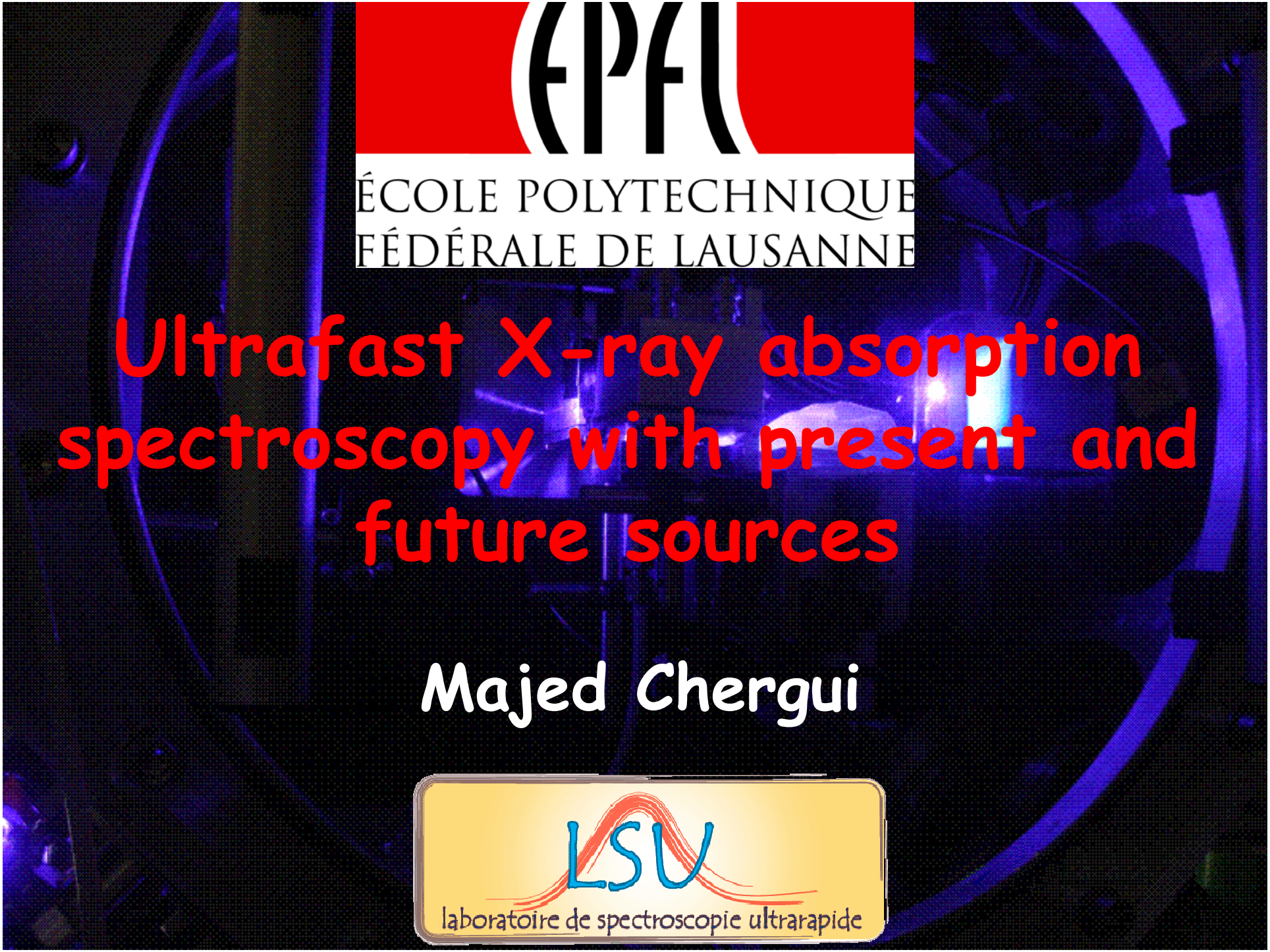
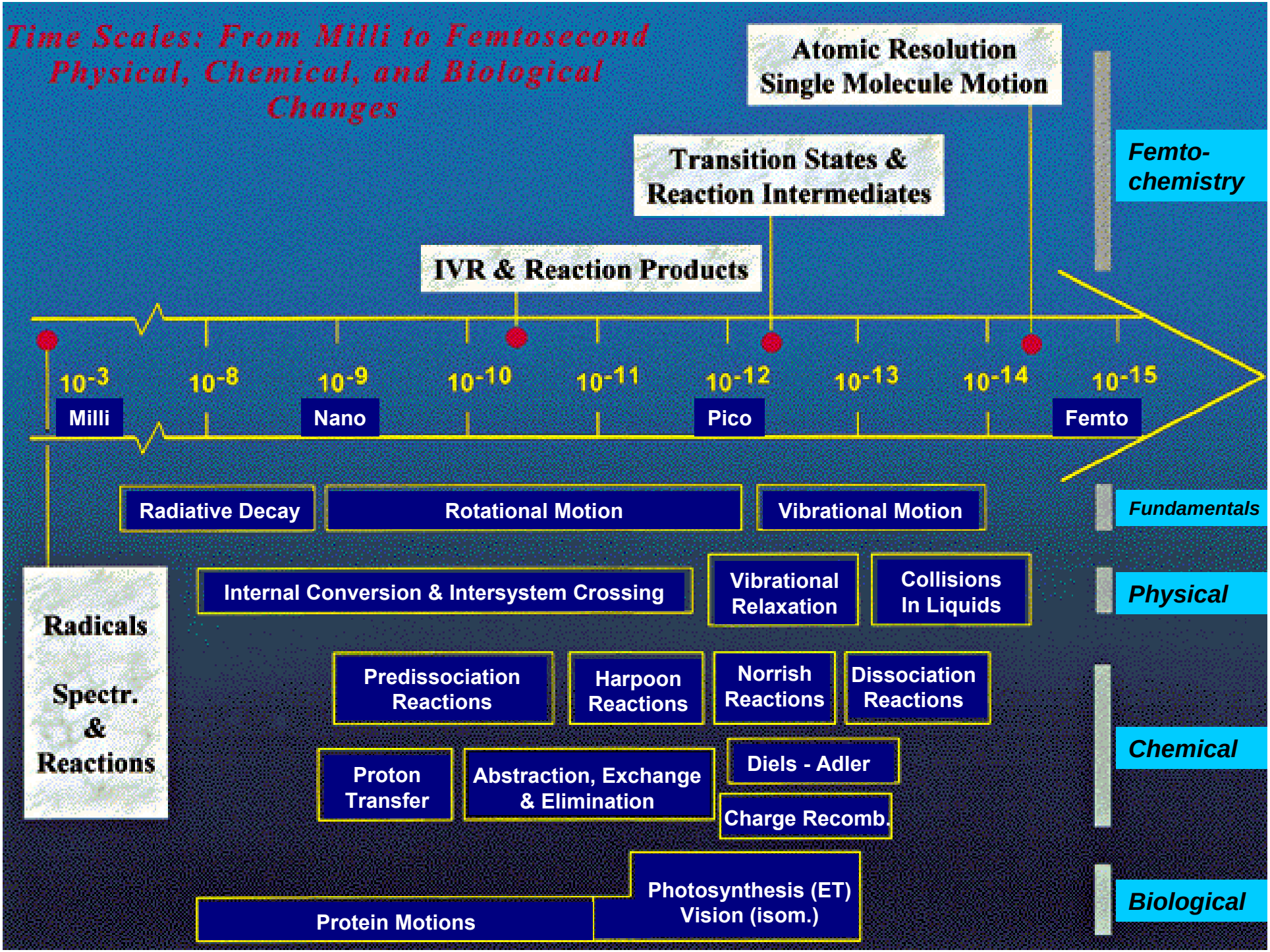

EPFL
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE
Ultrafast X-ray absorption spectroscopy with present and future sources
Majed Chergui
LSU
laboratoire de spectroscopie ultrarapide

"If you want to understand function, study structure"
(Francis Crick)

Function= sequence of events over time,
characterised by structural modifications

"If you want to understand function, study time-dependent structures"

Time resolution **Spatial resolution**

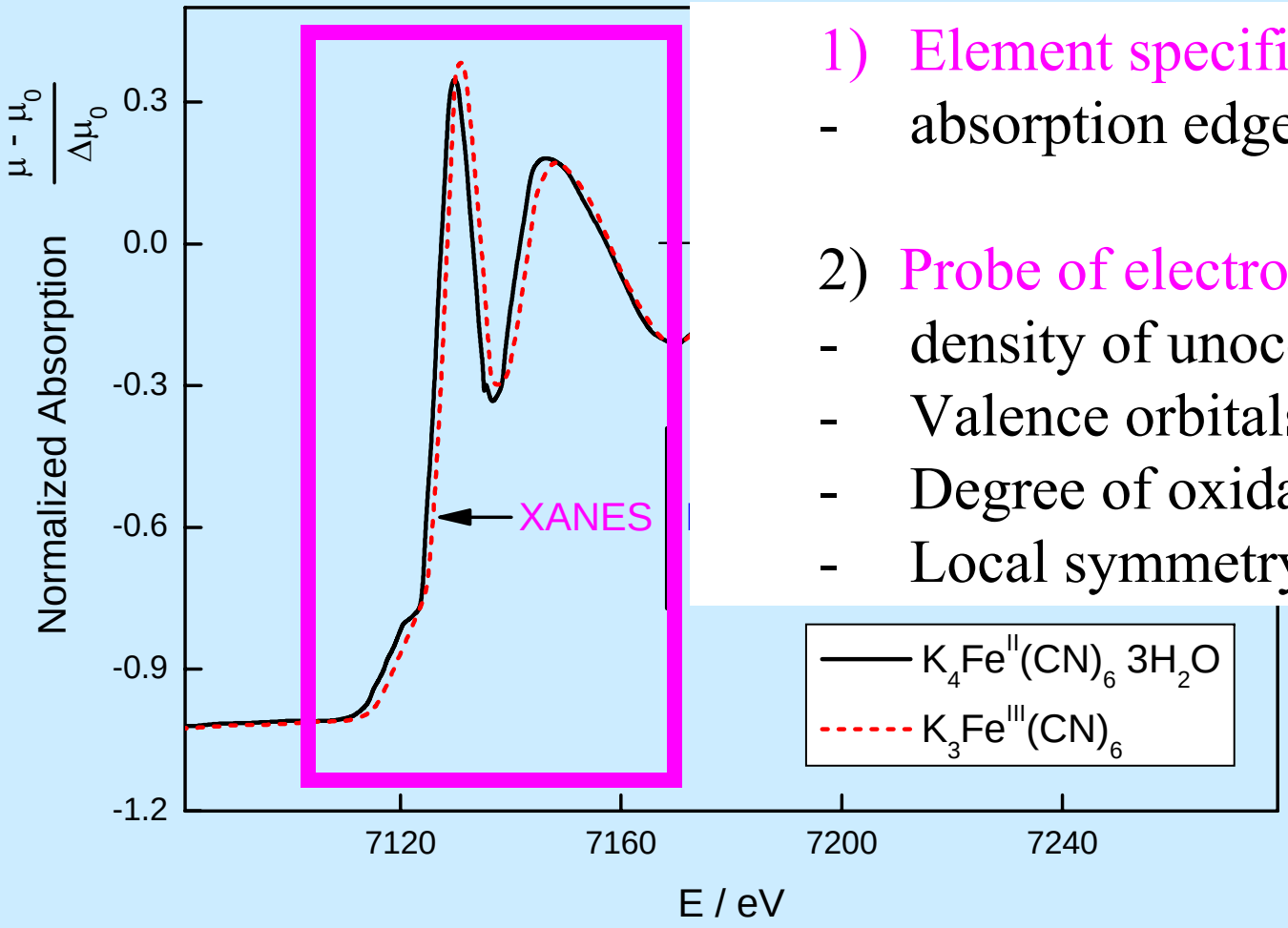

Time Scales: From Milli to Femtosecond Physical, Chemical, and Biological Changes
Atomic Resolution Single Molecule Motion
Transition States & Reaction Intermediates
IVR & Reaction Products
Femto-chemistry
10-3
10-8
10-9
10-10
10-11
10-12
10-13
10-14
10-15
Milli
Nano
Pico
Femto
Radiative Decay
Rotational Motion
Vibrational Motion
Fundamentals
Internal Conversion & Intersystem Crossing
Vibrational Relaxation
Collisions In Liquids
Physical
Radicals
Spectr. & Reactions
Predissociation Reactions
Harpoon Reactions
Norrish Reactions
Dissociation Reactions
Chemical
Proton Transfer
Abstraction, Exchange & Elimination
Diels - Adler
Charge Recomb.
Photosynthesis (ET) Vision (isom.)
Protein Motions
Biological

So ideally:

Note that:..

1) Detects both **electronic** and **molecular** structure changes
   - Electronic structure changes are the primary events in all chemical, biological and physical processes
   - These changes trigger or accompany (in non-adiabatic processes) geometric structural changes, i.e. nuclear motion
2) No long-range order
3) Local probe: Short time scales ↔ short distance scales
4) Liquids, solids, gases, proteins
5) Chemically selective

X-Ray Absorption: Overview

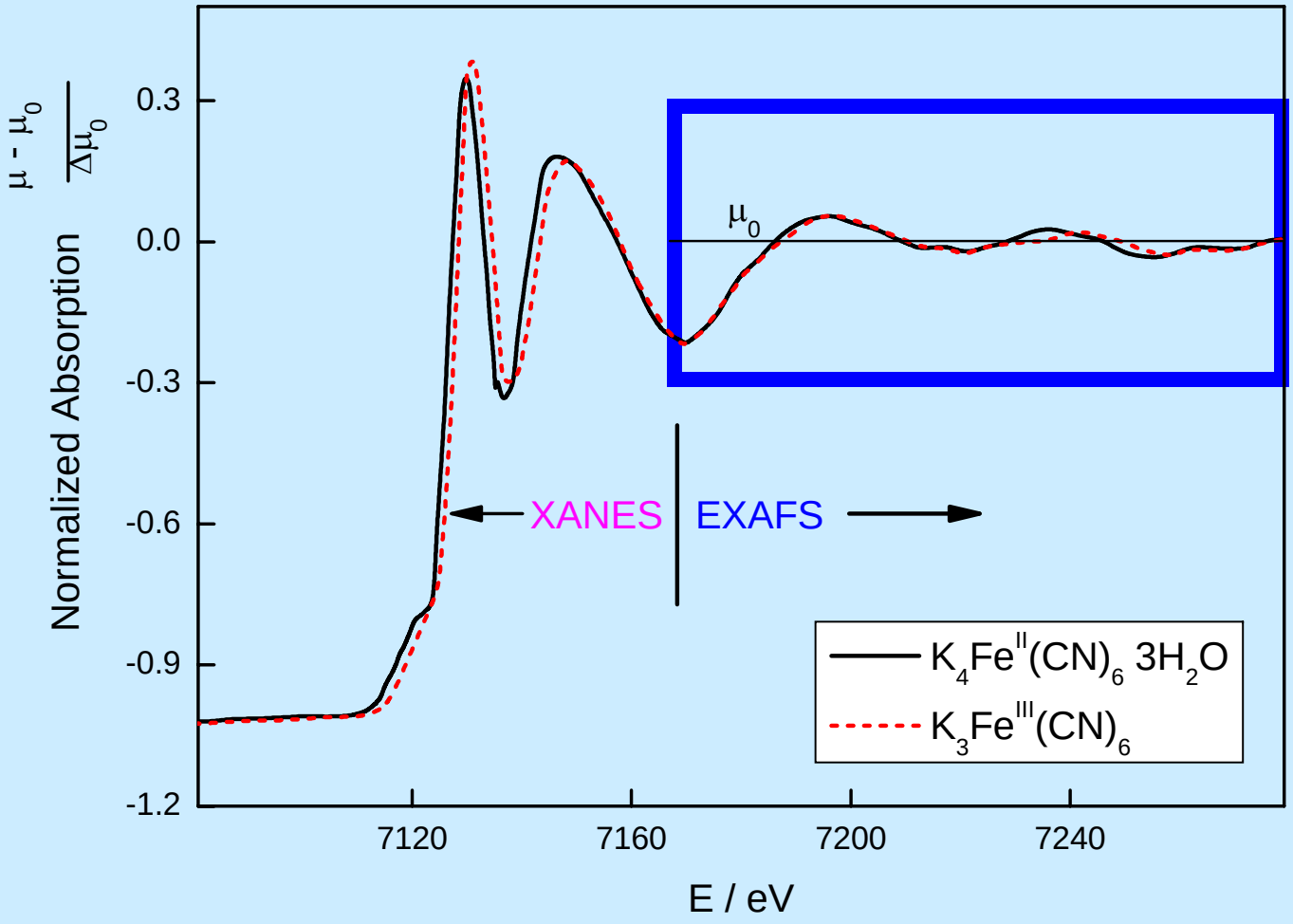


1) Element specific:
- absorption edge

2) Probe of electronic structure:
- density of unoccupied states
- Valence orbitals
- Degree of oxidation
- Local symmetry

