



*Picosecond X-ray absorption studies of
photochemical reactions in liquids*

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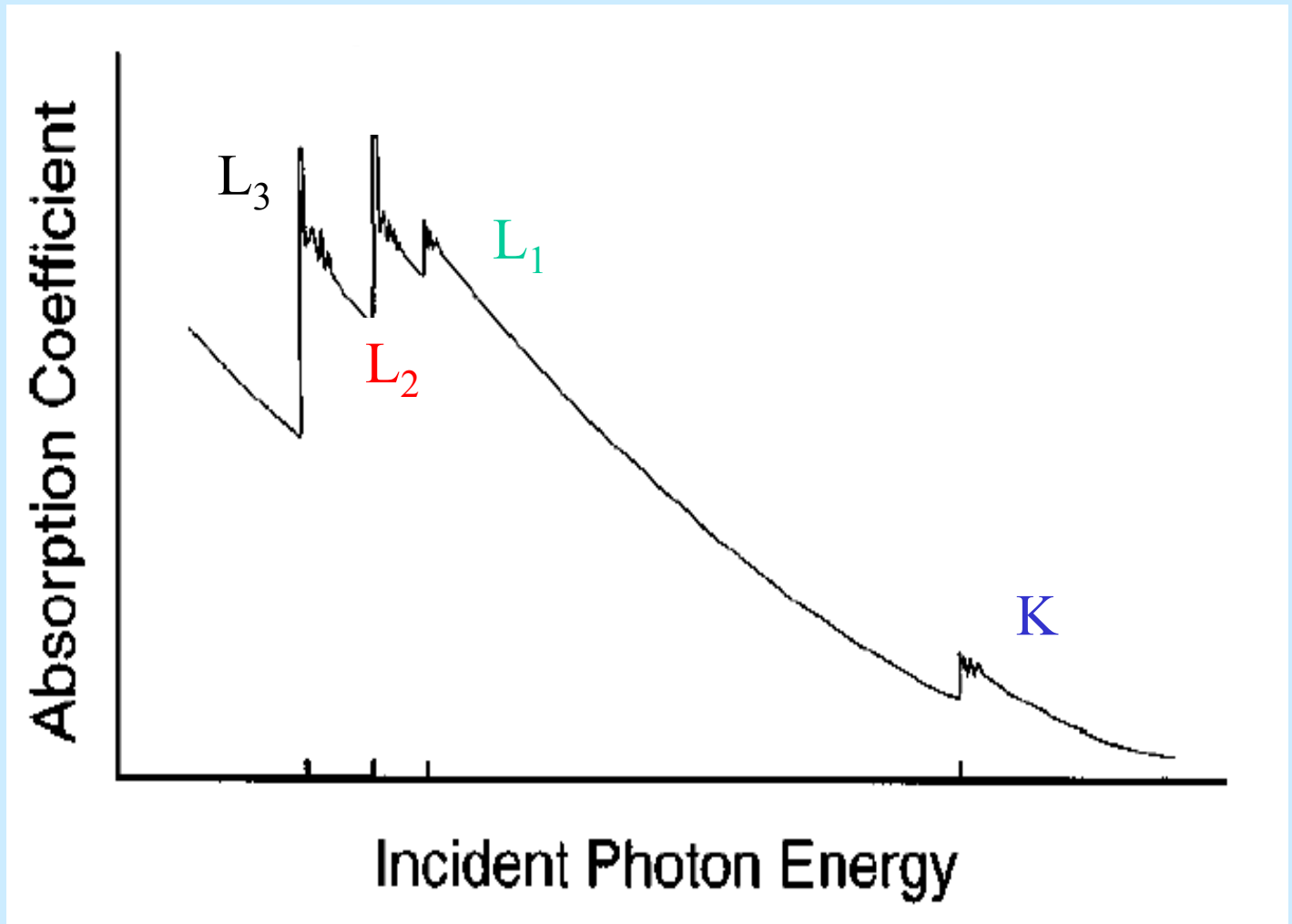
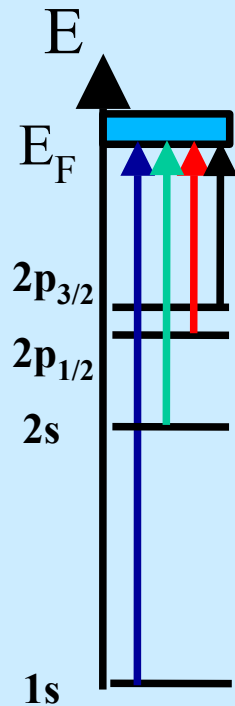
What's the aim ?

