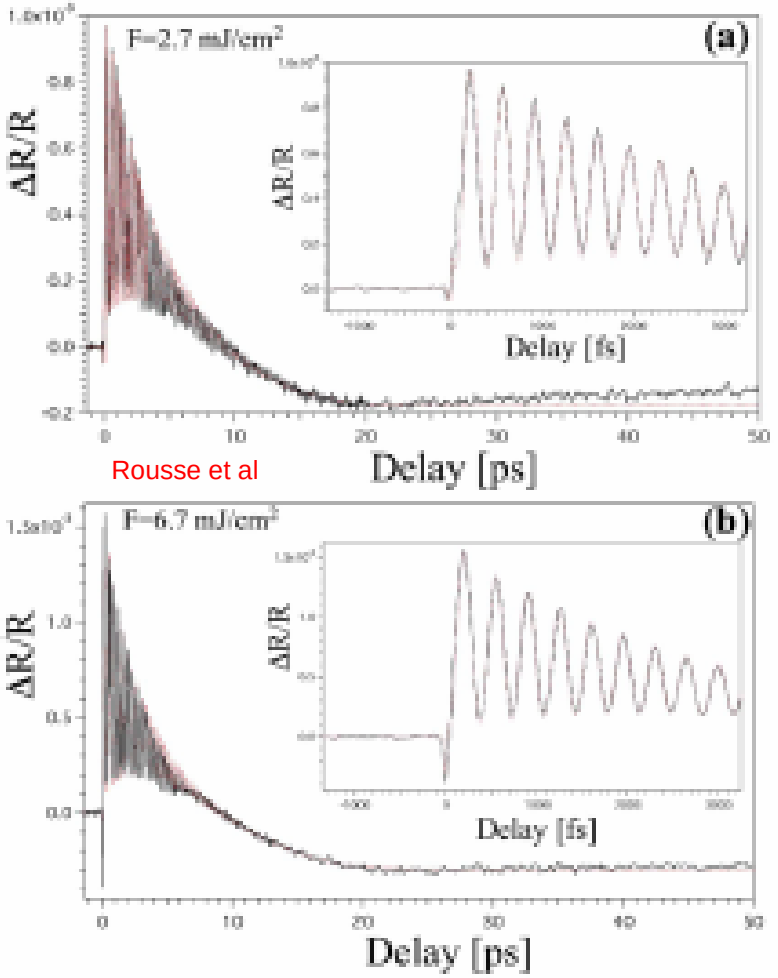
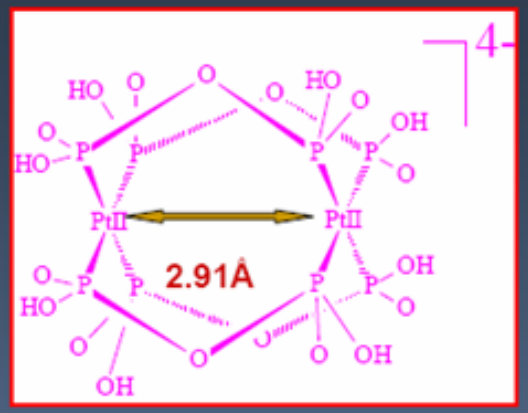


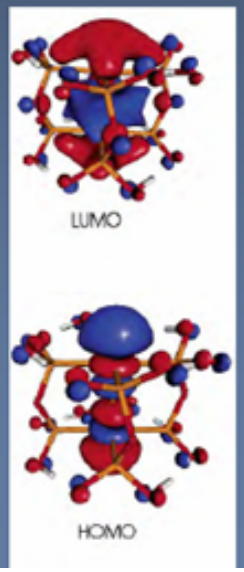
FIG. 1 (color online). Comparison between the experimental [solid (dark) line] and theoretical [dashed (red) line] behavior of the transient reflectivity: (a) excitation flux 2.7 mJ/cm^2 and (b) excitation flux 6.7 mJ/cm^2.

Chemistry in Solution : XAFS and XRD (P.C.)

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

50µs lifetime at 17K





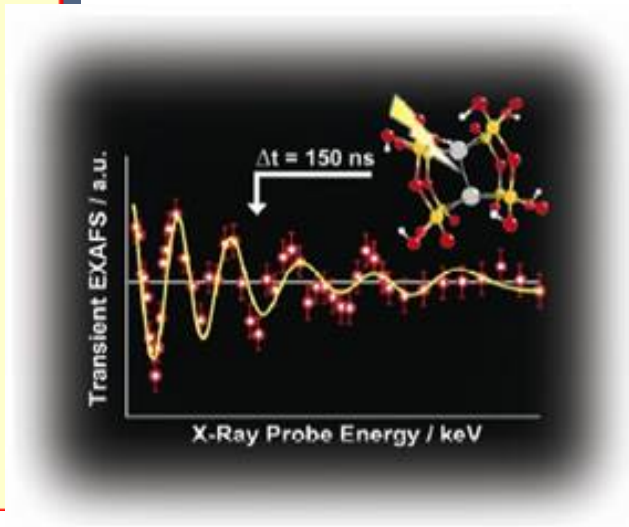
Contraction of Pt-Pt on excitation:

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

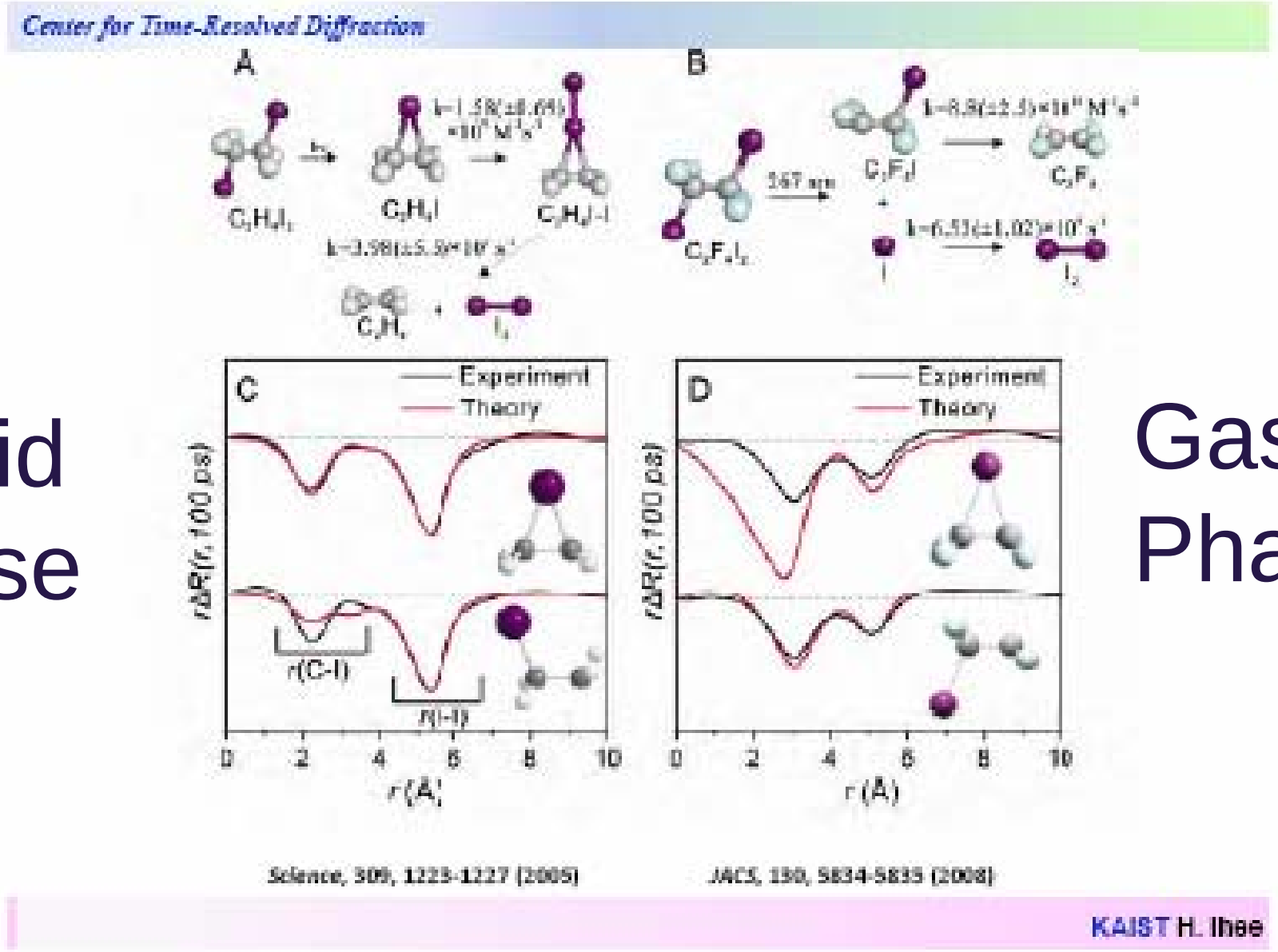
EXAFS
Solution (ethanol)
van der Veen et al 2009 RT: 0.31(5) Å