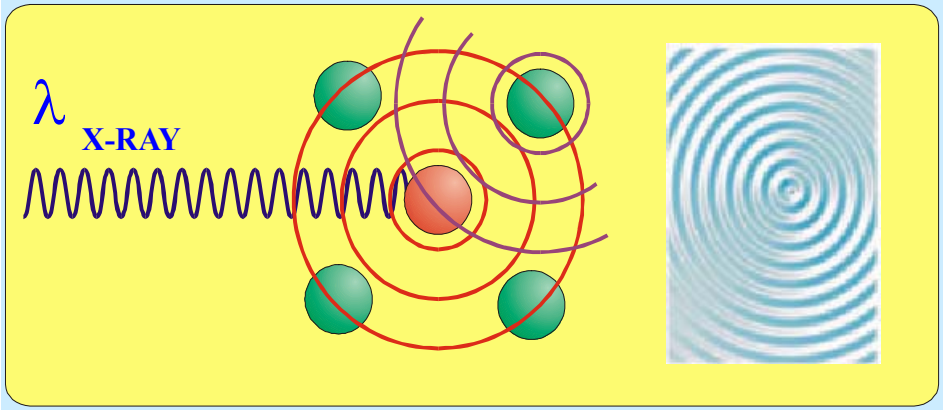
XANES=X-ray absorption Near Edge Structure

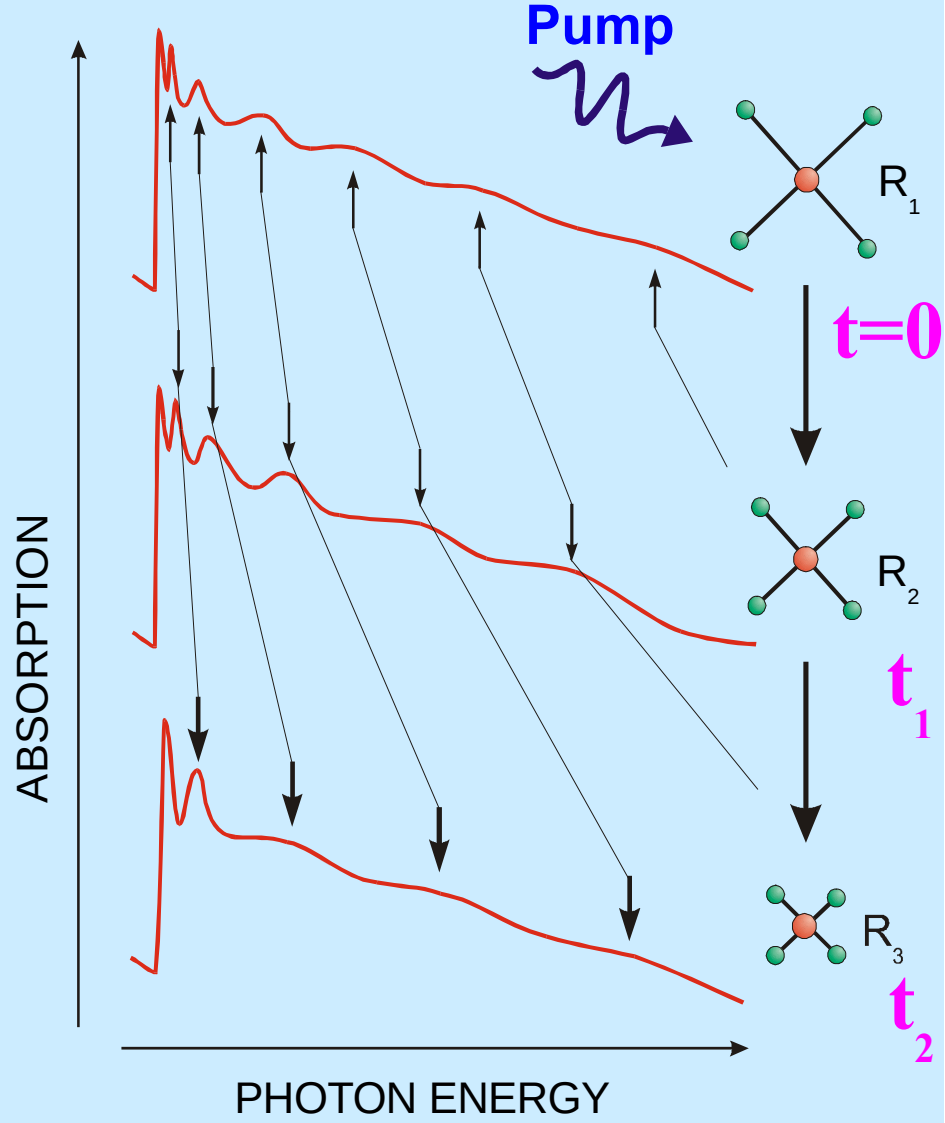
X-Ray Absorption: Overview



EXAFS=Extended X-ray Absorption fine structure

Structural Information via X-Ray Absorption (EXAFS)





- Single scattering events due to higher energy photoelectrons

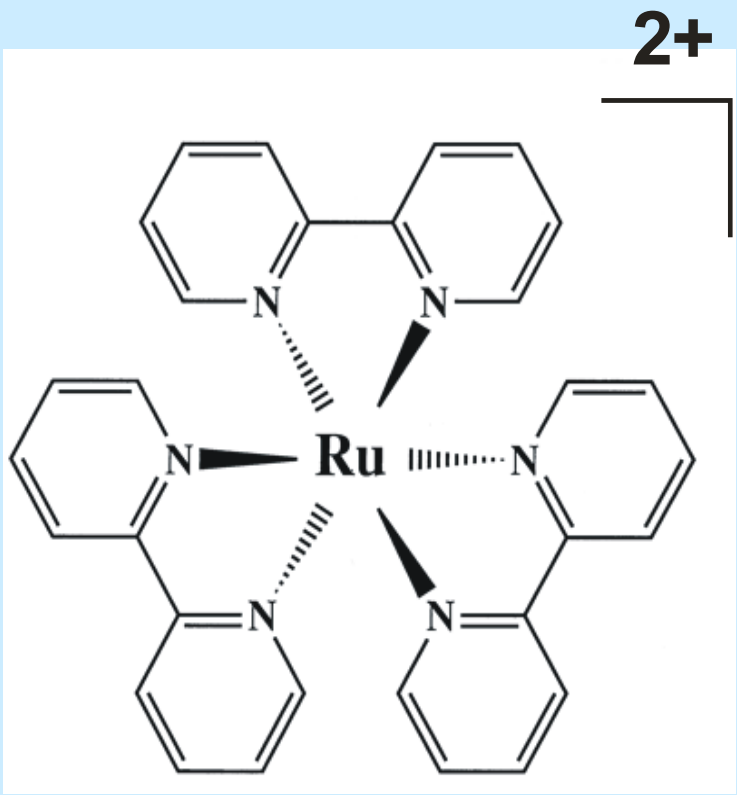
- Bond distances and coordination numbers from simple FT of energy spectrum

Contents

1. Intramolecular charge transfer
2. Spin-crossover compounds
3. Solvation dynamics in liquids
4. Future plans

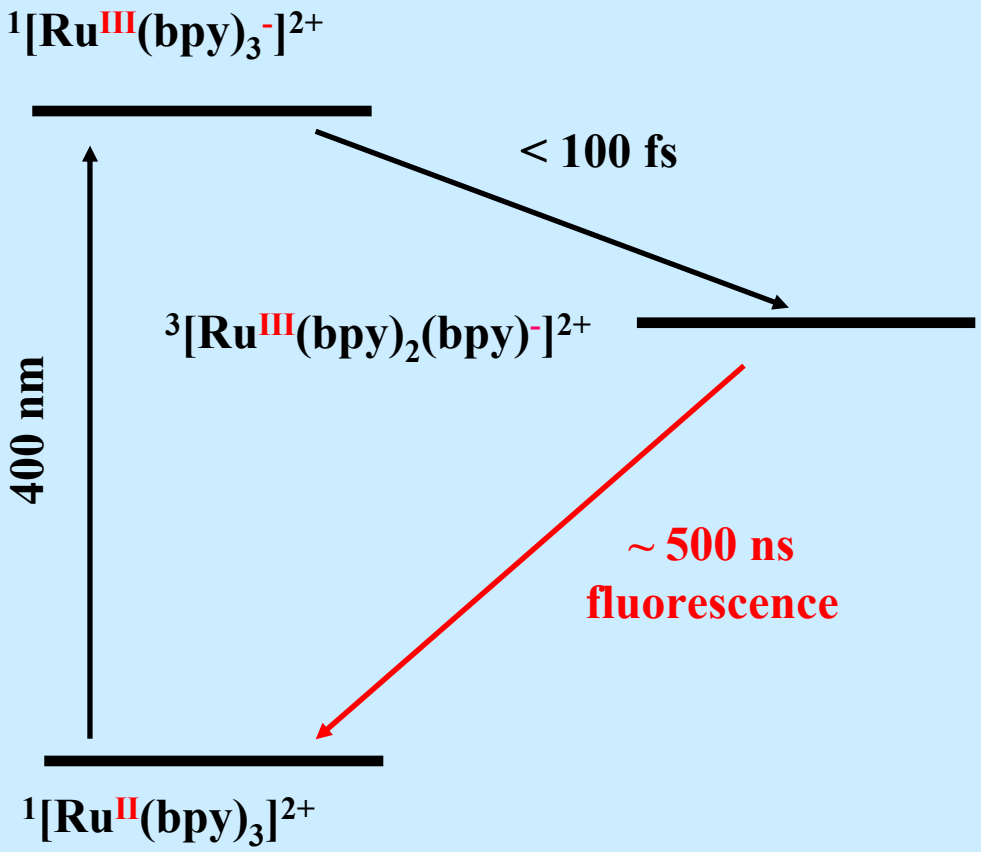
I. Electron Transfer Reactions

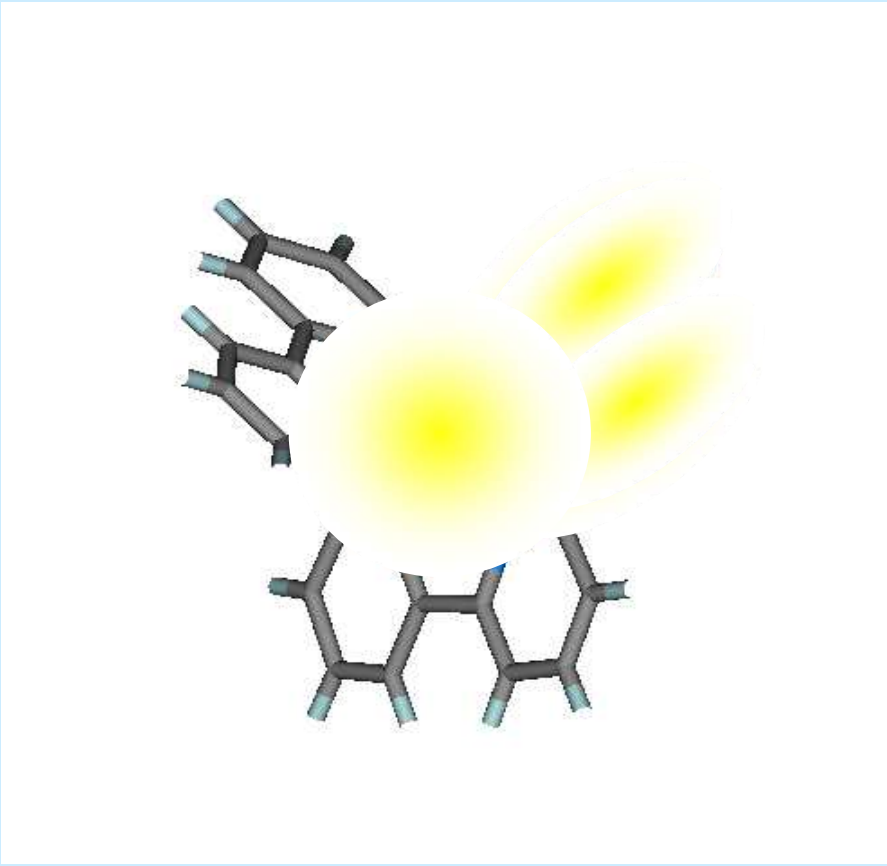
Aqueous $[Ru(bpy)_3]^{2+}$



- H-atom of coordination chemistry
- Photosensitizer
- Solar Cells
- Catalyst in Redox-Reactions
- Model for metalloproteins
- Marker in Biology,…