- **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**

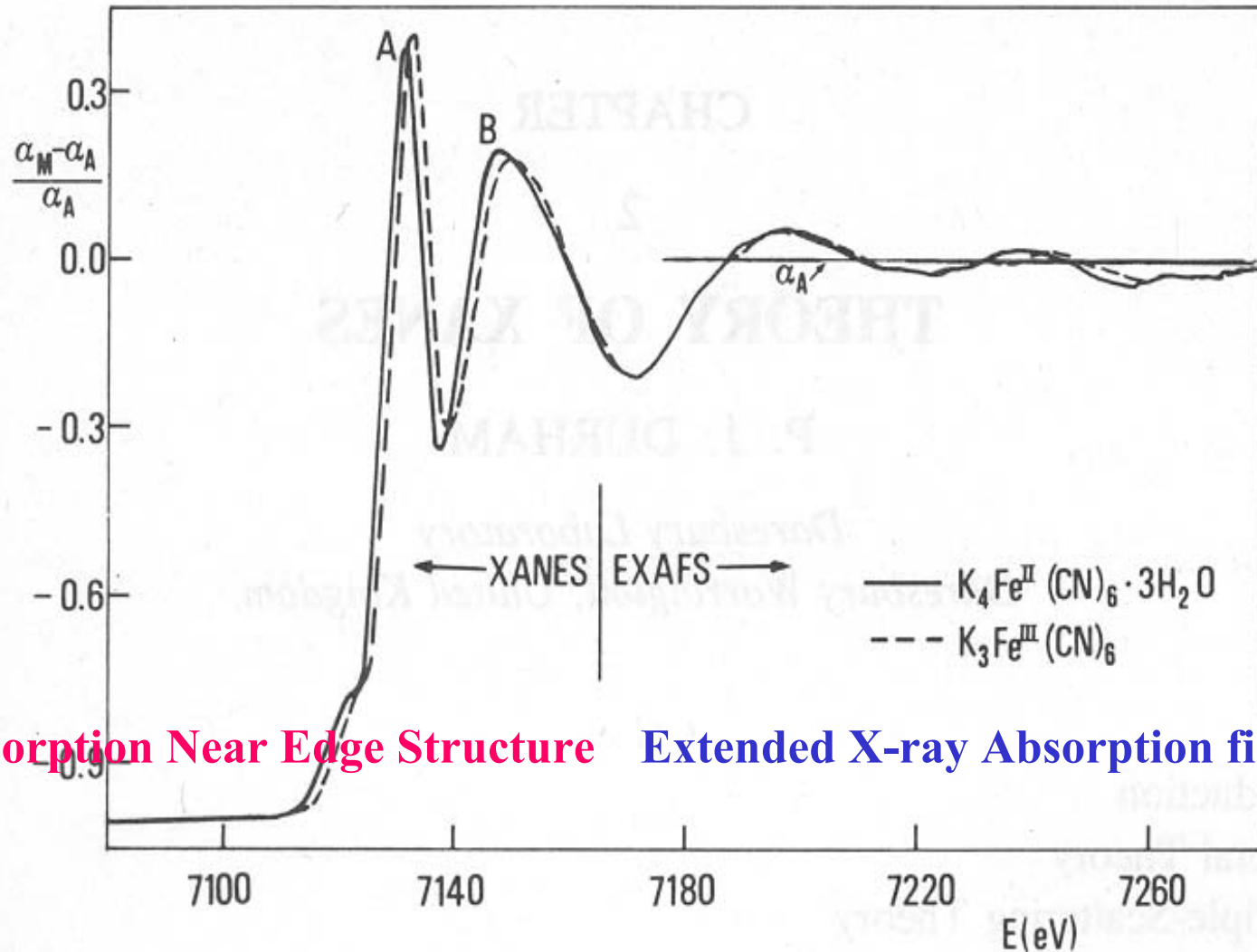
What's the issue?

- 1) Detect both electronic and structural changes**
- 2) No long-range order**
- 3) Implement in solids, concentrated and dilute disordered media, at surfaces and in the gas phase**
- 4) Chemical selectivity**