Spectroscopy
Solid State
Rice and Gray 1983: 0.21 Å
Solution (acetonitrile)
Leung et al 1999: 0.225 Å



Ultrafast Chemistry with XRD and UED

Liquid Phase

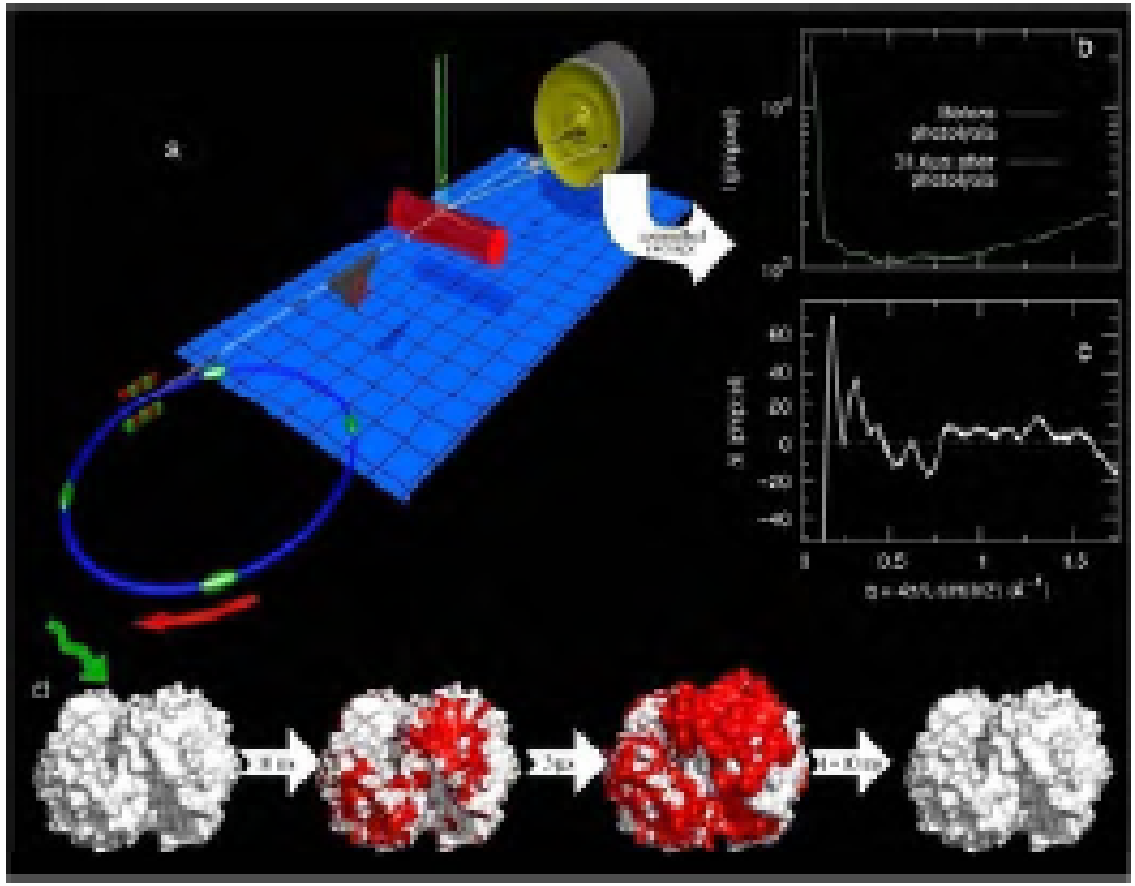


Gas Phase

Not ultrafast, but biologically relevant

Center for Time-Resolved Diffraction

Time-Resolved WAXS (TR-WAXS)



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

KAIST H. Ihee

Request(s), continued.. (K. Haldrup)

"Boundary conditions" for XFEL experiments

Molecular Movies

Referring to C. Bresslers "boundary-conditions" synopsis

ΔE/E ~ 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 mm)

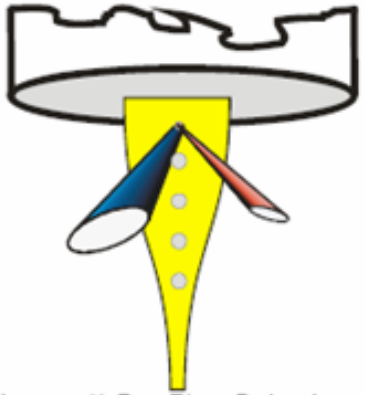
Experiments that can deal with burst mode operation are very attractive.

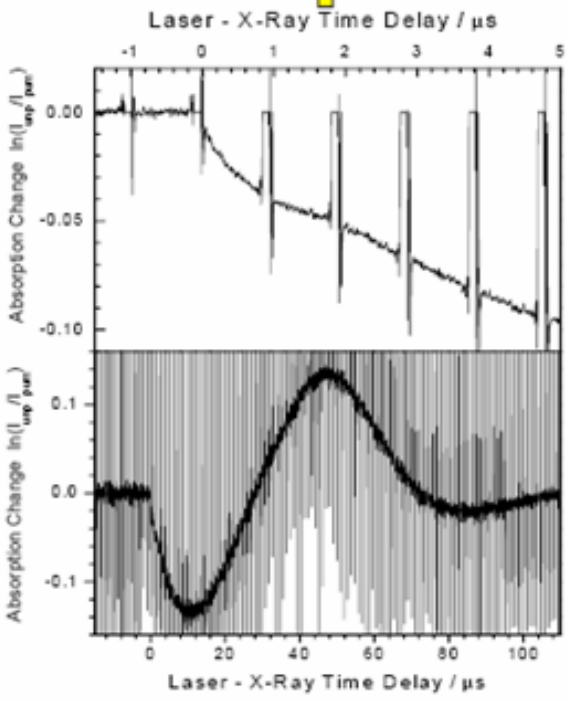
Low demands on angular resolution, 1mm^2 pixels OK