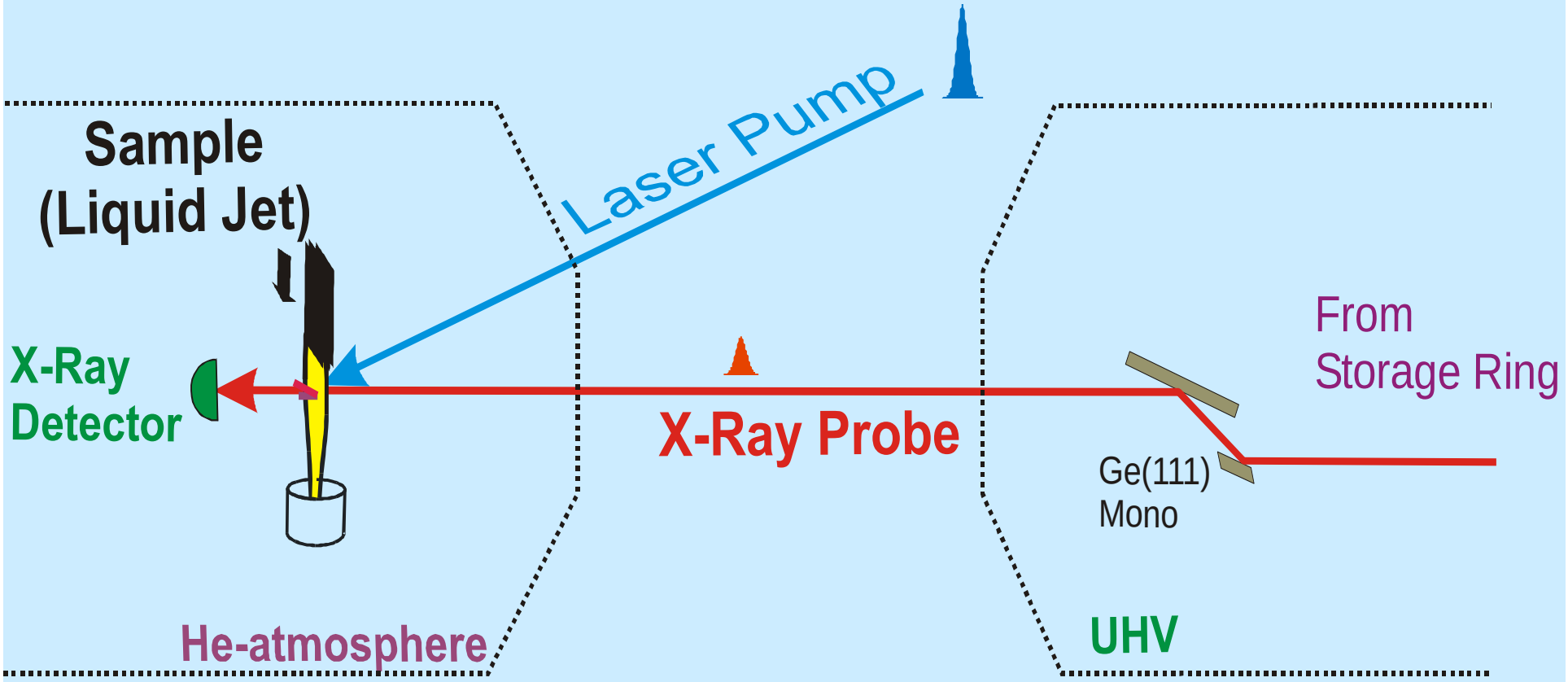
Photochemical Cycle of aqueous $[Ru(bpy)_3]^{2+}$



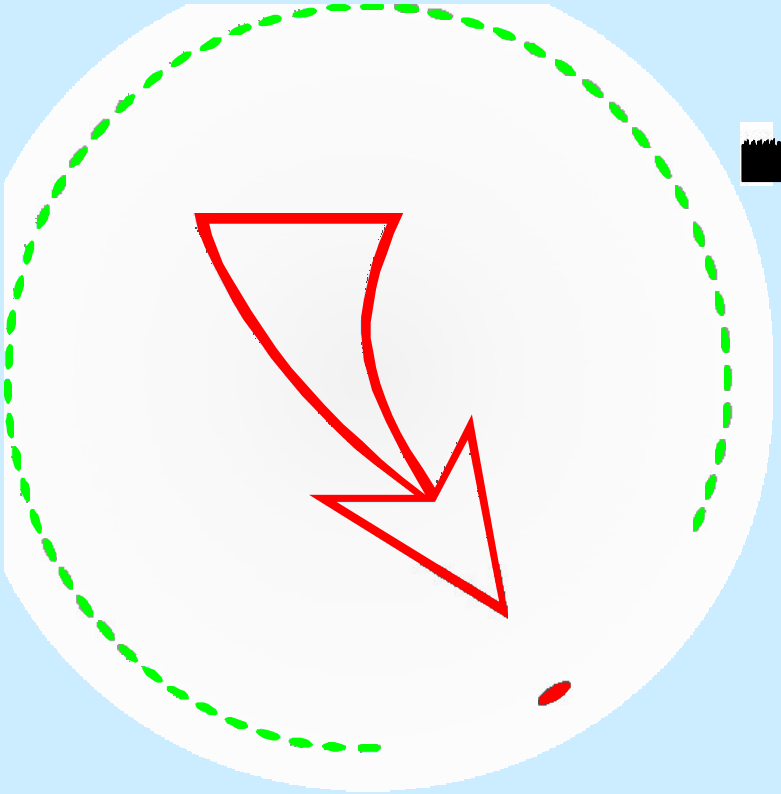


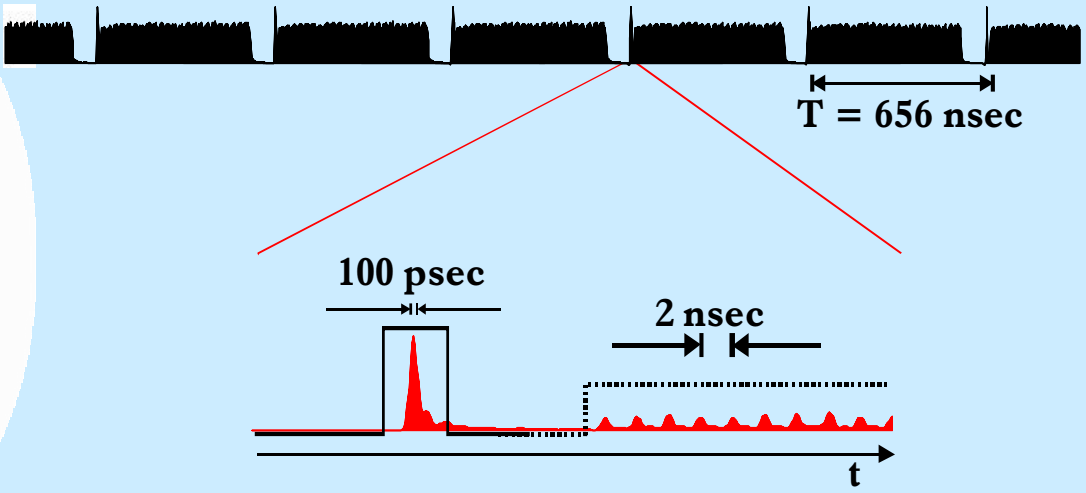
Laser-Pump X-ray-Probe Set-up

Bend Magnet Beamline 5.3.1 Advanced Light Source, Berkeley



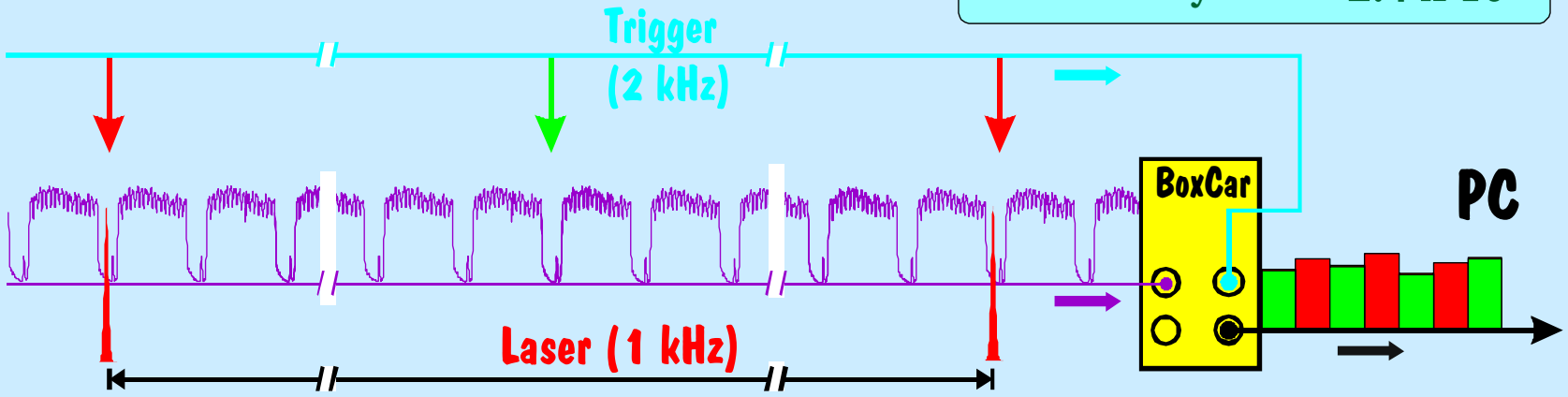
Data Acquisition Strategy



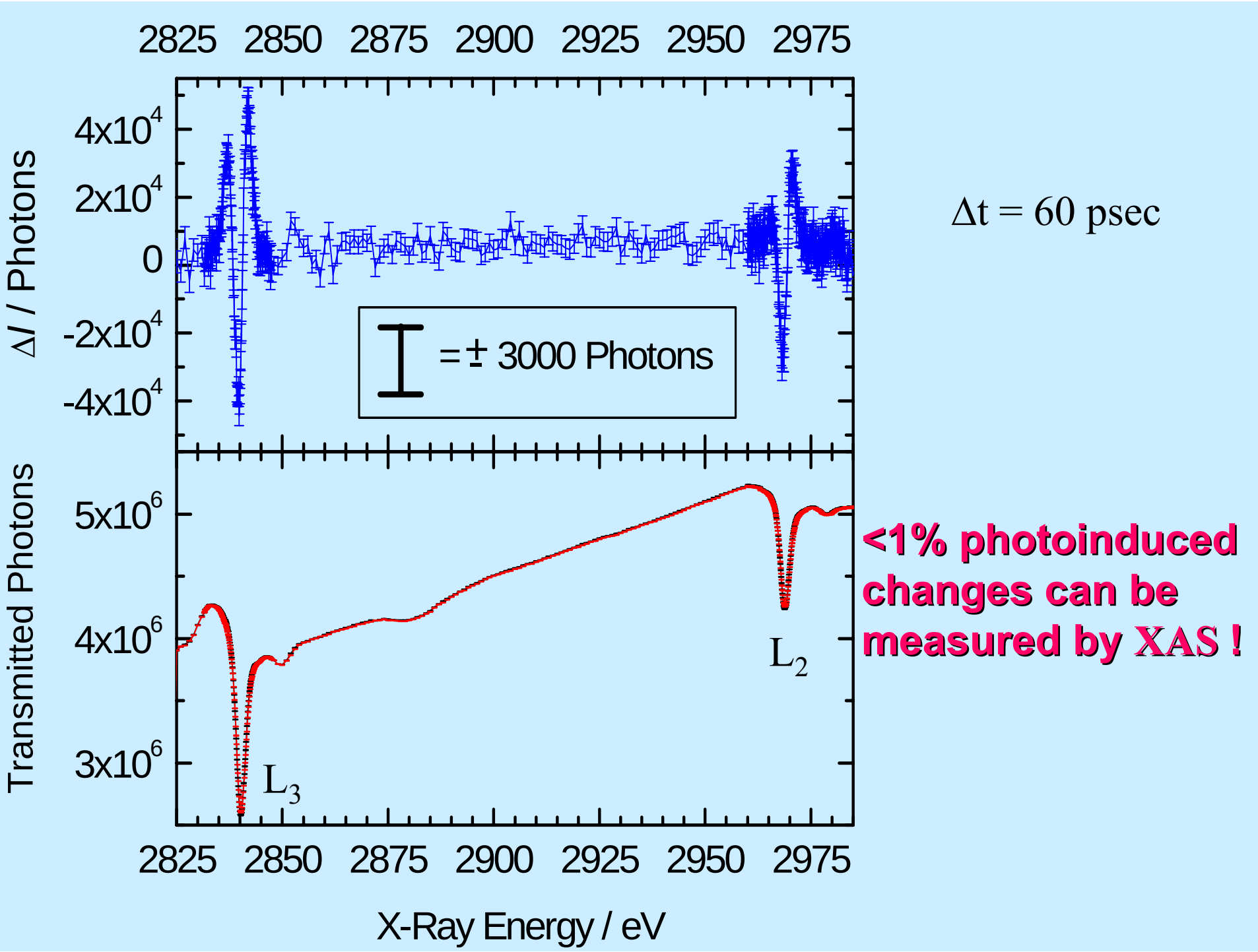


ALS "Camshaft" Mode

Usable X-Ray Flux = 2.4×10^{-6}



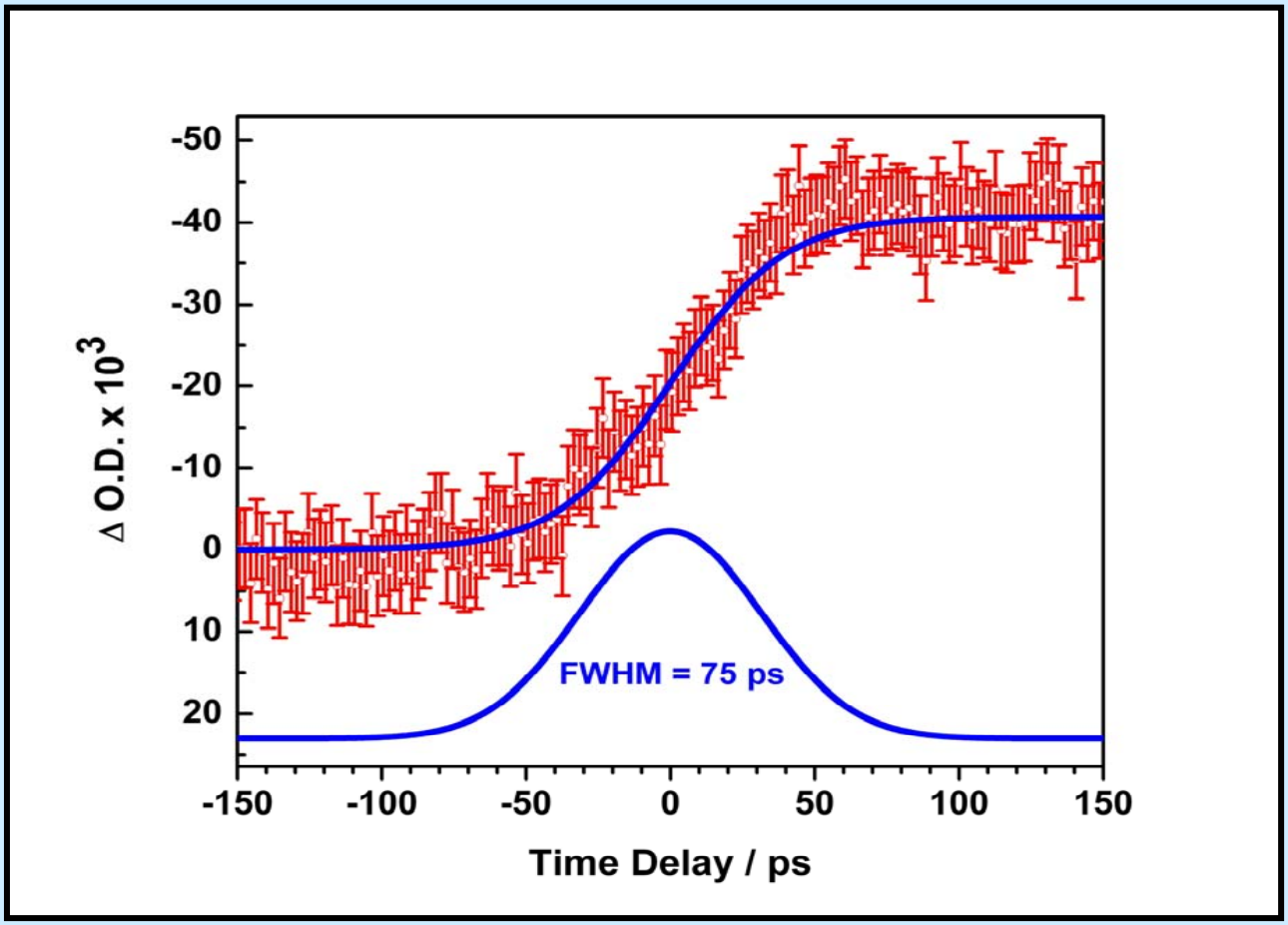
Saes *et al*, Rev. Sci. Inst. 75 (2004) 24



$\Delta t = 60$ psec

<1% photoinduced changes can be measured by XAS !