X-Ray Absorption: Overview



X-Ray Absorption: Overview



X-ray absorption Near Edge Structure

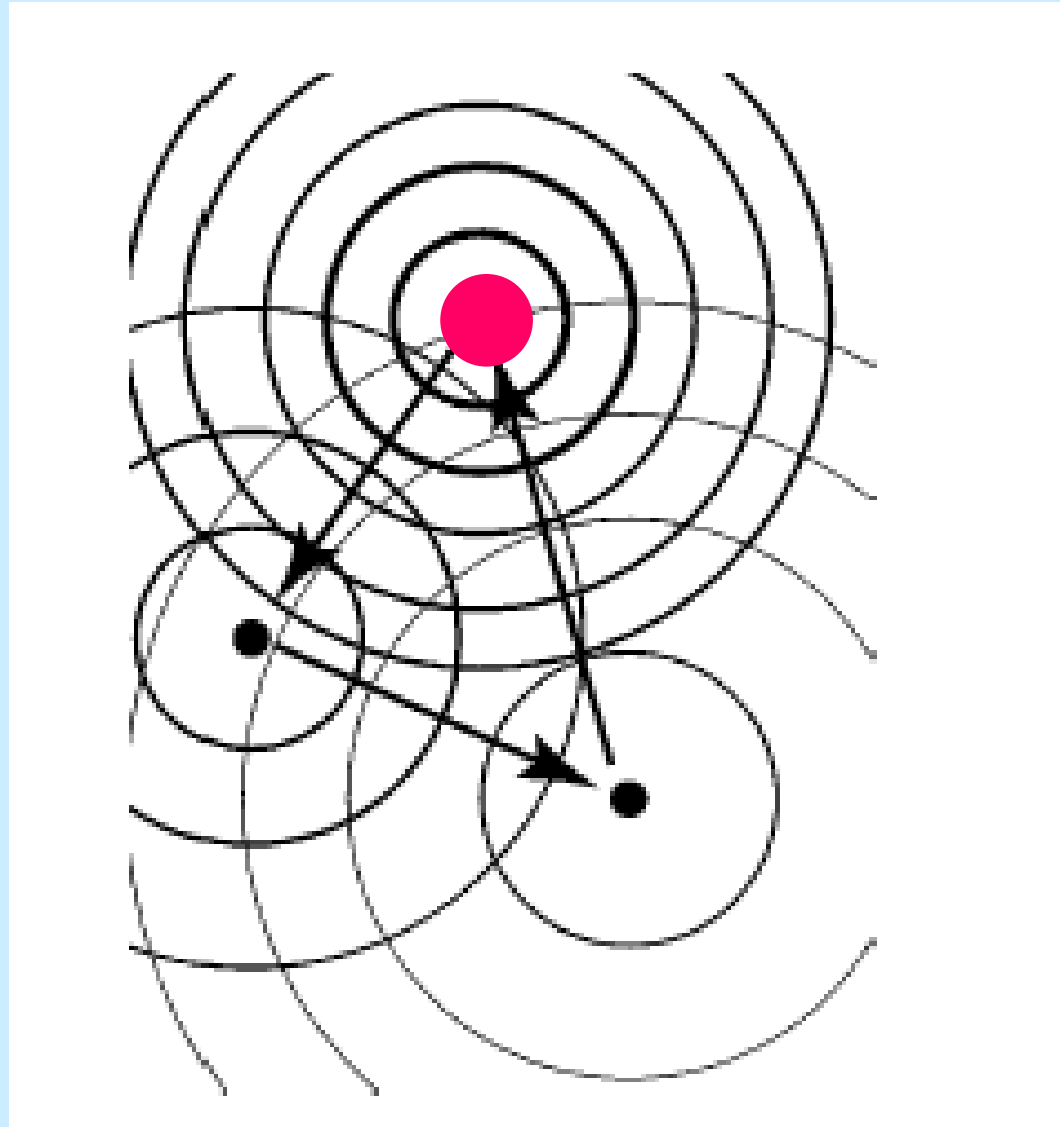
Extended X-ray Absorption fine structure

XANES: X-Ray Absorption Near Edge Structure

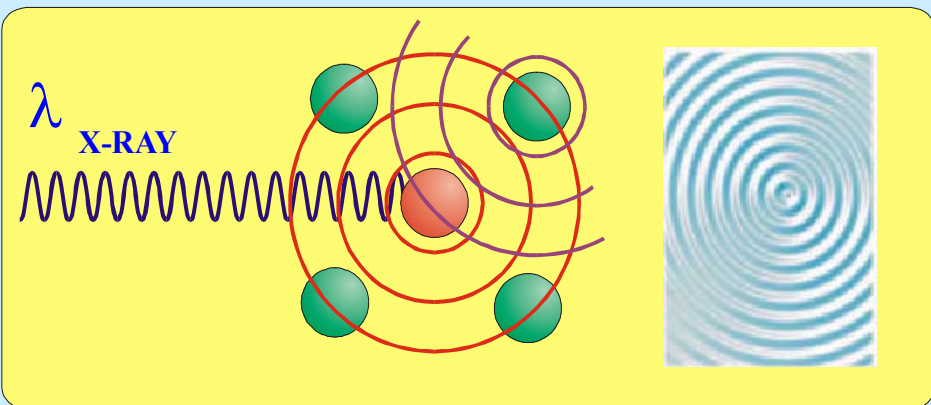
- 1) Element specific:
 - absorption edge