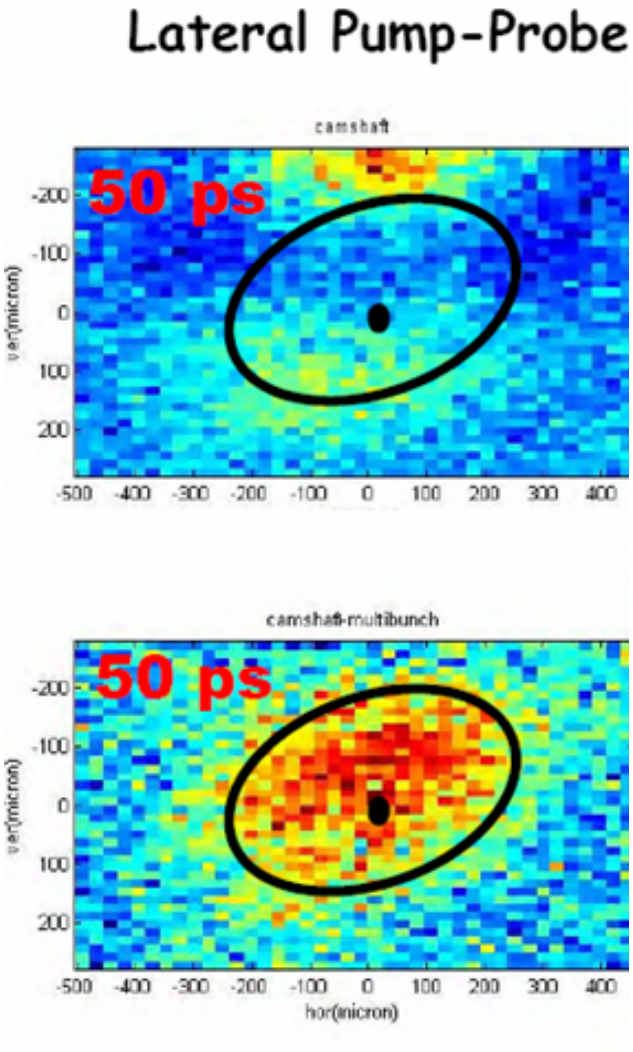
~0.5 mm^2 OK

Some significant challenges in this respect!
-Mainly to do with heating of sample and 5 MHz refresh

Liquid Phase Exp: Heatload Issues (here: laser)





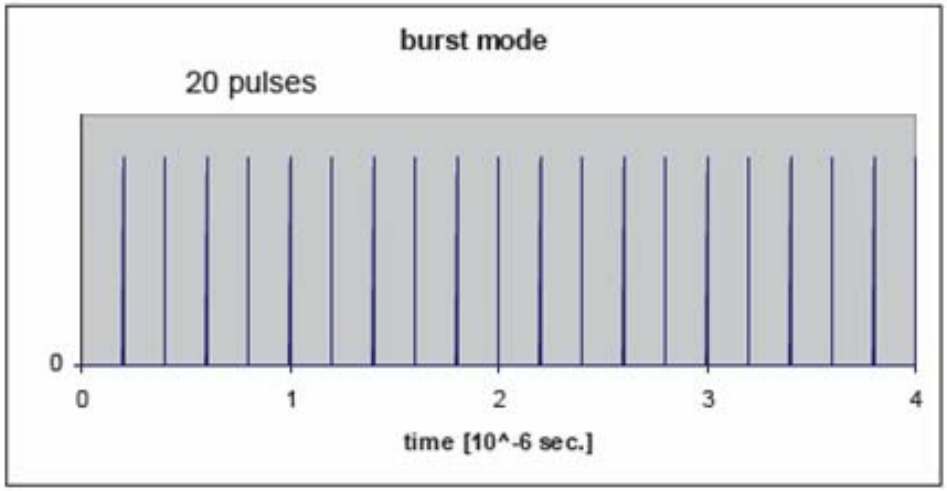


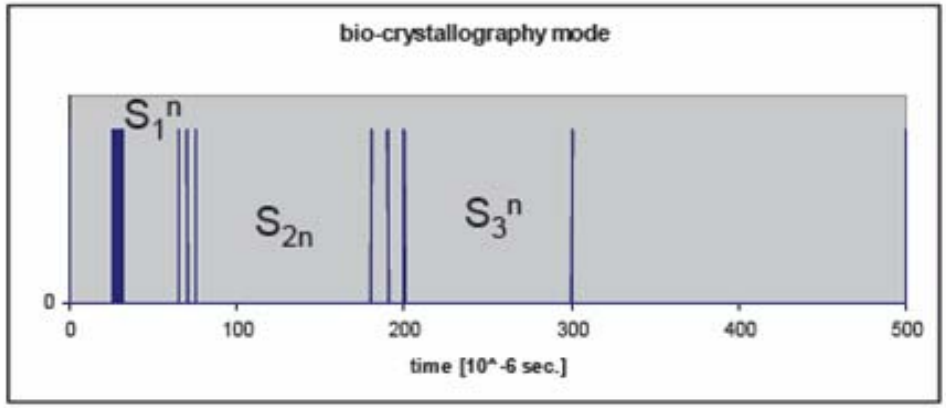
XAFS can correct for sample fluctuations…

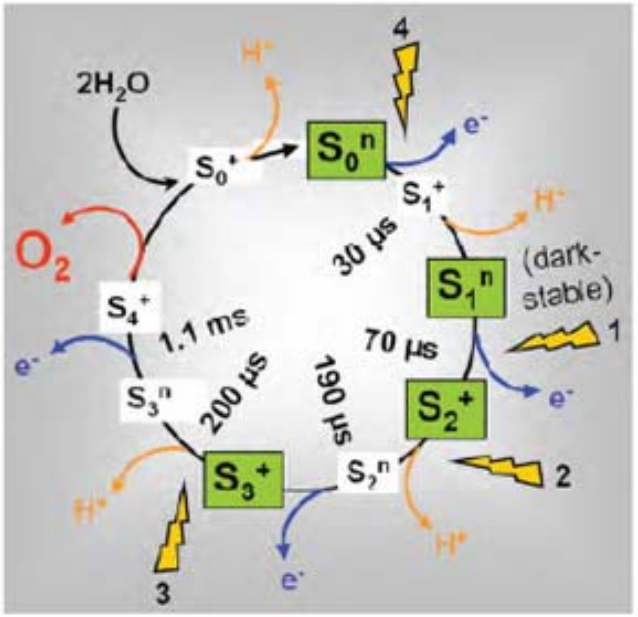
Gawelda et al.: to be published (2010)

Alke Meents (ca. 30 pulses max)

Bunch train structure for biological crystallography







Tolerable dose for organic / biological molecules

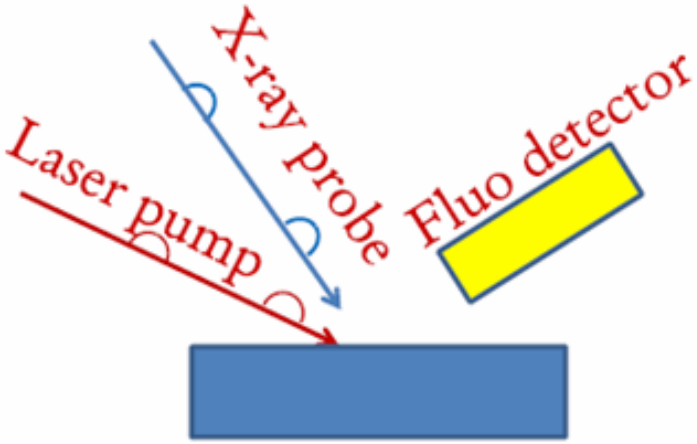
- Dose limit in marcomolecular crystallography at 100 K: 20 - 30 MGy
- Dynamics in proteins need T > 260 K – otherwise 'frozen states'
- Dose limit at 300 K: ~ 0.3 MGy, at 260 K ~ 0.8 MGy