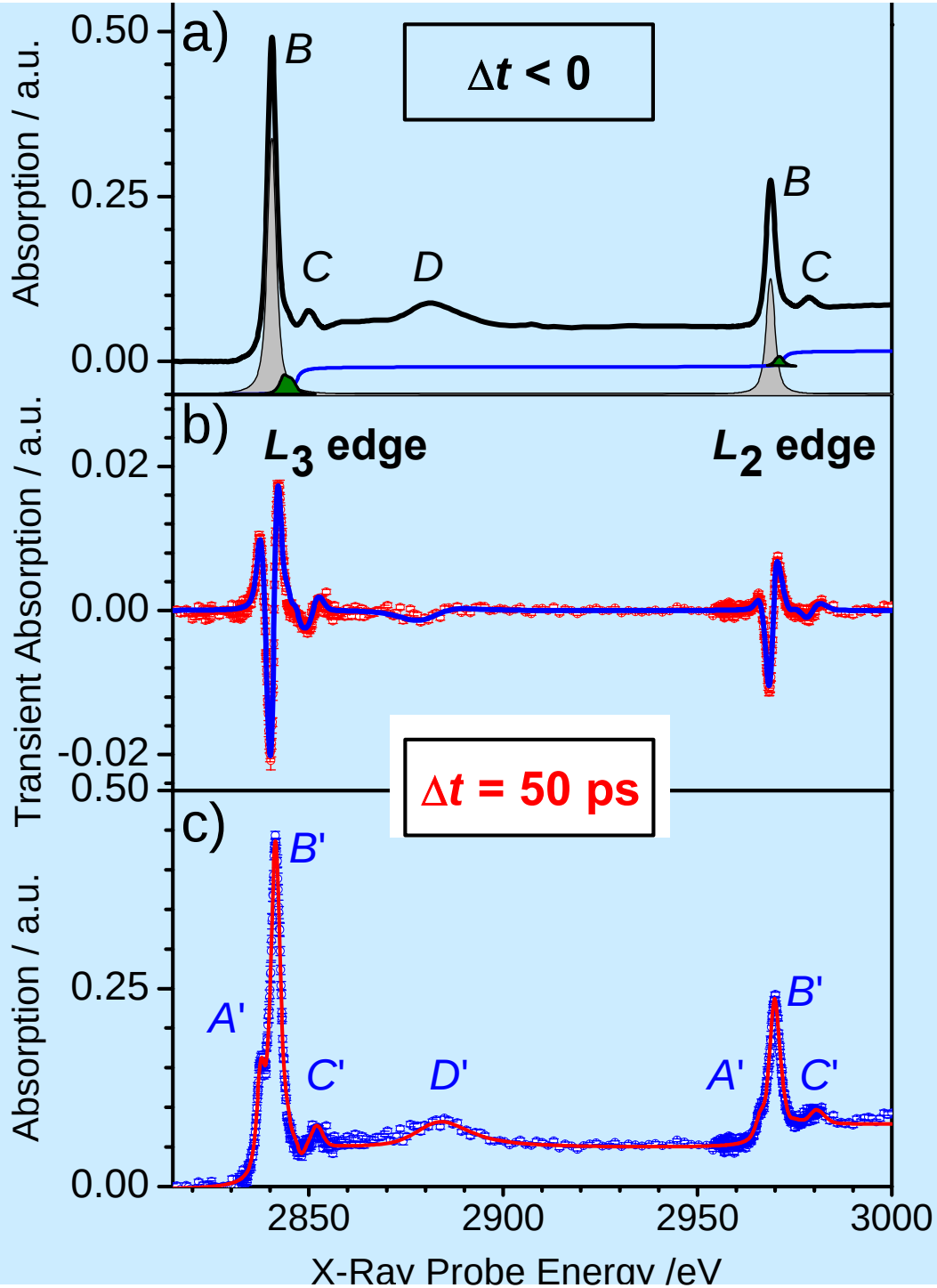
Real-Time Laser/X-Ray Cross-Correlator

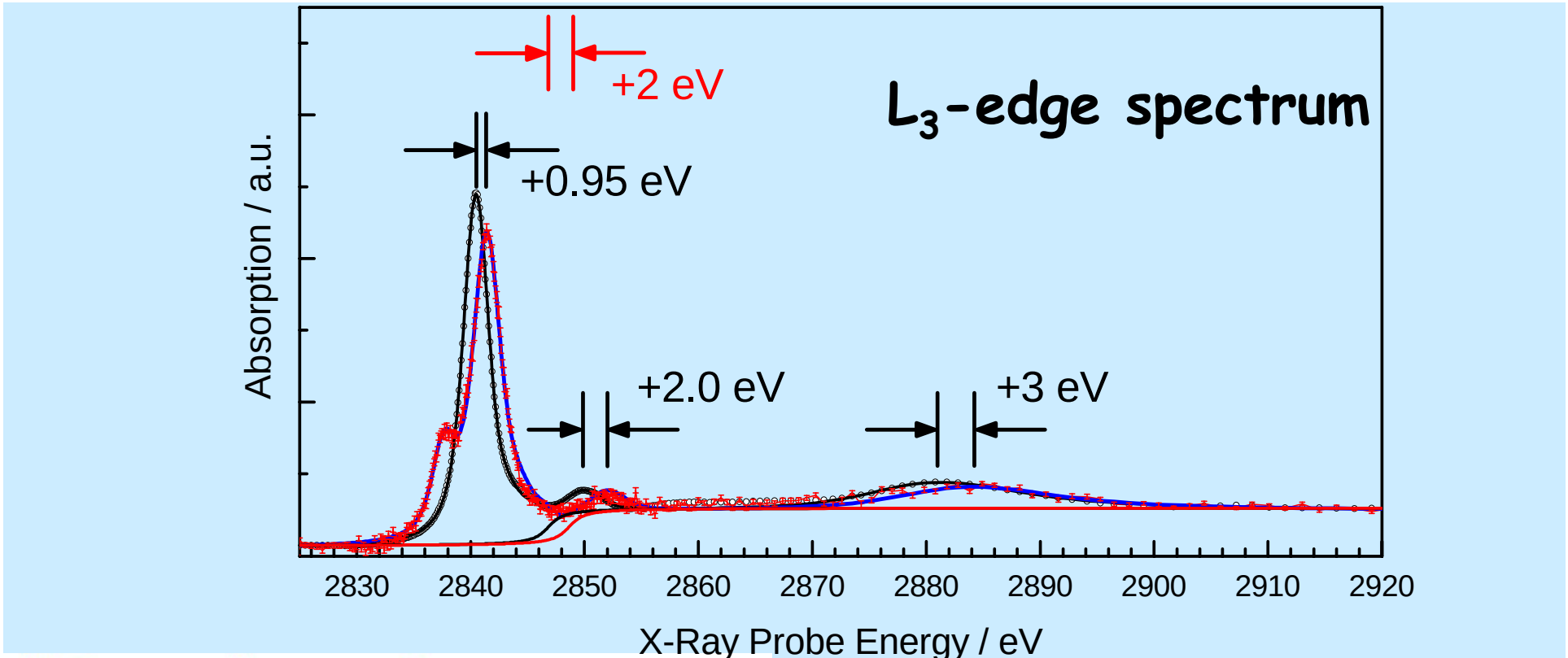


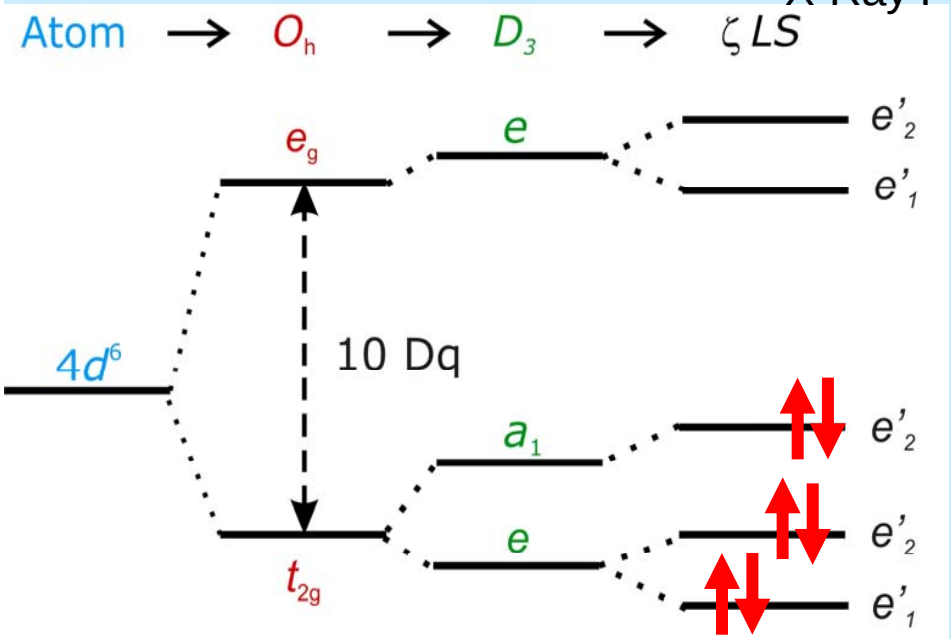
- **Short scan times ≤ 10 min**
- **Adjustable time delay between laser and x-ray pulses up to nsec and more**

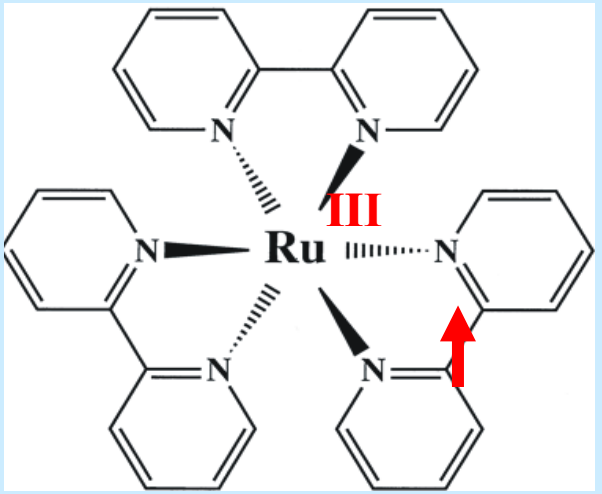
Timing jitter ≤ 10 ps accuracy

M. Saes *et al*, Synch. Rad. News 16 (2003) 12


a)
B
Δt < 0
B
C
D
C
0.50
0.25
0.00
Absorption / a.u.
b)
L3 edge
L2 edge
0.02
0.00
-0.02
Transient Absorption / a.u.
Δt = 50 ps
c)
B'
A'
B'
C'
D'
A'
C'
0.50
0.25
0.00
Absorption / a.u.
2850
2900
2950
3000
X-Ray Probe Energy /eV







Saes *et al*, Phys. Rev. Lett. 90 (2003) 47403

Multiplet structure calculations

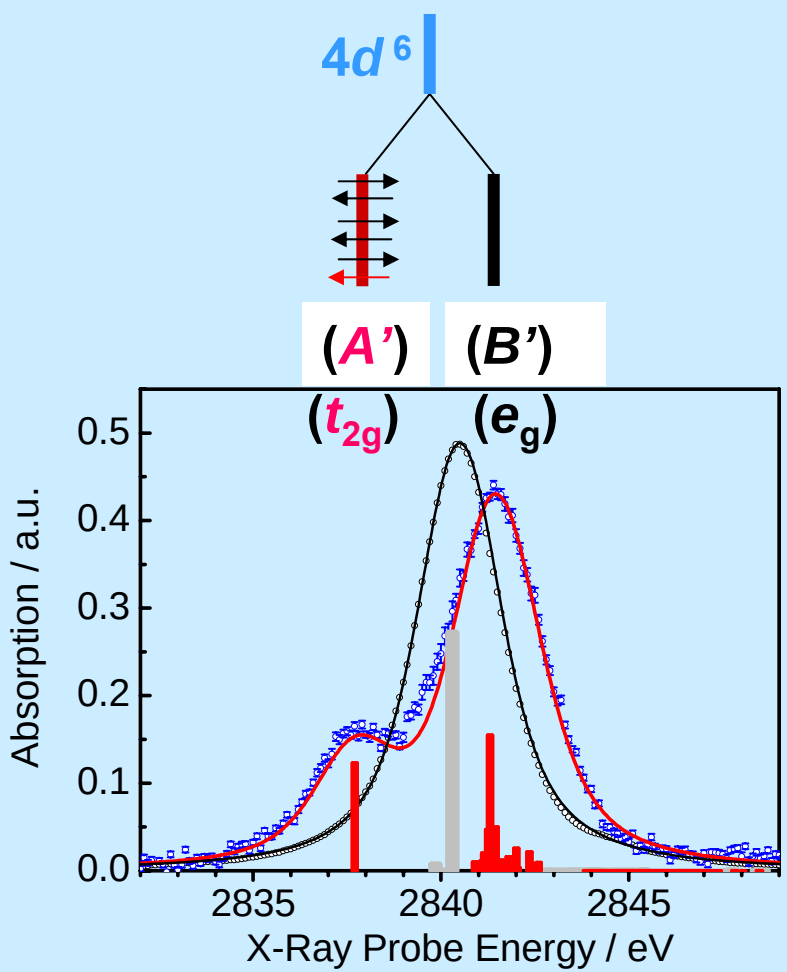
(de Groot, Coord. Chem. Rev. (2005))