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

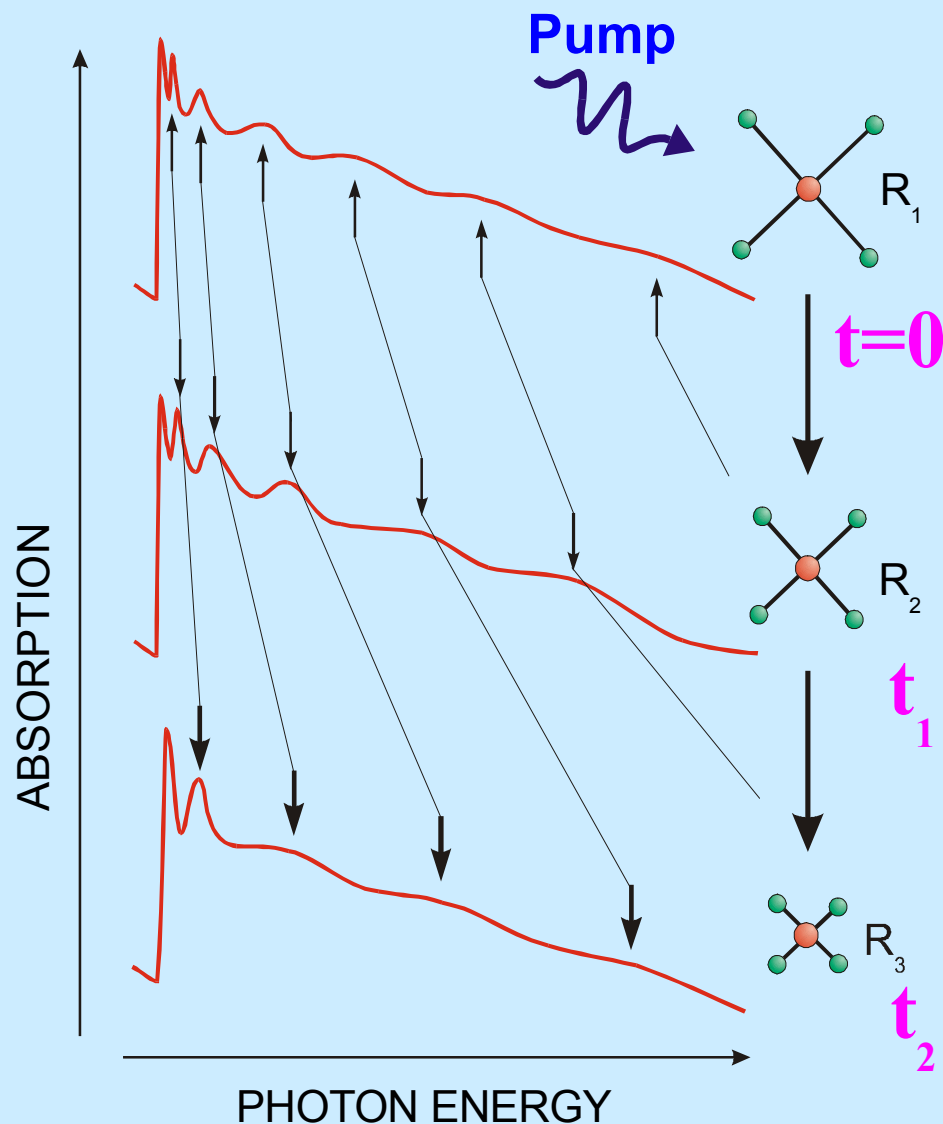
- 3) Bond distances and bond angles:
 - Multiple scattering of low-energy photoelectrons
 - Resonances above ionization