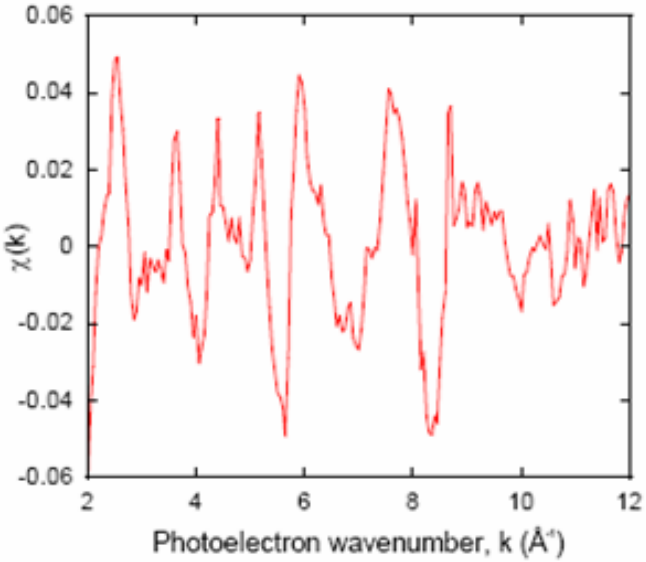
XFEL scenario:

- Beam size: 200 x 200 μm^2.
- Energy: 12 keV
- Crystal of 200 x 200 x 200 μm^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

- Pumb – 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)

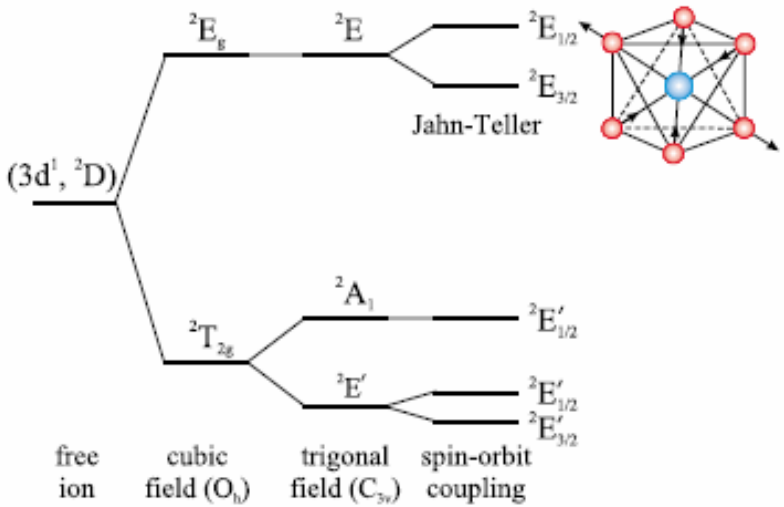
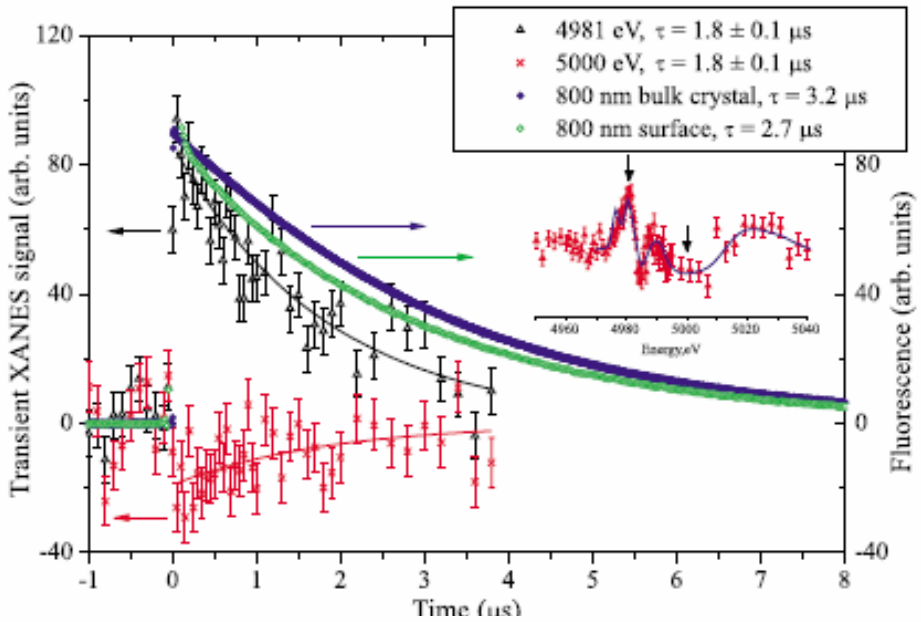
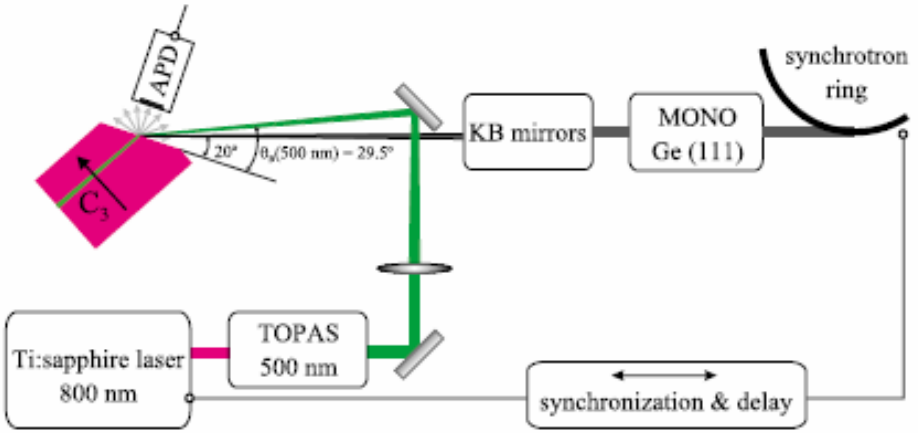


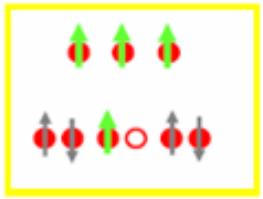
FIG. 1. (Color online) Electronic structure of the Ti^{3+} ions in the Al_2O_3 crystal.