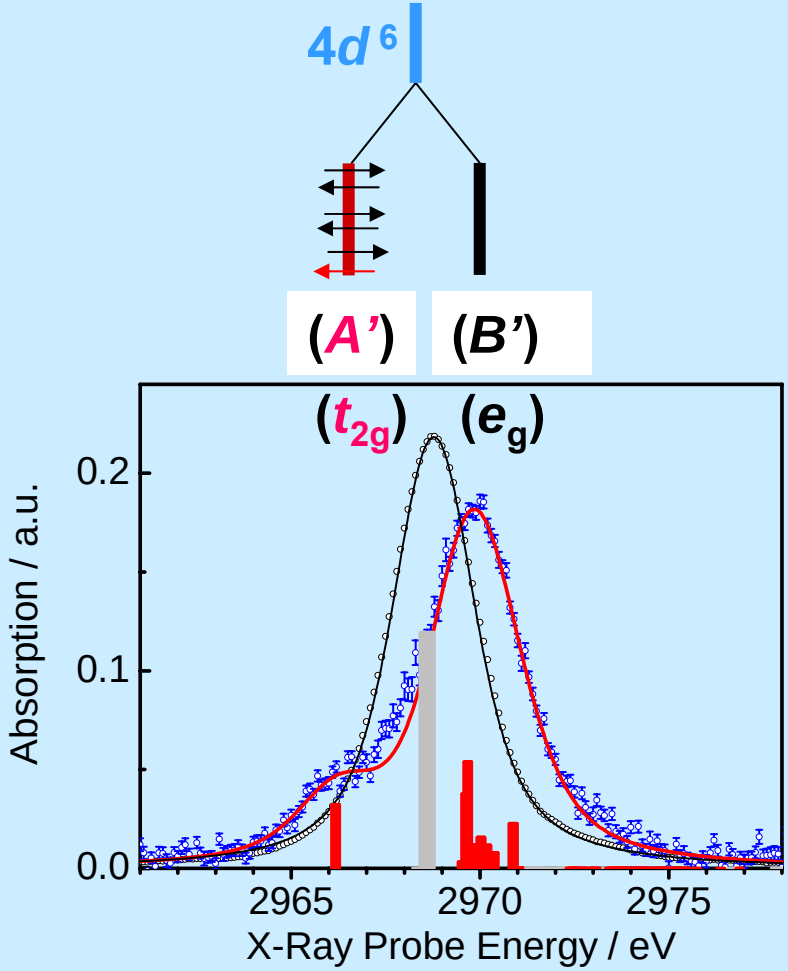
$$H = H_{atom} + H_{Ligands}$$

H_{atom}: kinetic energy, Coulomb terms, e-e correlations, spin-orbit coupling

$H_{Ligands}$: octahedral and trigonal field contributions, written as superposition of spherical harmonics

Comparison of experimental and simulated line shapes





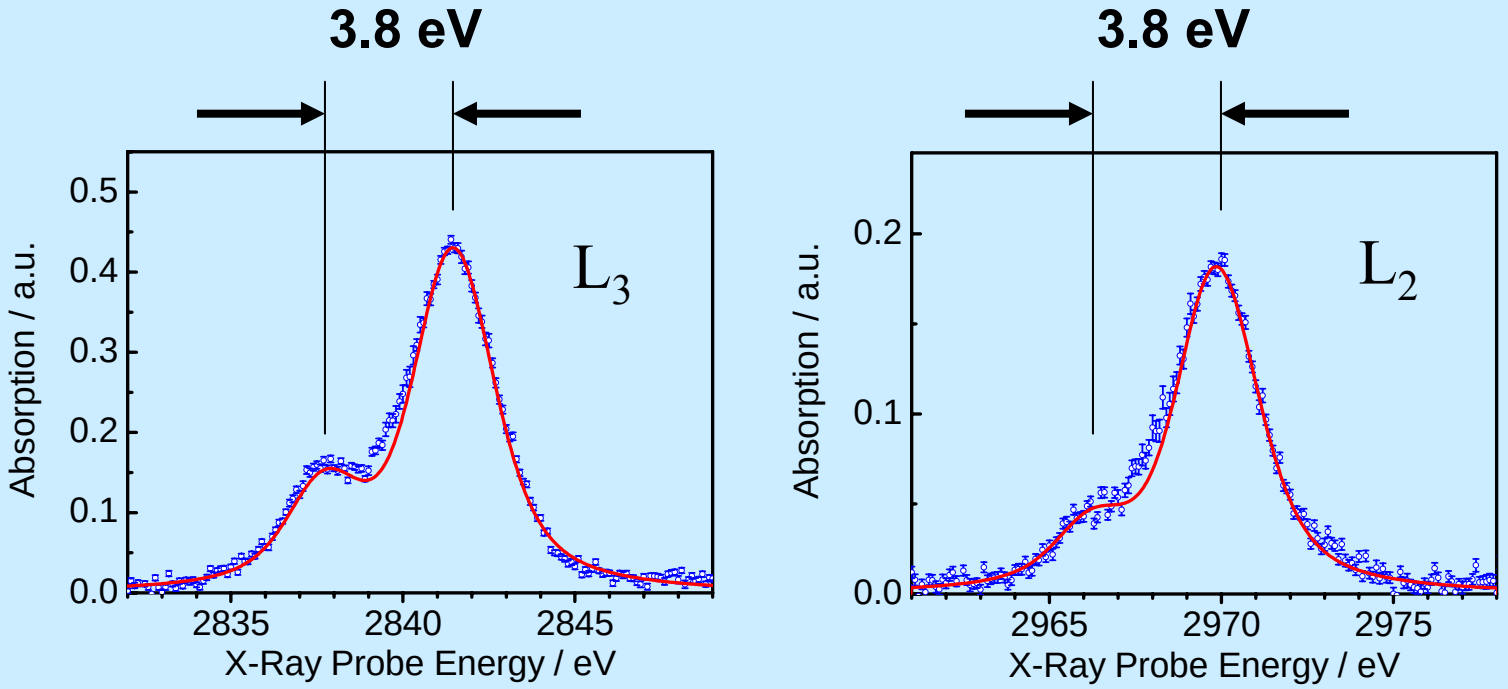
W. Gawelda *et al.*, submitted to JACS

Ligand field theory: Information about the Transient *Structure*

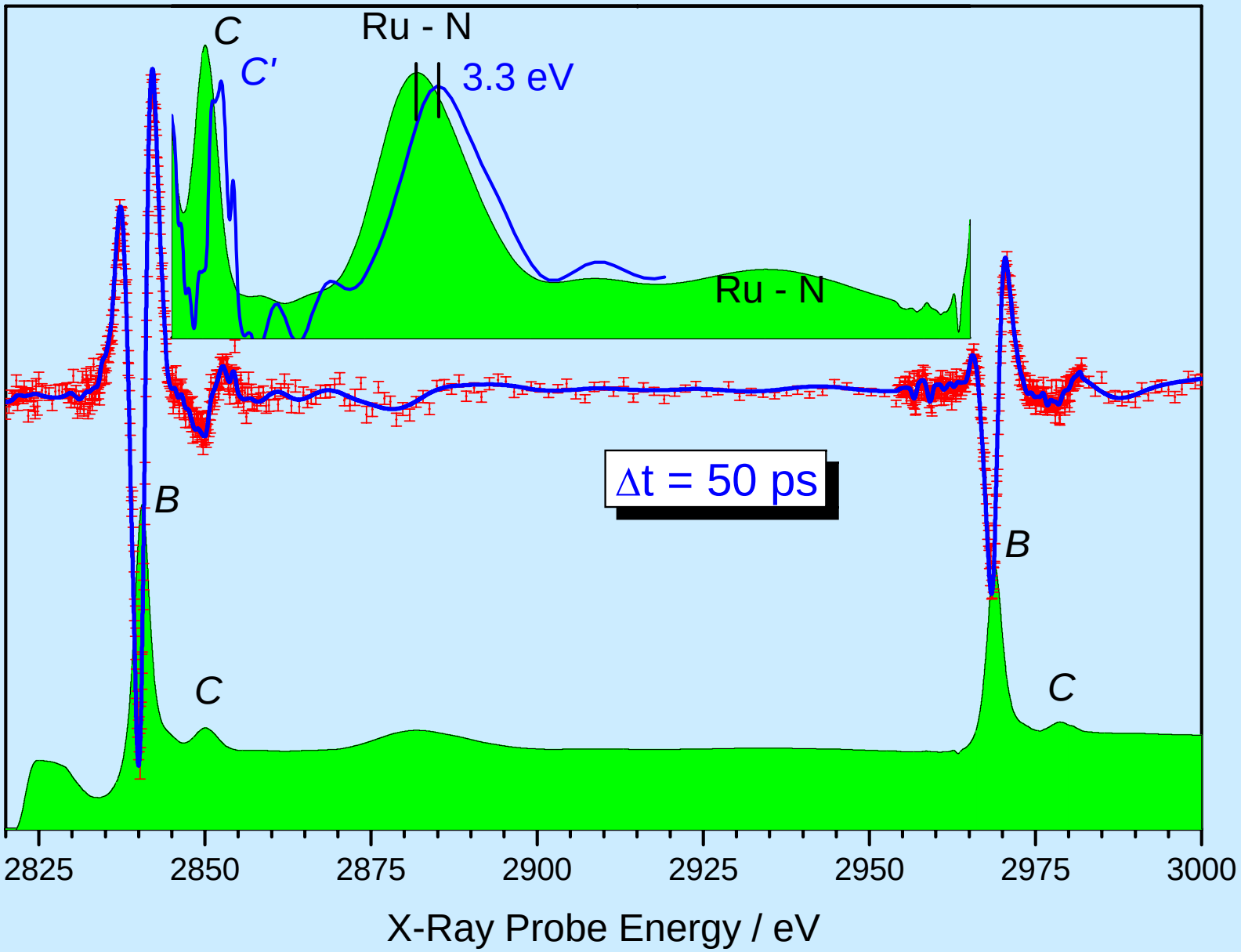
$$\frac{10Dq^{ES}}{10Dq^{GS}} = \left(\frac{R^{GS}_{Ru-N}}{R^{ES}_{Ru-N}}\right)^5 \Rightarrow \Delta R_{Ru-N} = R^{gs}_{Ru-N}\left[\left(\frac{\Delta E_{gs}}{\Delta E_{es}}\right)^{1/5} - 1\right]$$

ΔE (10Dq) (ground - excited) = -0.15 eV

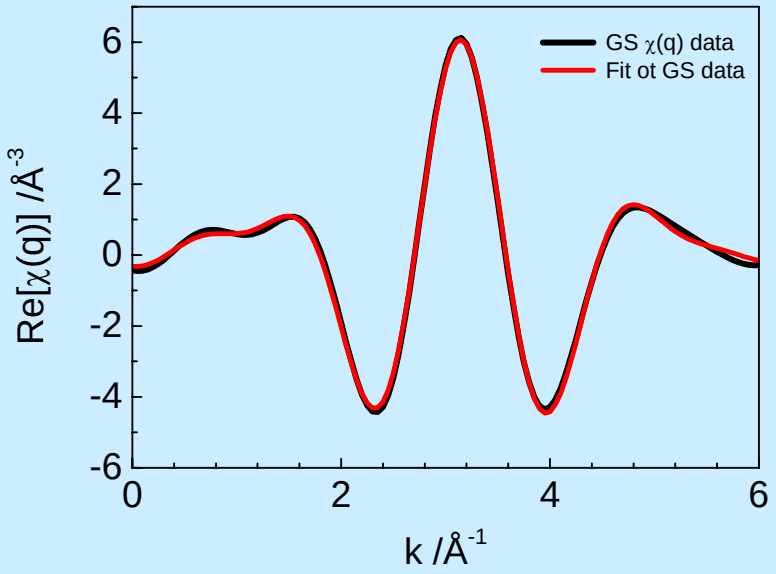
→ ΔR = -0.02 Å



Structure from transient EXAFS

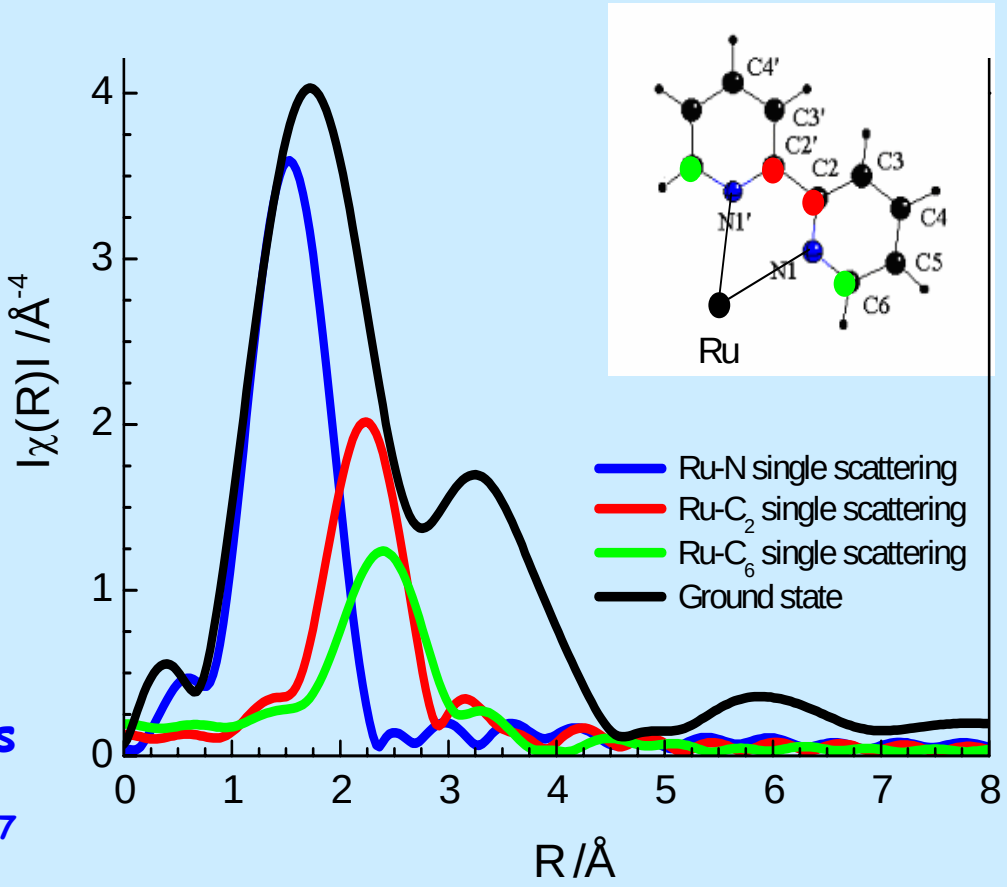


Ground state EXAFS Data



FEFF 8.20 – Theoretical backscattering amplitudes and phases

A.L. Ankudinov et al., Phys. Rev. B, 65 (2002) 104107



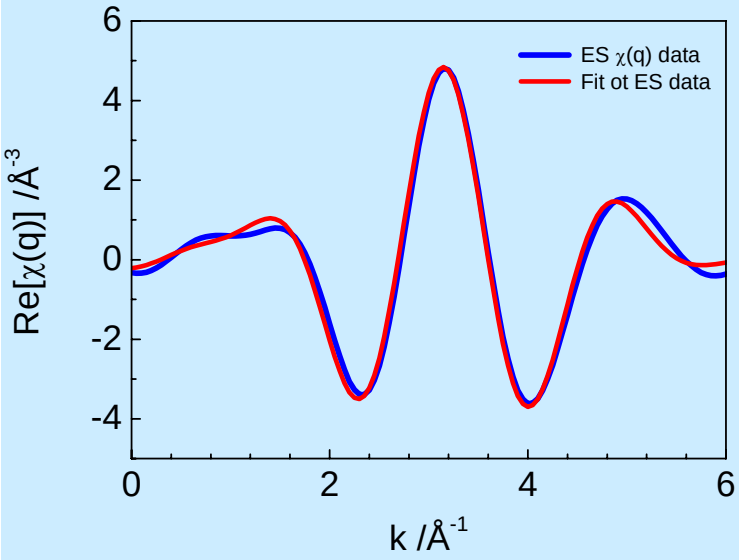
✓ Good agreement with x-ray crystallography