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

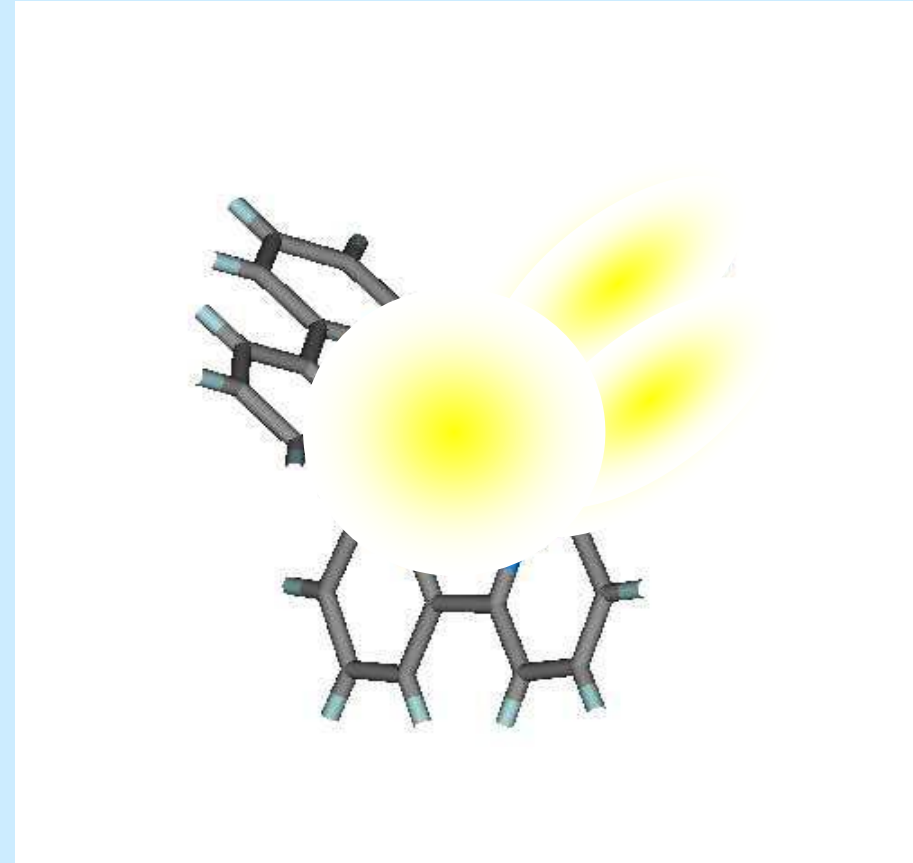
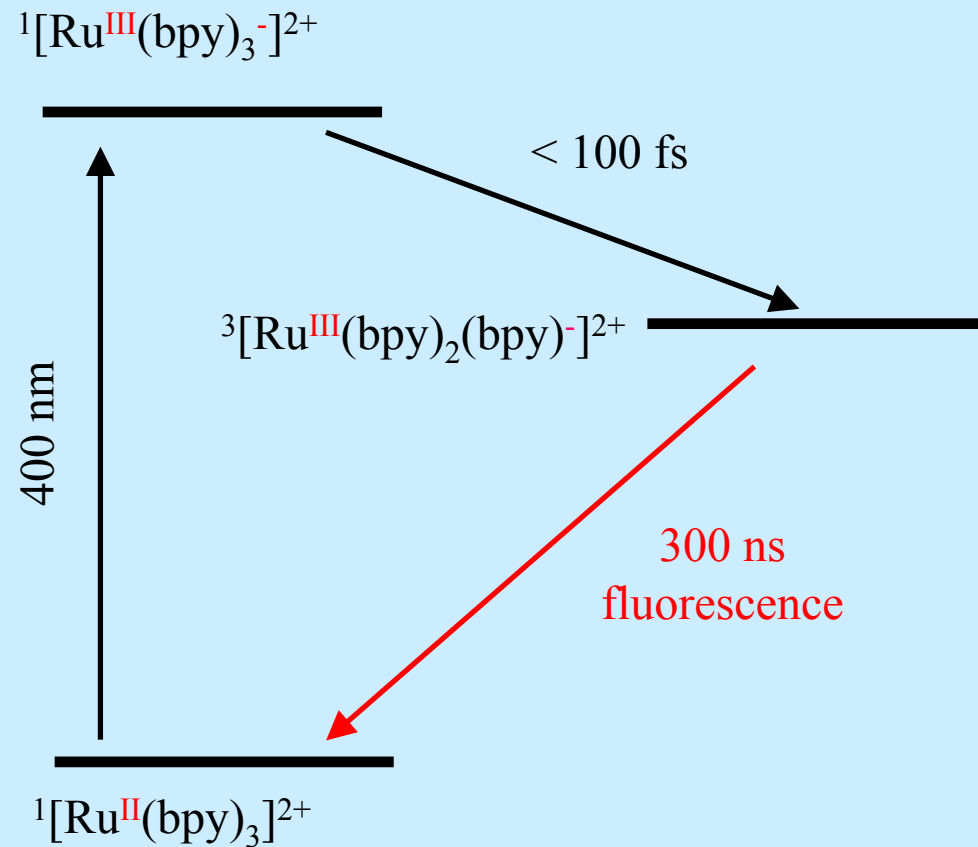


Electron transfer reactions

- Fundamental in Chemistry and Biology
- Rates depend critically on the coupling of the electron motion to the nuclear motions within the molecule
- Short-lived intermediates