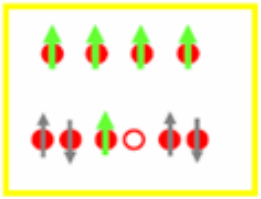


Chemical sensitivity of Kβ Emission

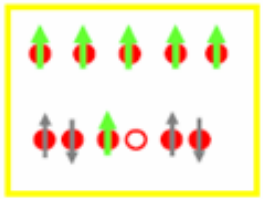
MnF_4: S=3/2

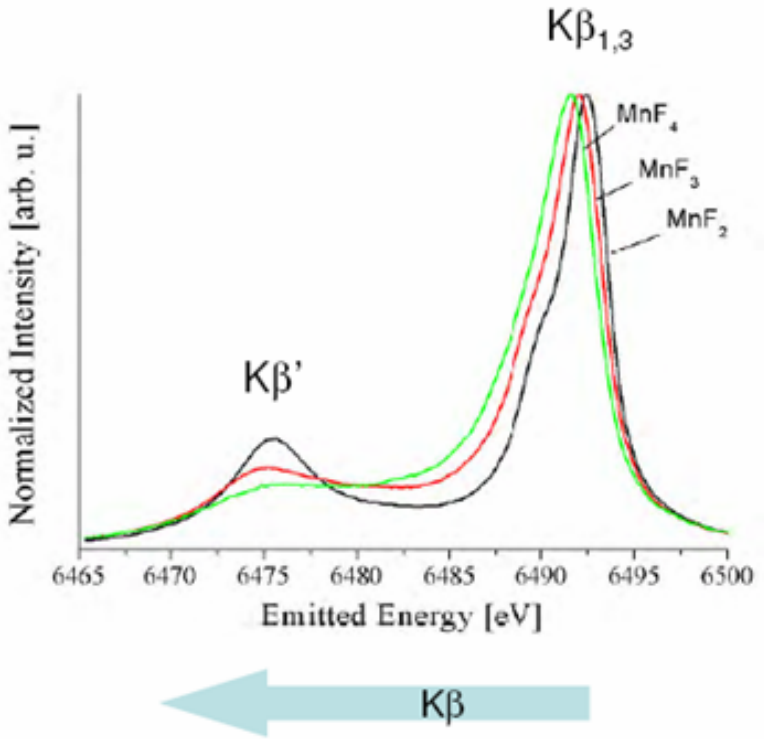


MnF_3: S=2



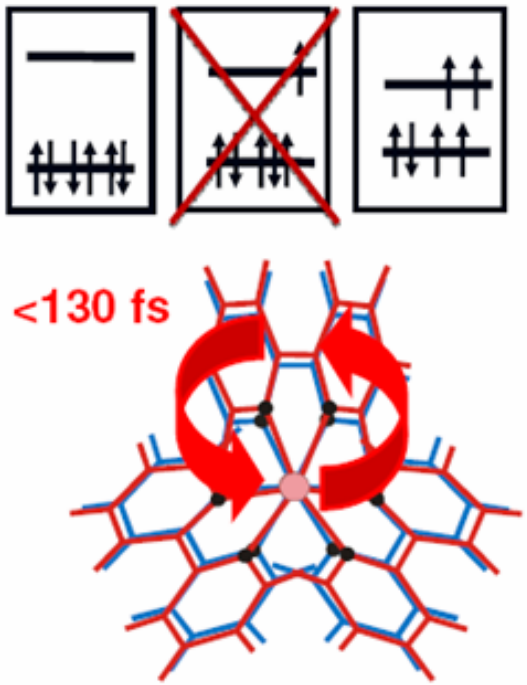
MnF_2: S=5/2

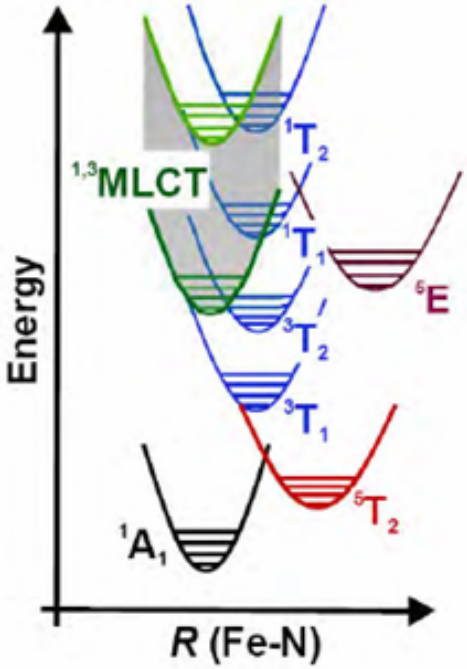


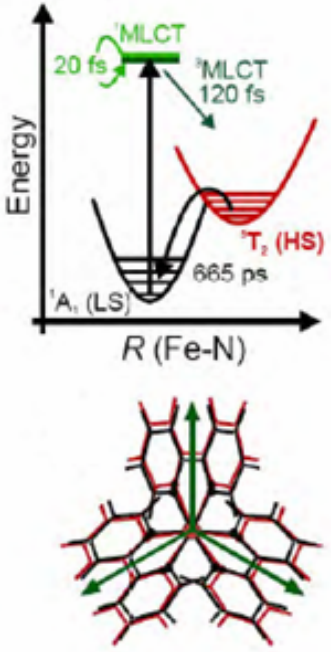


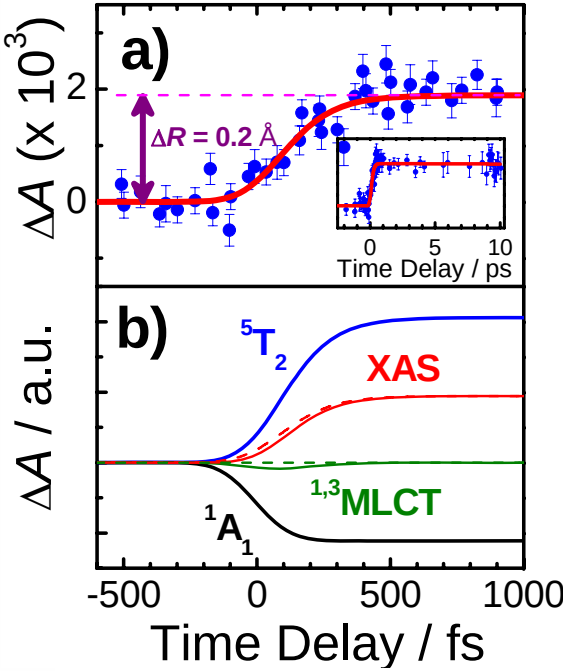
Wang et al. Phys. Rev. B 56, 4553 (1997)

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









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)

TR-XES (ps) → LCLS XPP proposal (fs)