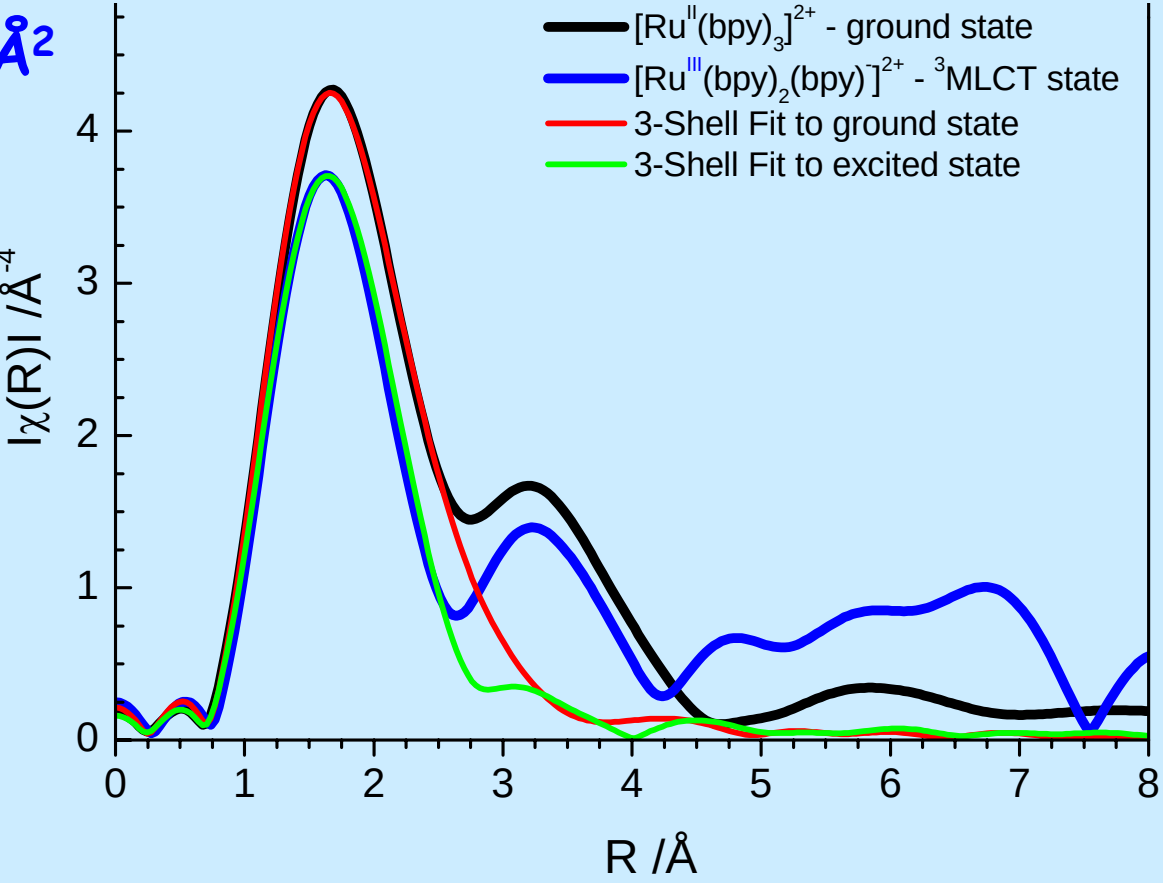
Transient EXAFS Data @ Δt=50ps

ΔR (Ru-N) = - 0.037 (0.02) Å

σ^2_{gr} (Ru-N) = 0.009 Å²

σ^2_{ex} (Ru-N) = 0.01 Å²





Summary

- *Weak Ru-N bond contraction (0.02 to 0.04 Å)!*

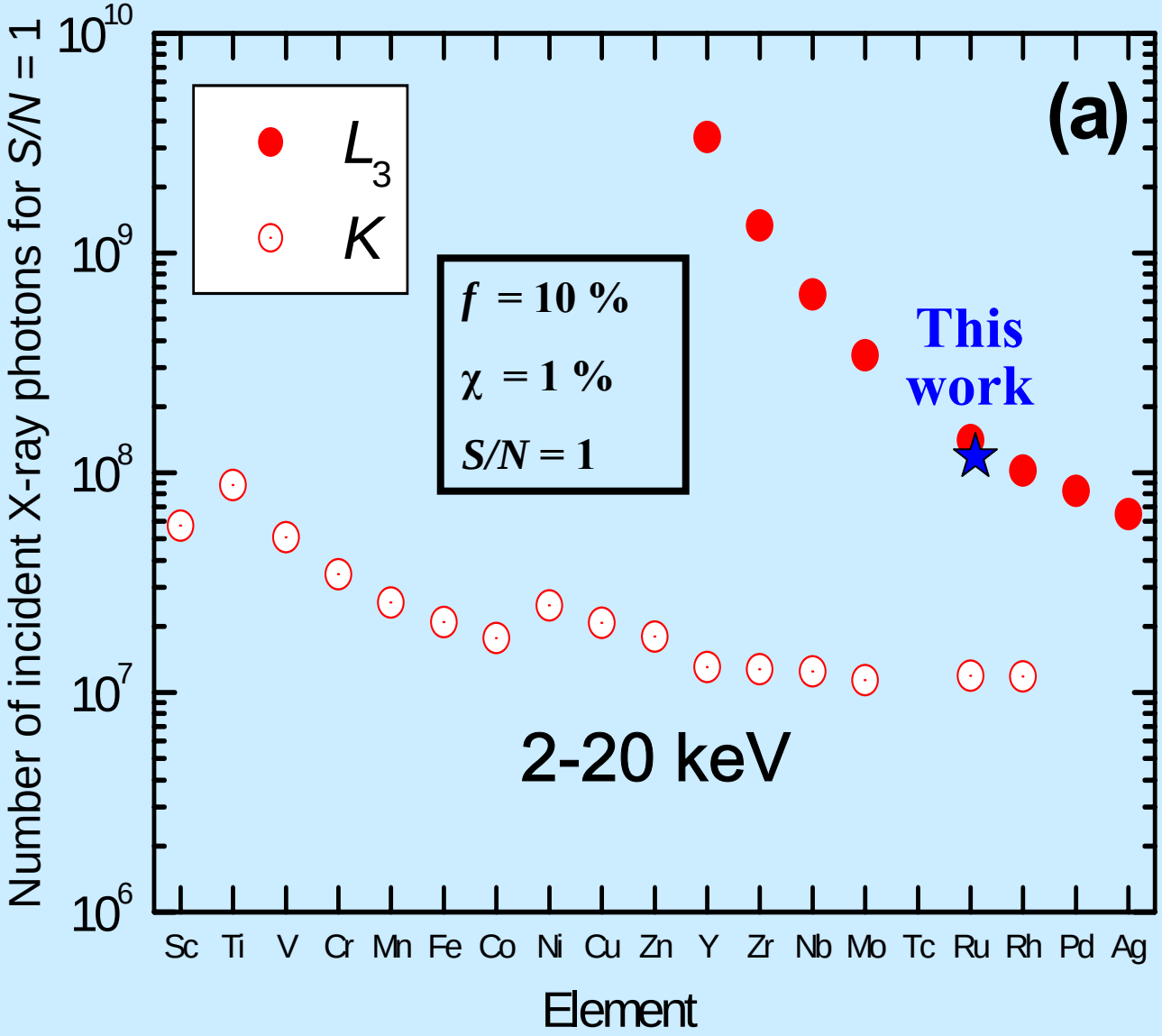
- Electrostatic and polarisation forces (contraction) counterbalanced by reduced π-backbonding (elongation) and steric effects.

- *Implications for intermolecular electron transfer:*

- Efficient, due to small reorganisation between gs and es.

- In good agreement with XRD data on $Ru^{II}(bpy)_3$ and $Ru^{III}(bpy)_3$ and high rates of self exchange between them.

Calibrating future EXAFS experiments on aqueous Metal Compounds



Bressler and Chergui, Chem. Rev. (2004)

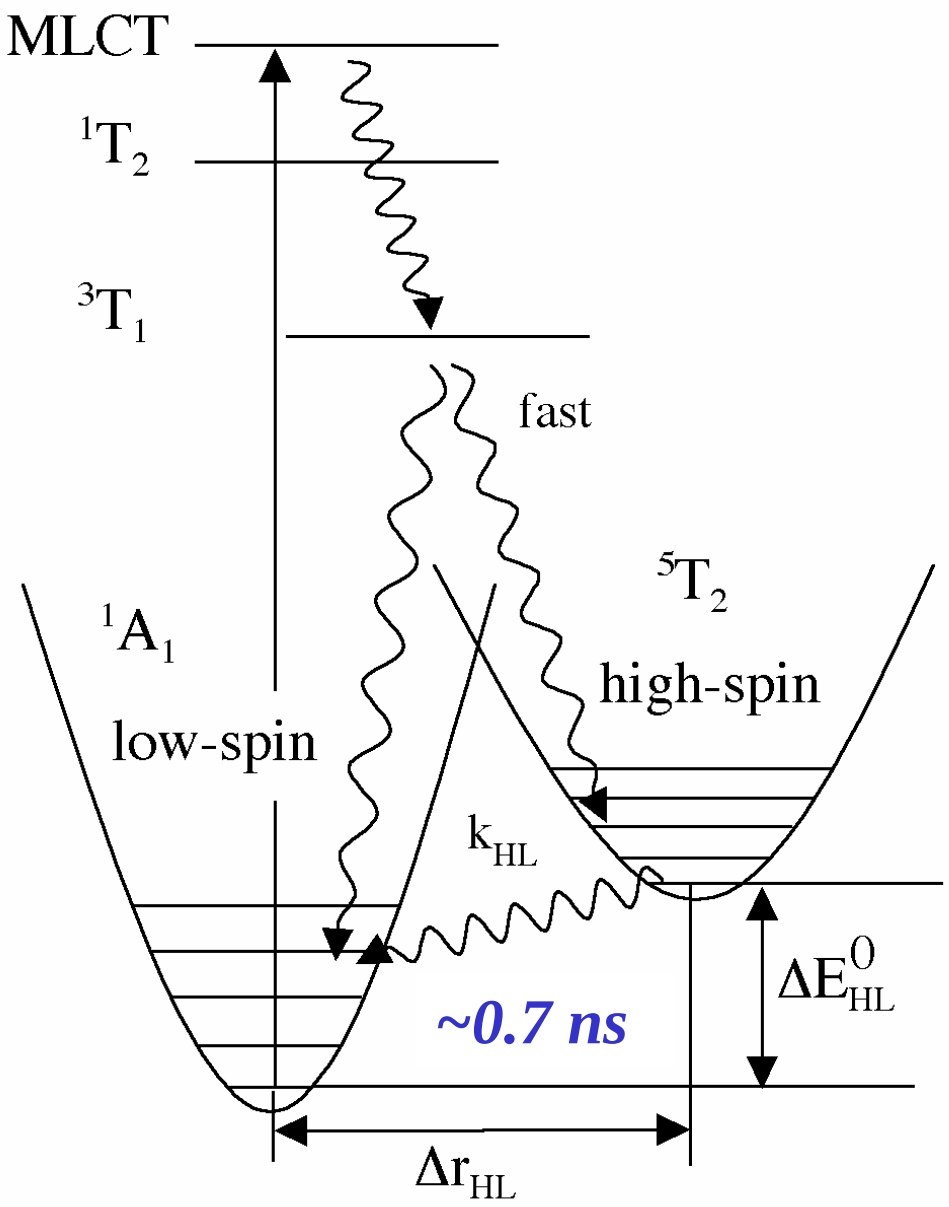
→Swiss Light Source in Villigen

μ^f-XAS Beamline

(undulator + laser-slicing wiggler)

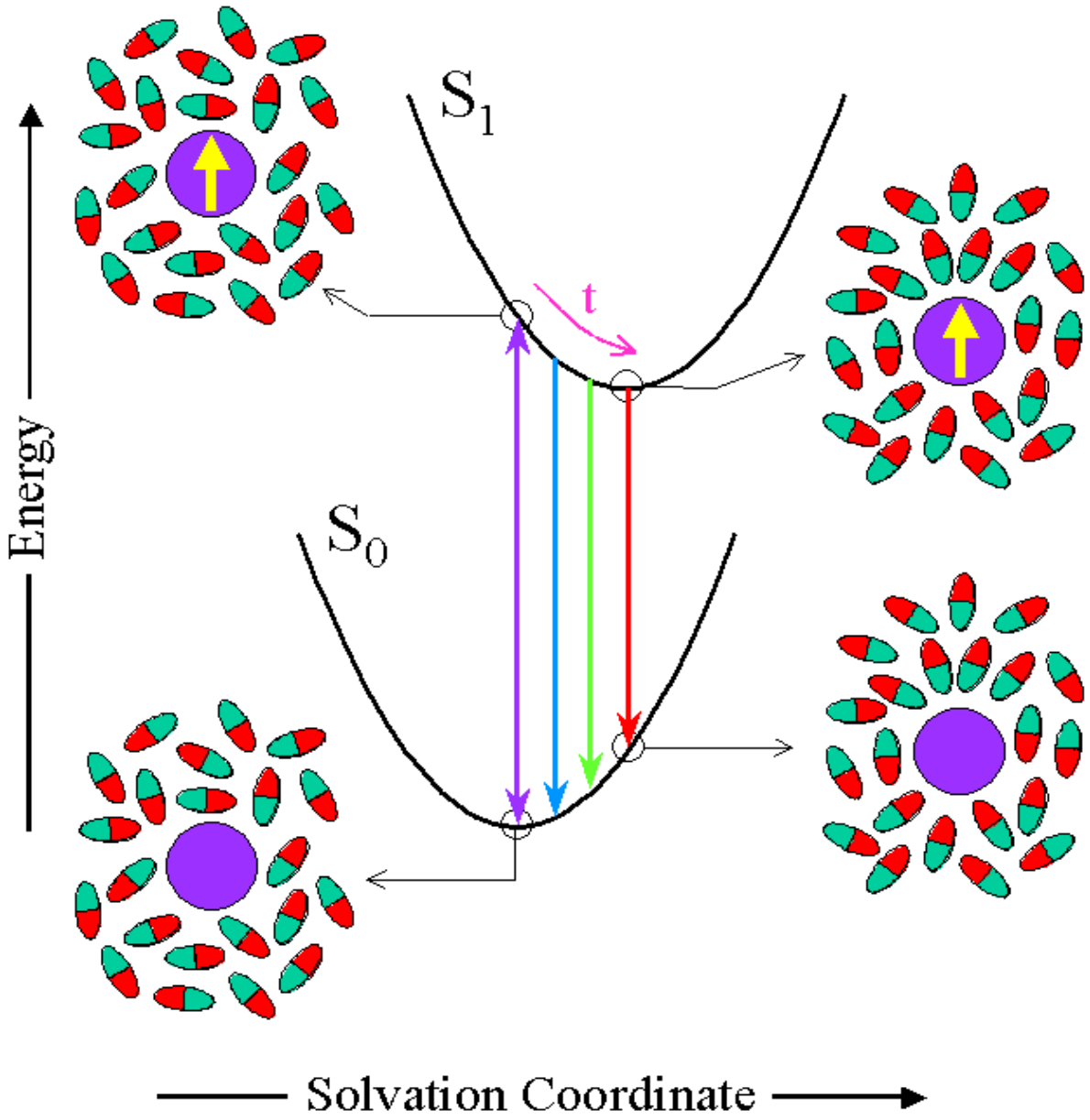

Our new playground…
KG
30 8 2005

II. Spin-crossover compounds



- Magnetic data storage
- Information technology
- $Fe^{II}(bpy)_3$ and $Fe^{III}(terpy)_2$
- Short lived at RT, long lived at LT
- At LT, HS lifetime governed by Δr_{HL}