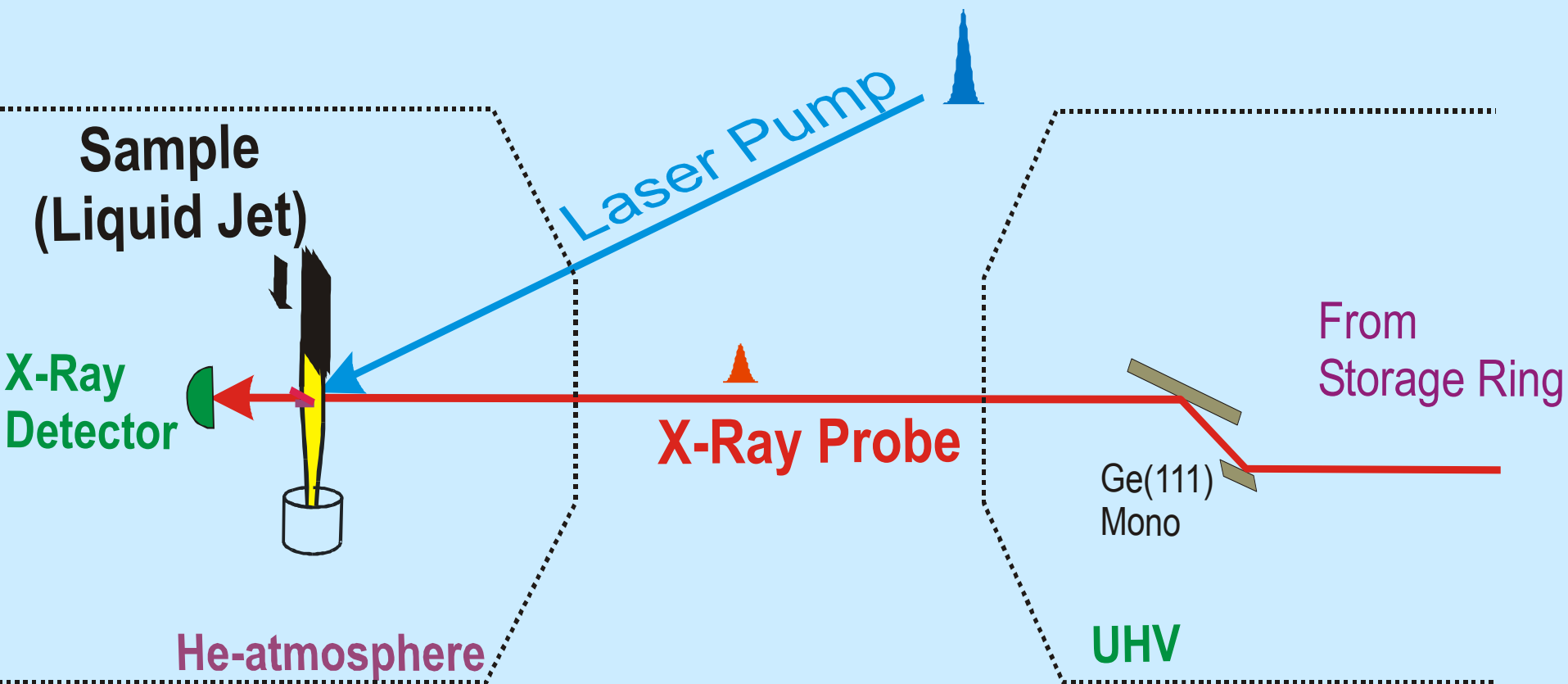
Photochemical Cycle of aqueous $[Ru(bpy)_3]^{2+}$

- H-atom of coordination chemistry
- Solar Cells
- Photosensitizer
- Catalyst in Redox-Reactions
- Marker in Biology,...



Laser-Pump X-ray-Probe Set-up

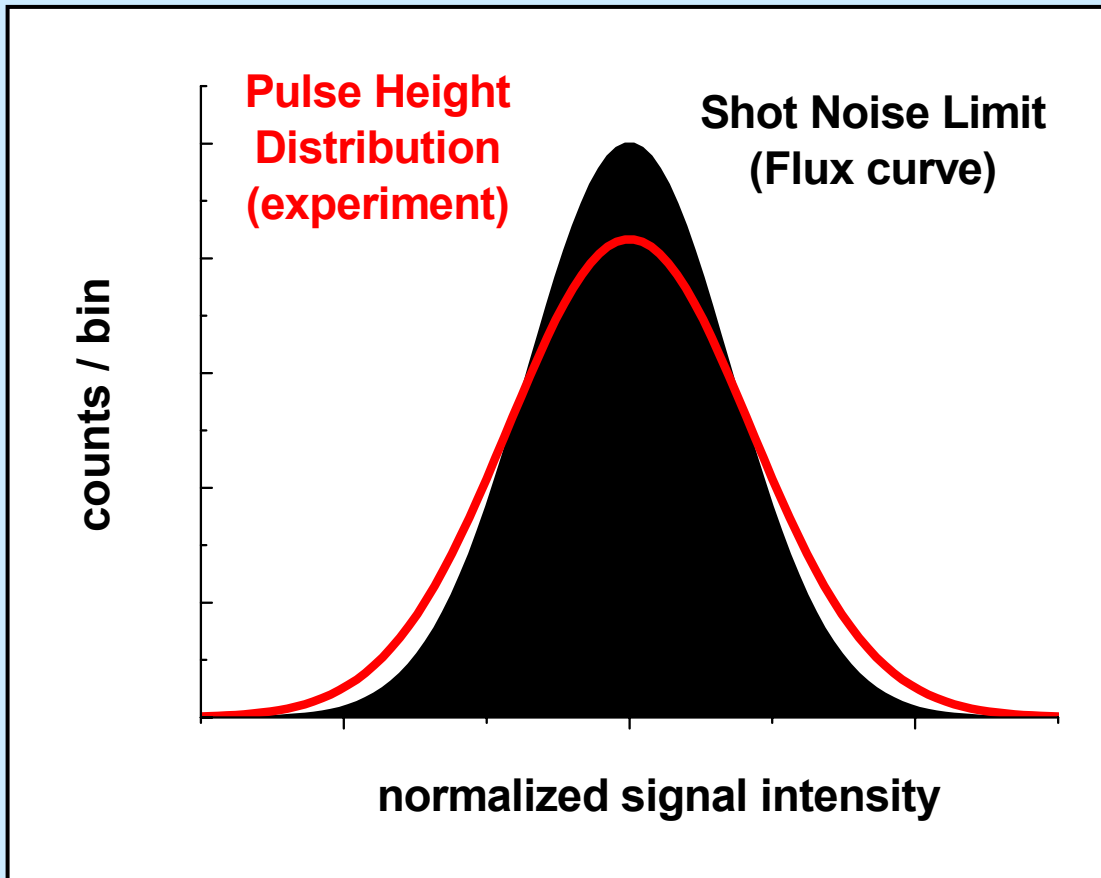
Bend Magnet Beamline 5.3.1 Advanced Light Source, Berkeley