Non-resonant Kα spectroscopy

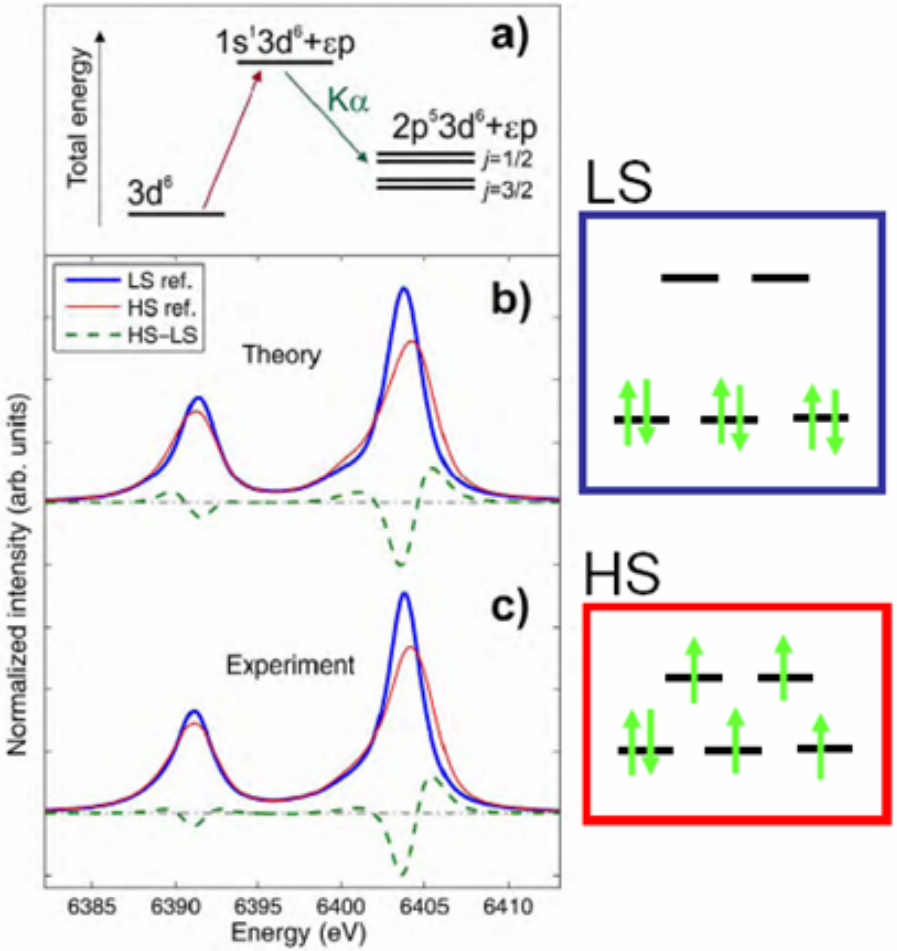
Crystal field mulitplet model

10Dq = 1 eV

10Dq = 3 eV

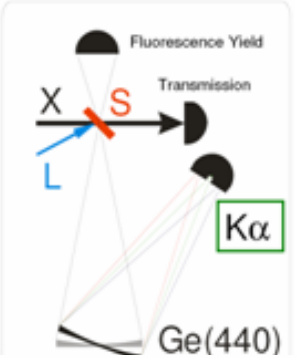
$[Fe(phen)_2(NCS)_2]$

$[Fe(bpy)_3]Cl_2$

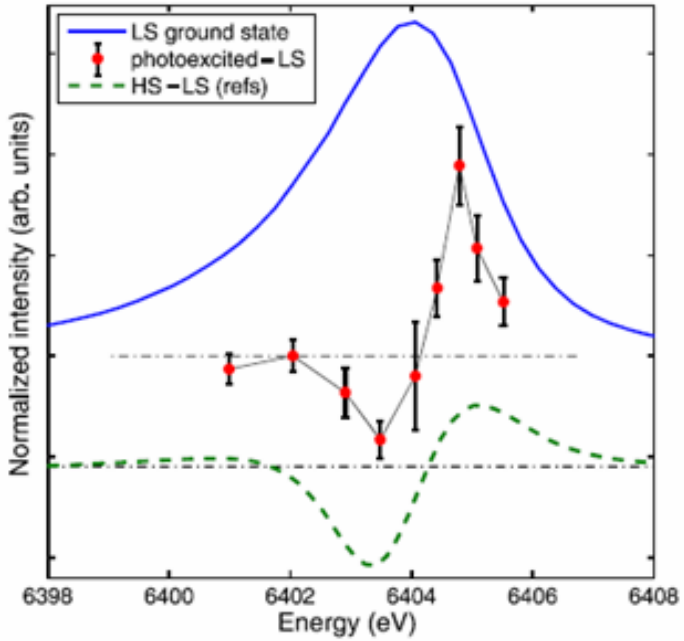


LS

HS



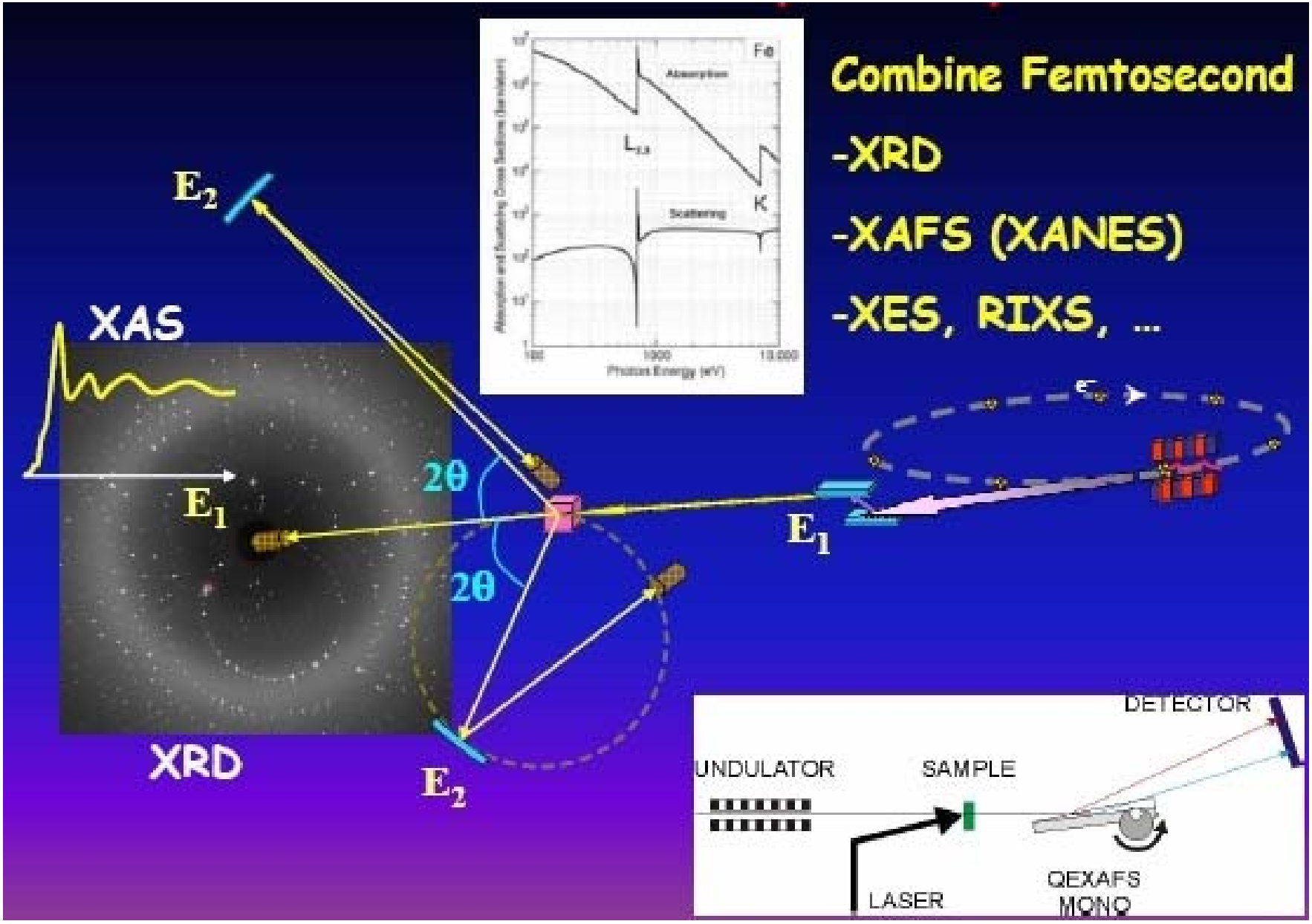
60 ps delay between laser and x-ray pulse



Direct measurement of change of Fe spin state.

G. Vankó, … Ch. Bressler, submitted

FXE Instrument: complementary observables



Current status of evaluation

- 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)

Monochromator issues

- 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)?

Checklist

- 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 %?)