III. Solvation Dynamics

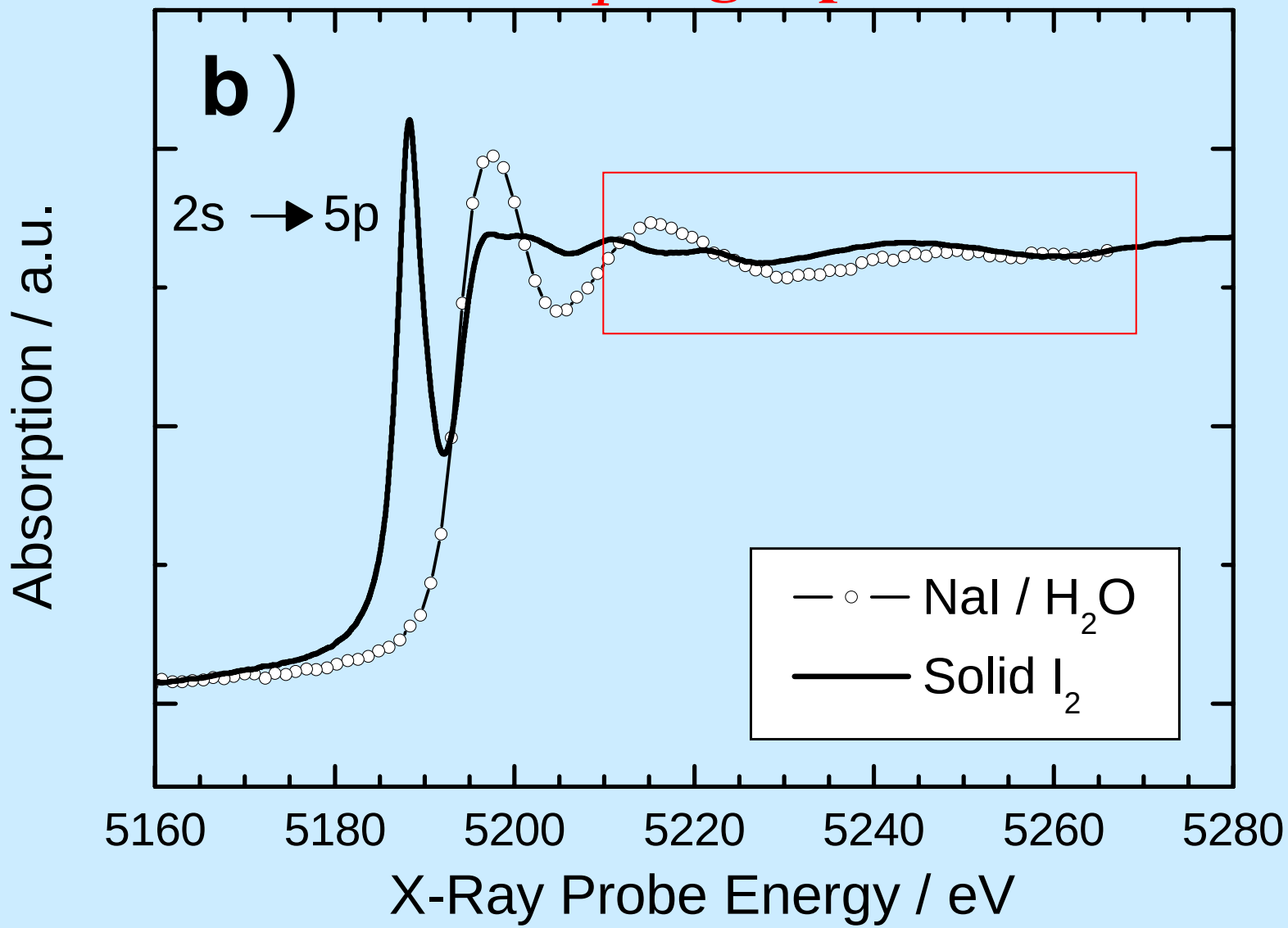


Our strategy:

- I^- or Br^- ions in water

- I^- (Br^-) + $(H_2O)_n$ + $h\nu_{UV}$ → I^0 + $(H_2O)_m$ + $e^-_{aq.}$

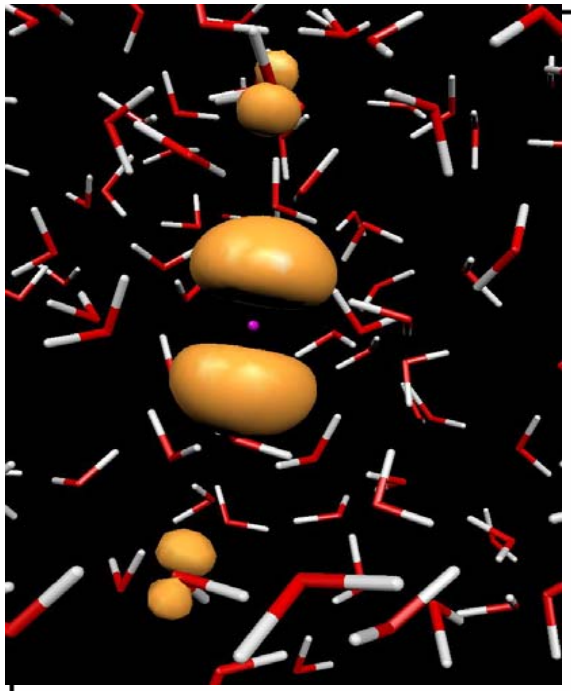
Static L_1-edge spectra



$I^- \equiv Xe\ (5p^6)$

I in 183 water molecules

Radial distribution for water oxigens

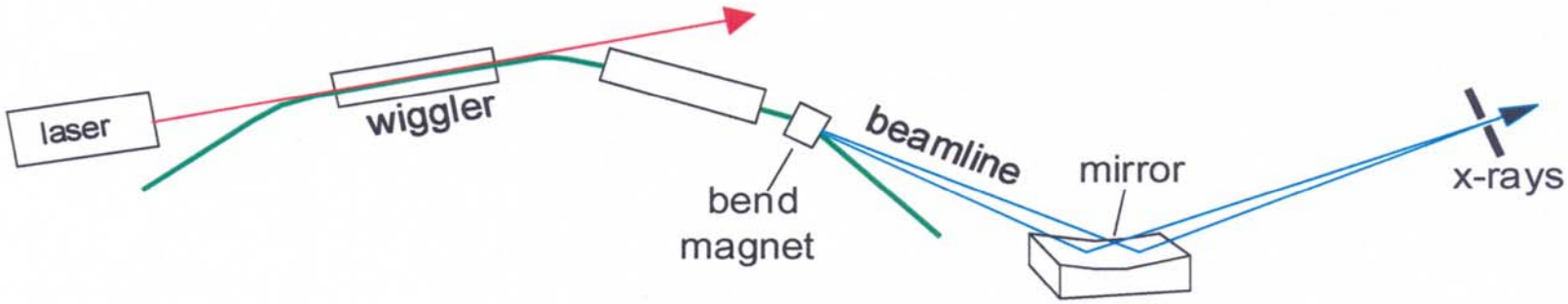


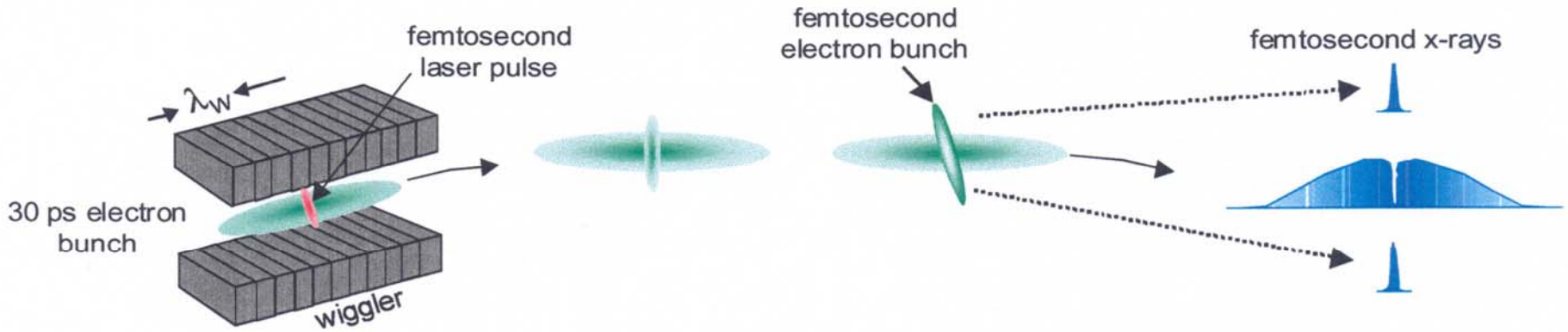
Future

- Higher temporal resolution: slicing scheme and Streak Cameras at Synchrotrons

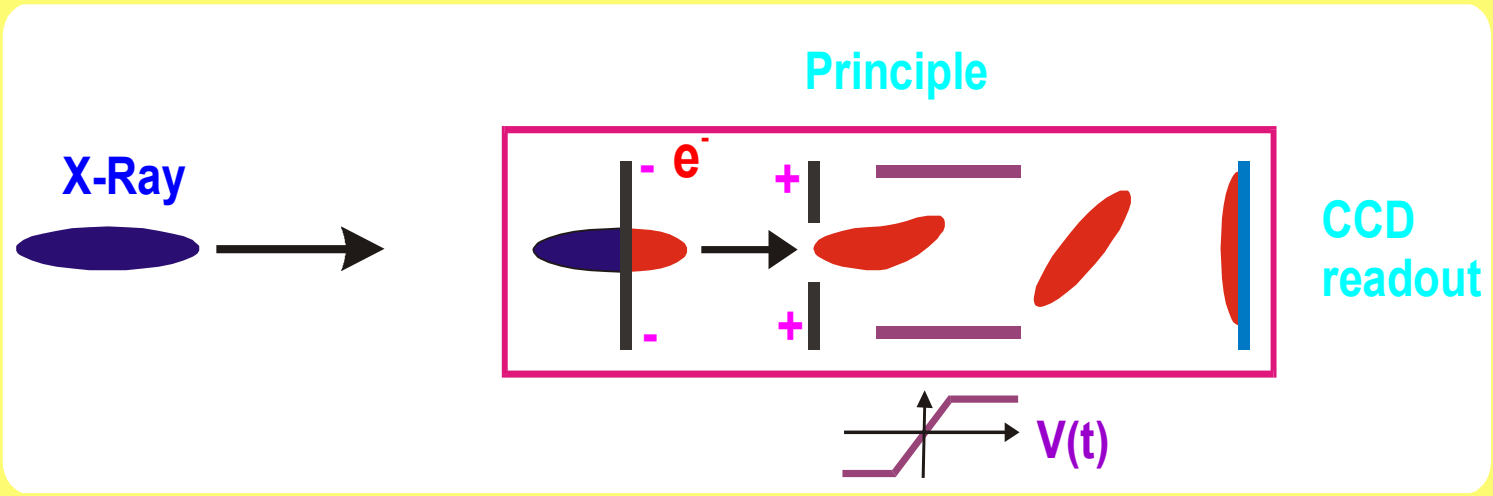
- Higher Flux and higher temporal resolution: ERLs and FELs

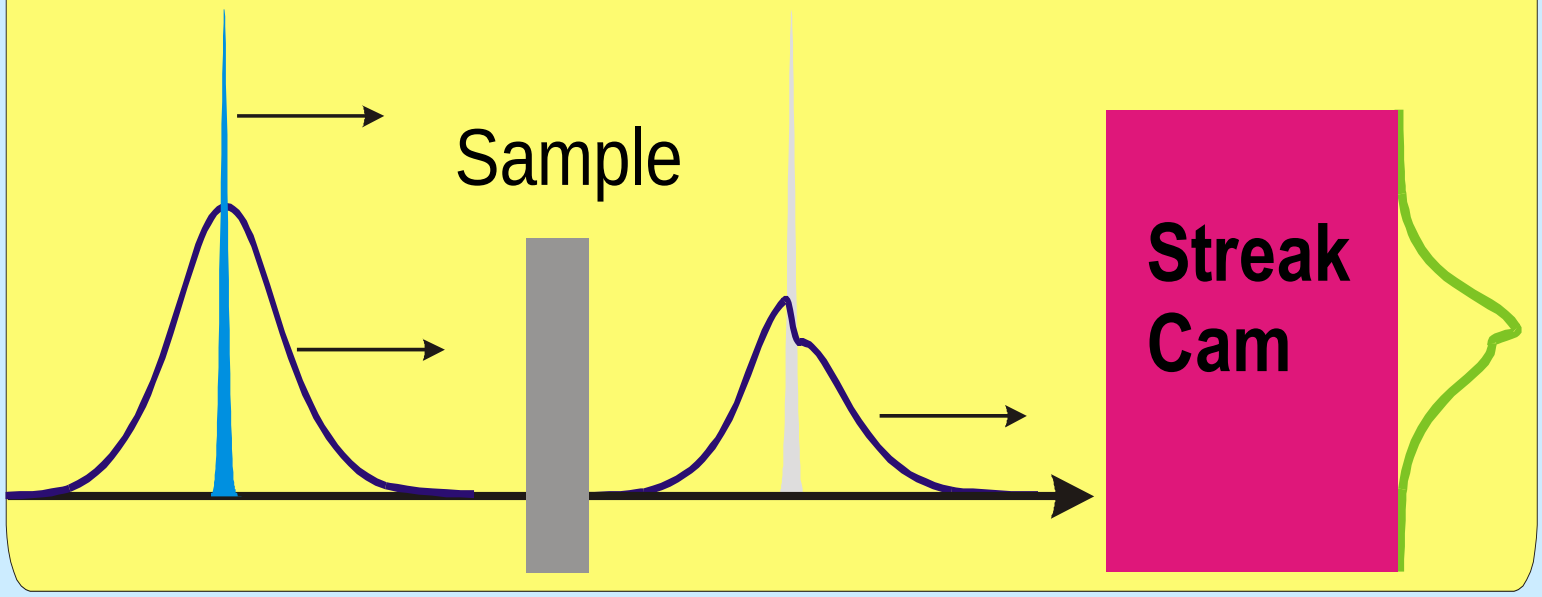
Femtosecond X-Ray Pulses at a Synchrotron