Boundary conditions

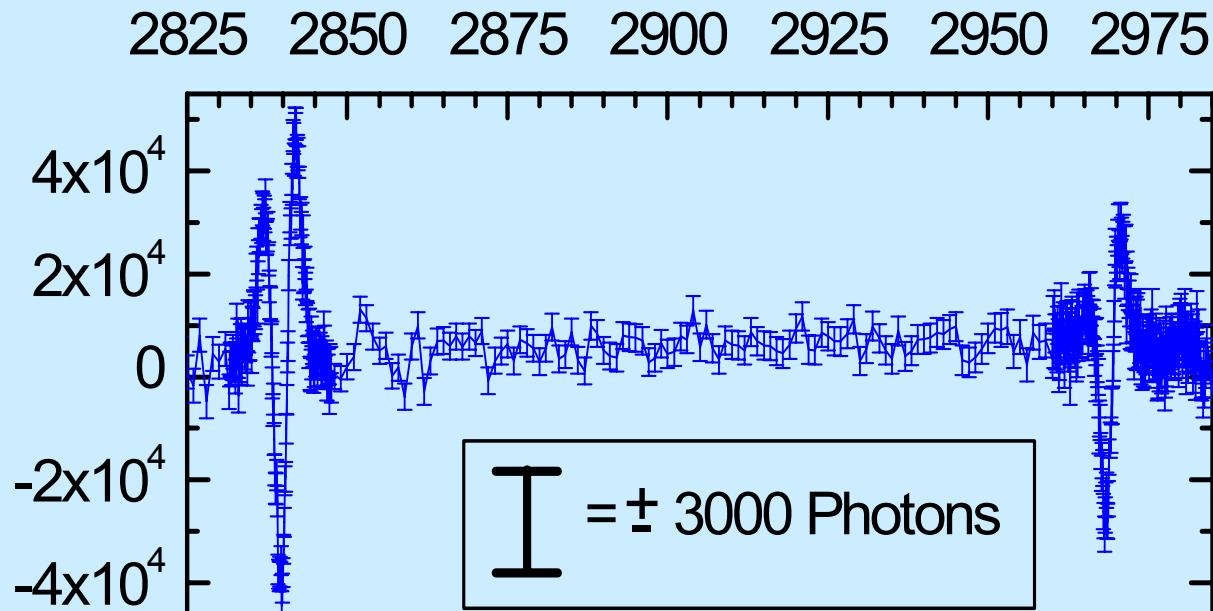
- Temporal and spatial overlap of X-ray and laser pulses
- Sample configuration: solute absorption cross-section mismatch, solvent absorption, solute concentration and sample thickness (Bressler *et al*, JCP 2002)
- X-ray Fluxes: shot noise limit

Saes et al, Rev. Sci. Inst. (Jan. 2004)