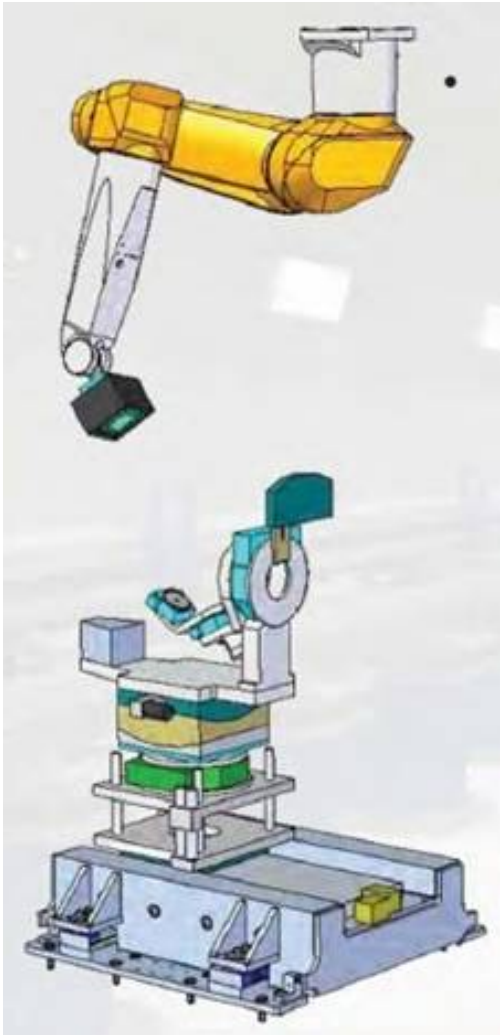
Checklist cont'd

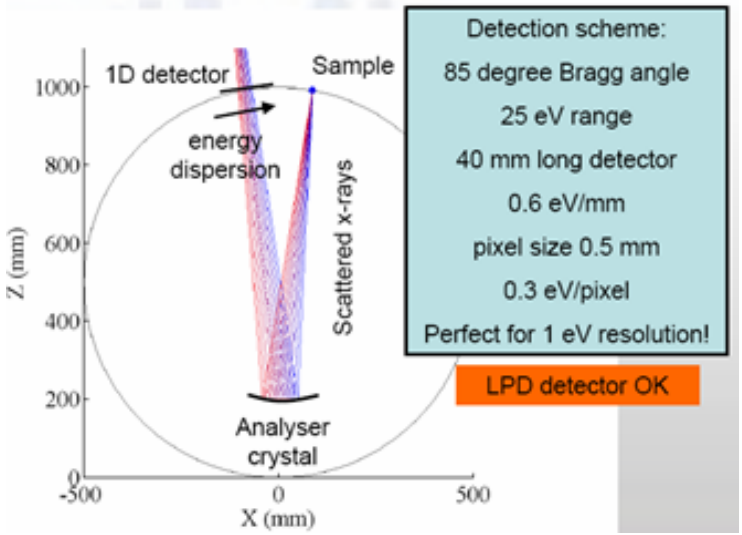
- Timing issues
  - femtosecond desired (10 ? 50? 100?)

- 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…

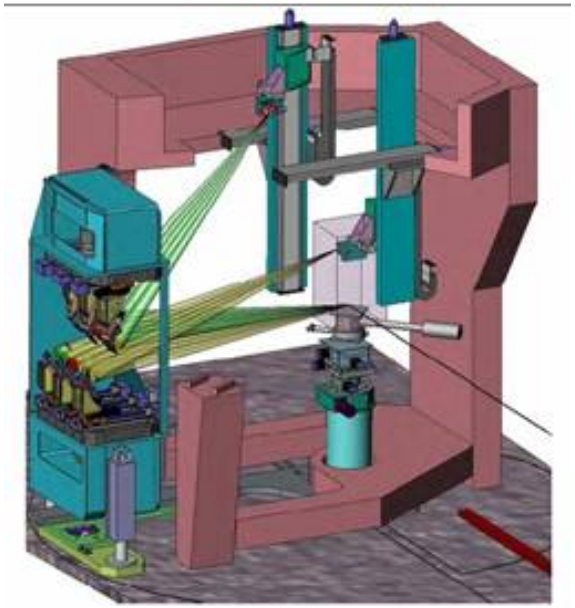
Possible ingredients to the FXE end station

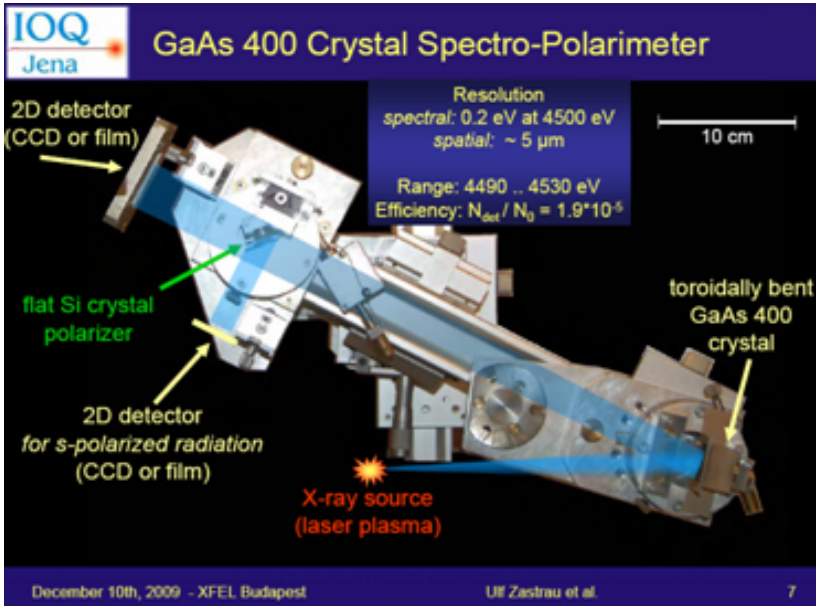




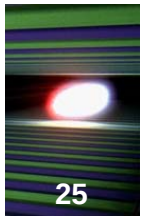
- XANES received a quite large demand, thus a 1 % dispersive setup would be mostly appreciated

Combination of two spectrometers





The End



The End

Solid state experiments (E. Collet)

Multi-step spin-crossover Photo-switching

M. Lorenc 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

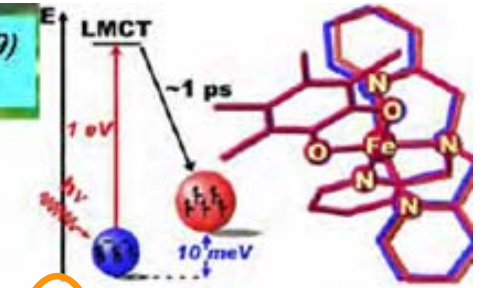
Step 2.
elastic stress induced by propagating sound waves
volume expansion (10ns-10 µs)

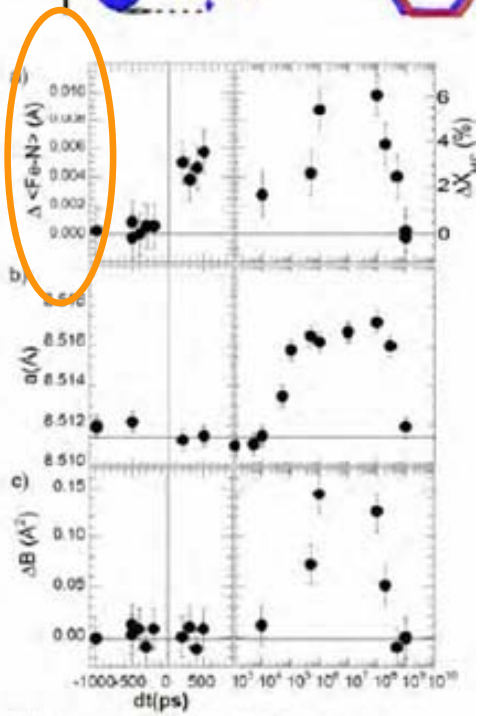
Step 3.
slower diffusive heating processes through the lattice (µs-ms), delayed thermal population of HS state

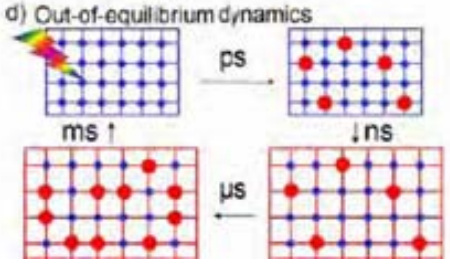
Out of equilibrium thermodynamics:

-Early stage: E=Nhν
N Photoconverted molecules i.e. =5% fraction

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



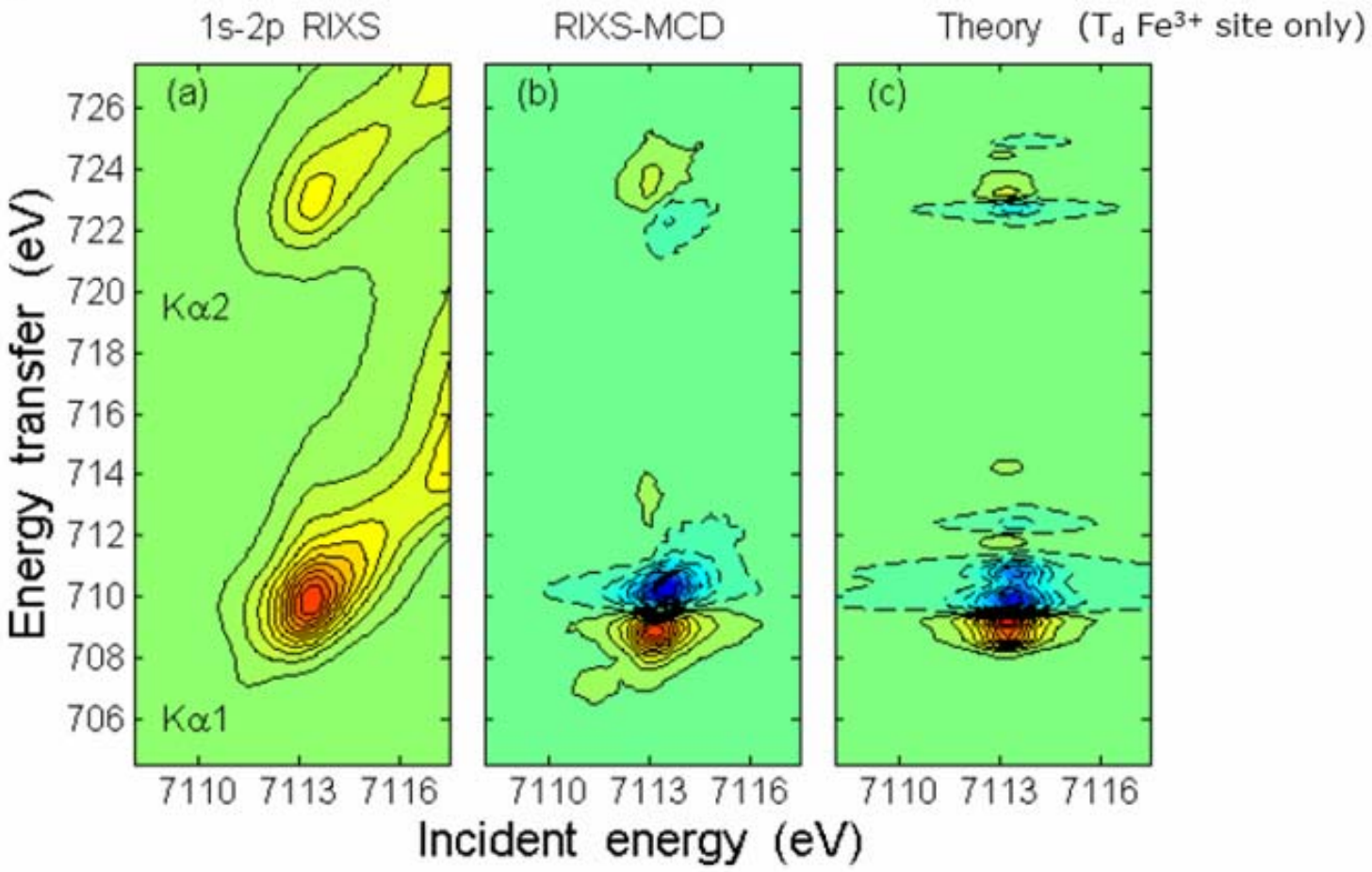




RIXS (Sikora)

ESRF ID26

1s2p RIXS-MCD: Fe_3O_4

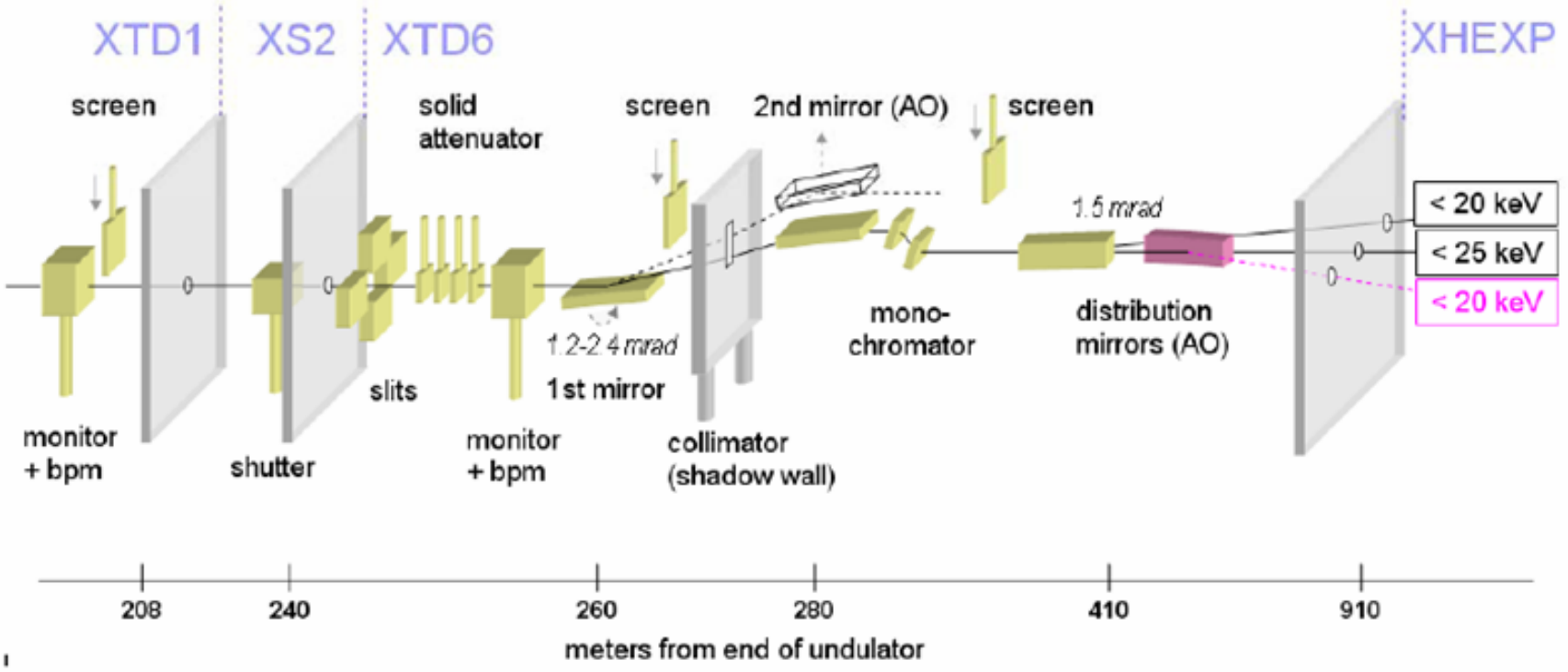


M.Sikora, A. Juhin, T.-C. Weng, C. Detlefs, P. Sainctavit, F. de Groot, P. Glatzel

X-ray Optics and Beam Transport

European XFEL SASE 2

SASE 2 beamline



Current status of evaluation

- 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