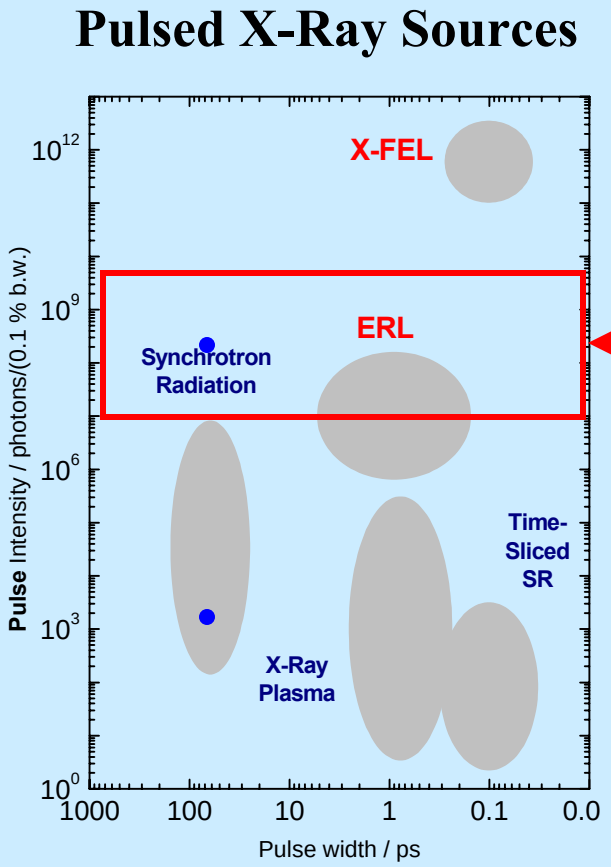


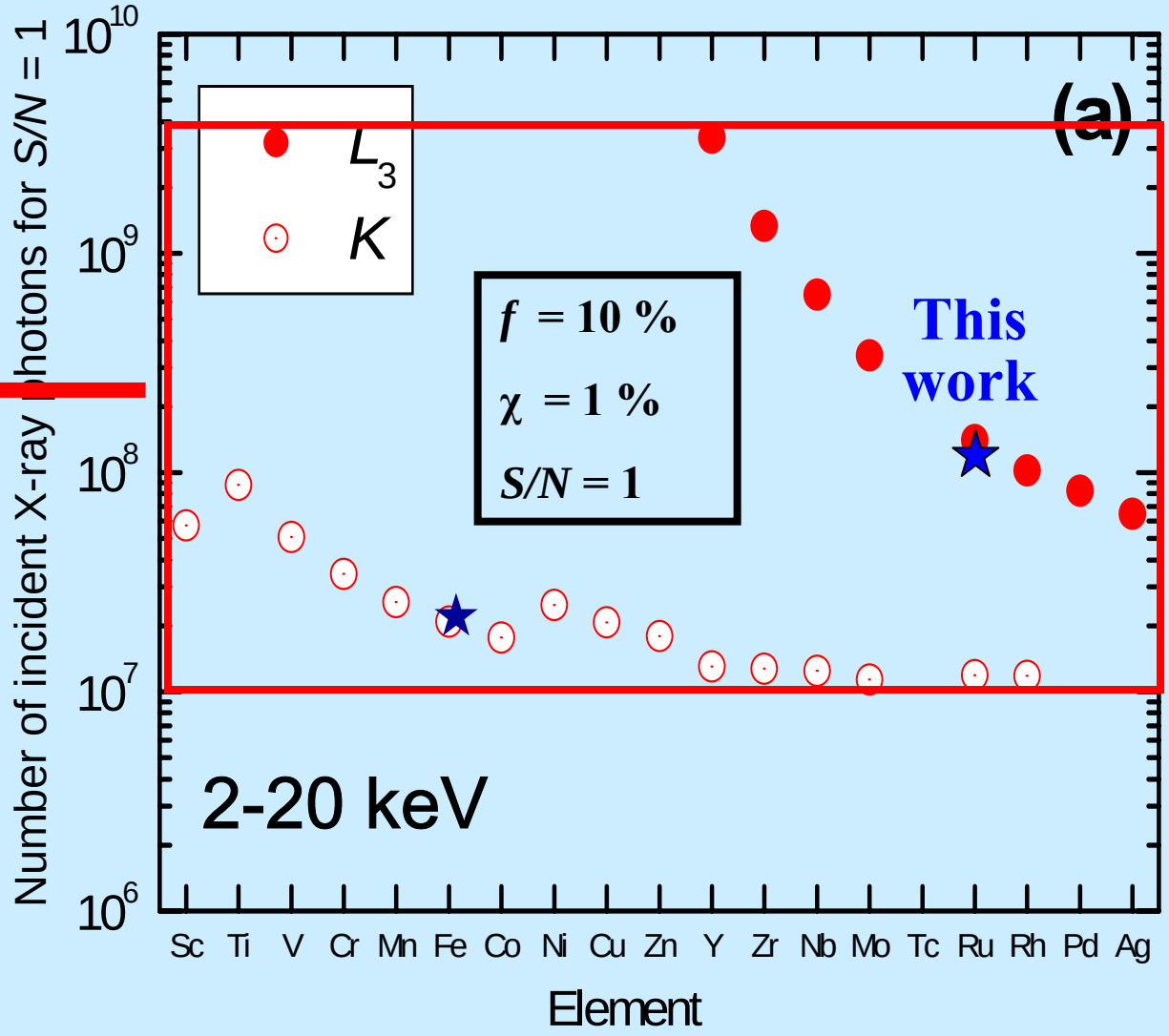
Ultrafast X-Ray Streak Cameras





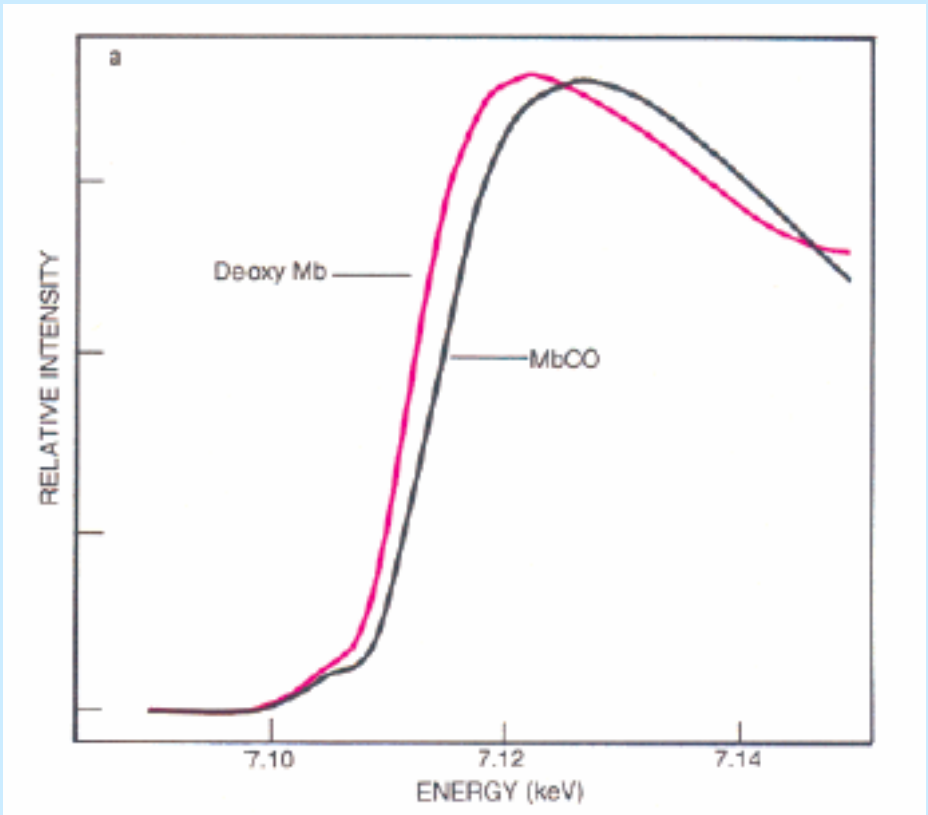
Ultrafast *EXAFS* on Transition Metal Compounds

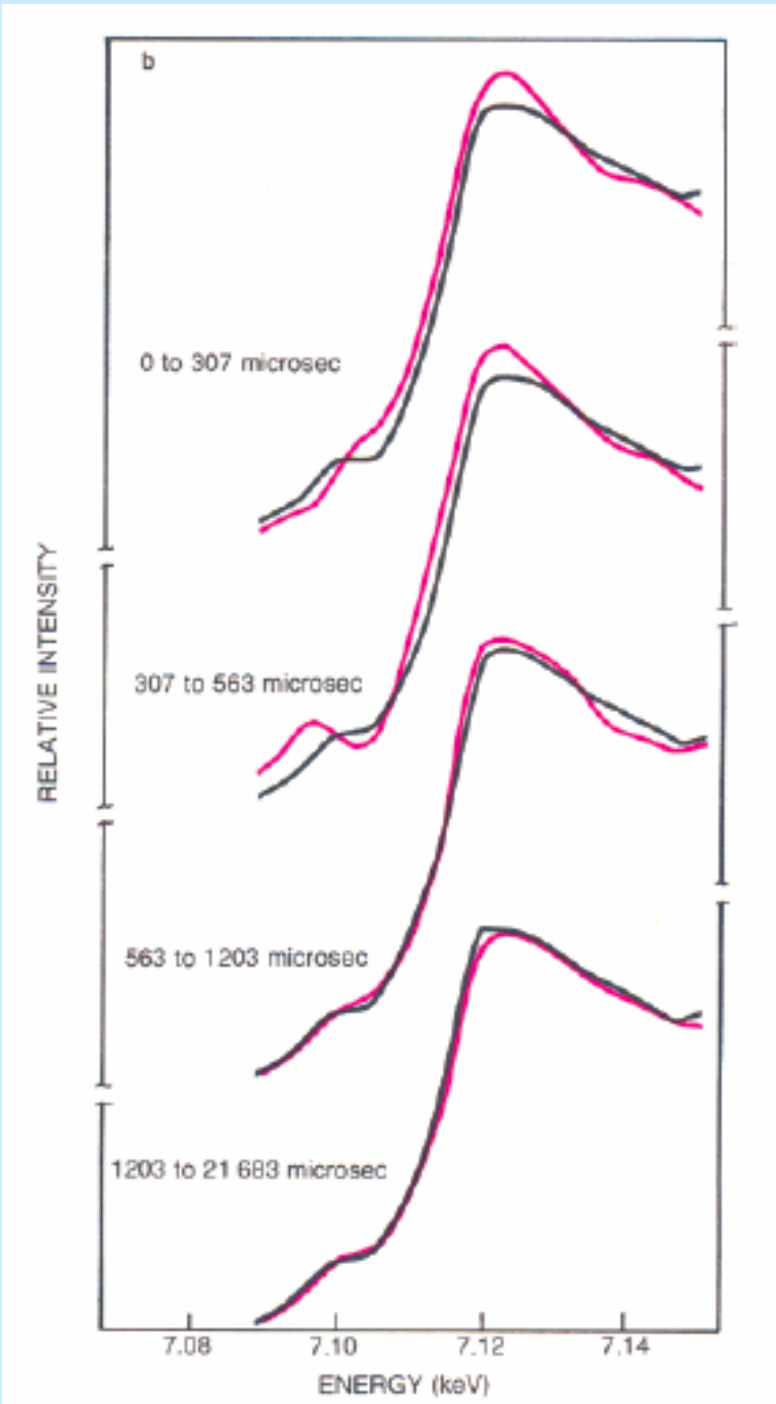




Bressler and Chergui, Chem. Rev. (2004)

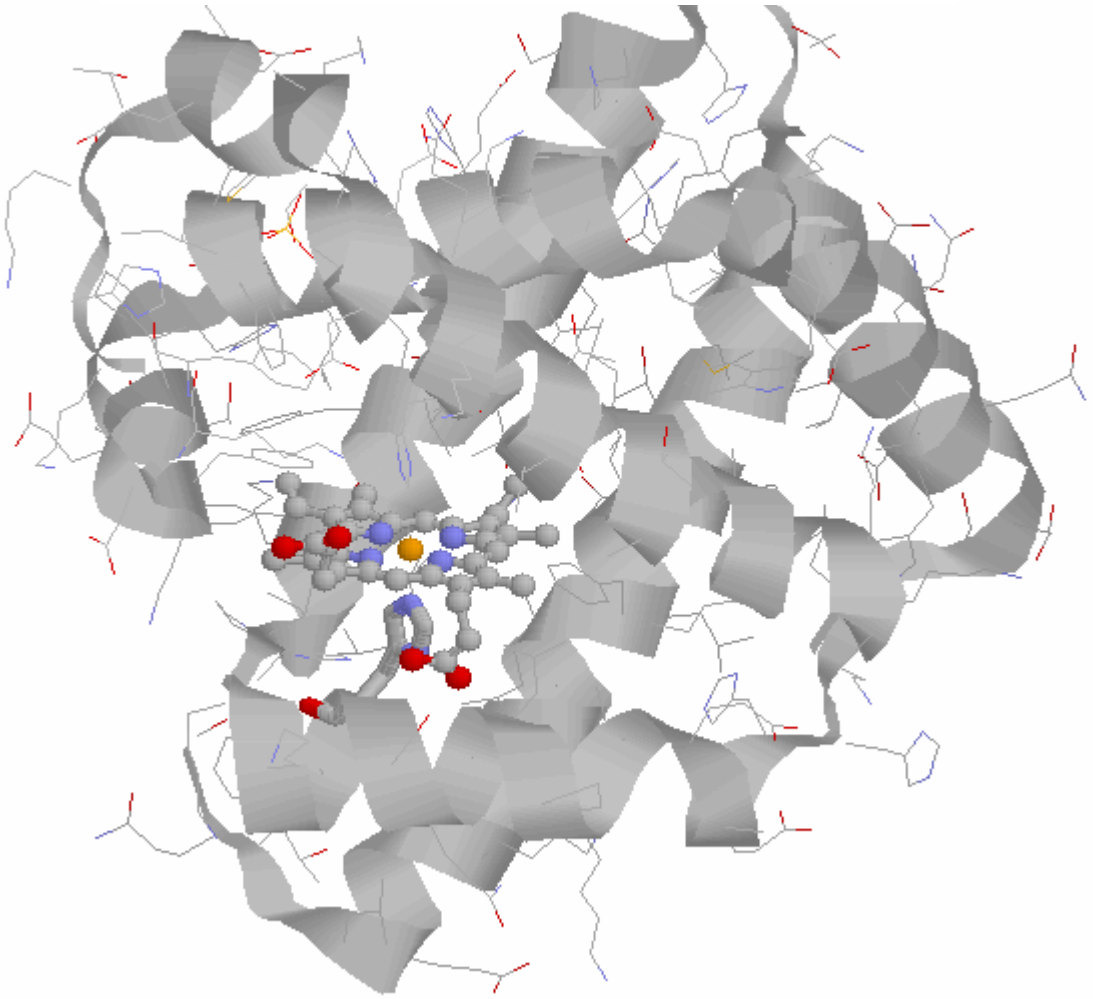
First time-resolved X-ray experiment





Mills et al, Science 223 (1984) 811

Hemoglobin I from *L. pectinata*



Ferric Heme system, binds CN and H_2S

Ultrafast recombination in < 5ps (Helbing *et al*, Biophys. J. (2004))

Members and Collaborations

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

SWISS LIGHT SOURCE SLS

BERKELEY LAB

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Yuri Zaushitsyn
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Ursula Röthlisberger

CHF: Swiss NSF, SLS, EPFL