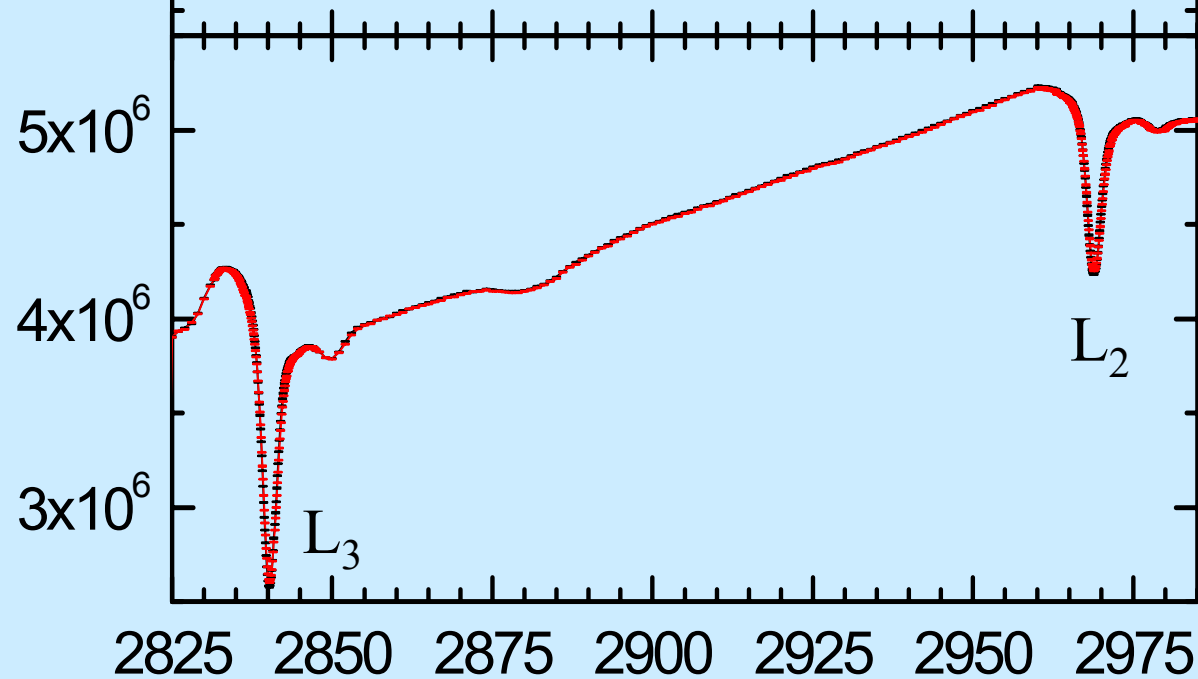


Saes et al, Rev. Sci. Inst. (Jan. 2004)

ΔI / Photons



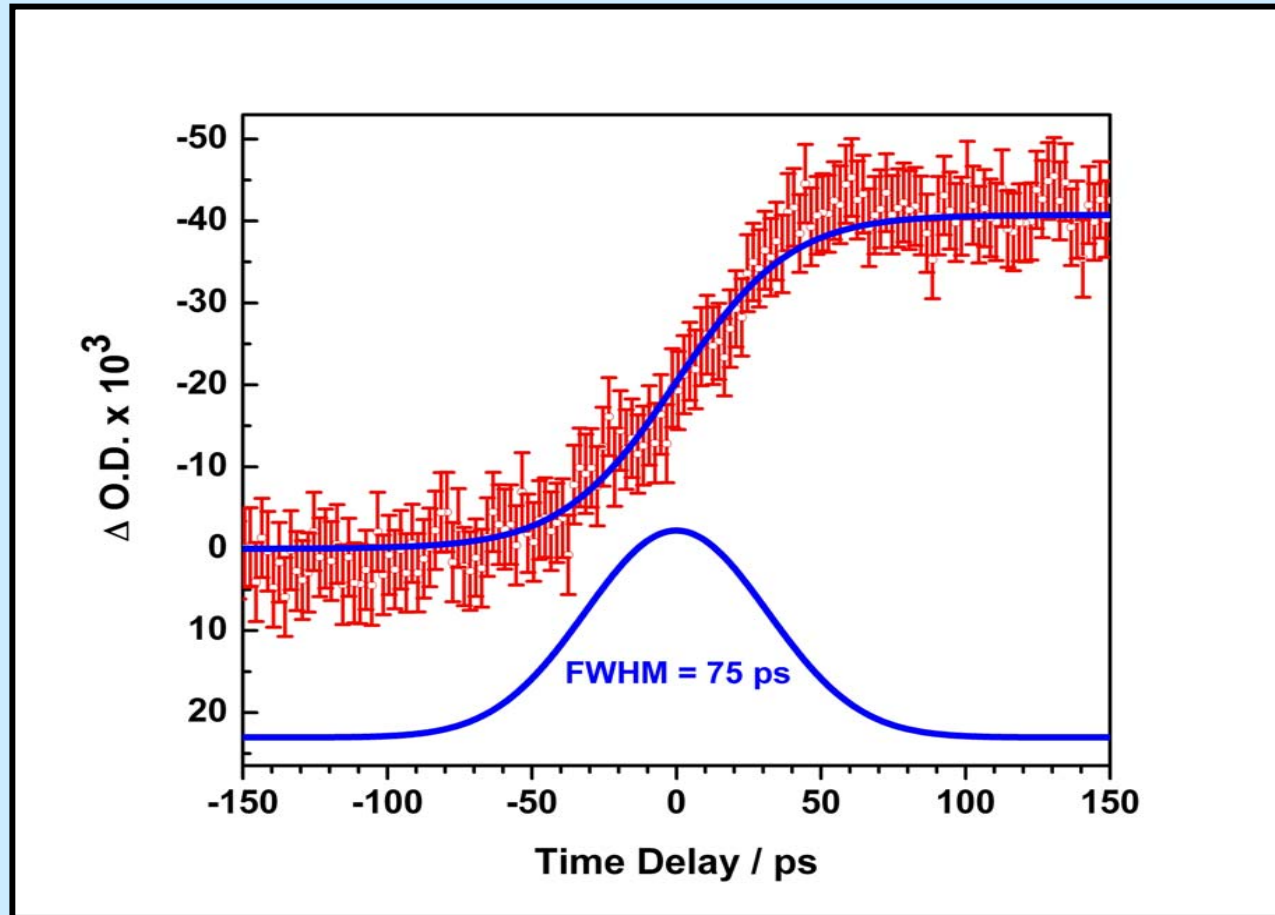
Transmitted Photons



<1% photoinduced changes can be measured by XAS !

X-Ray Energy / eV

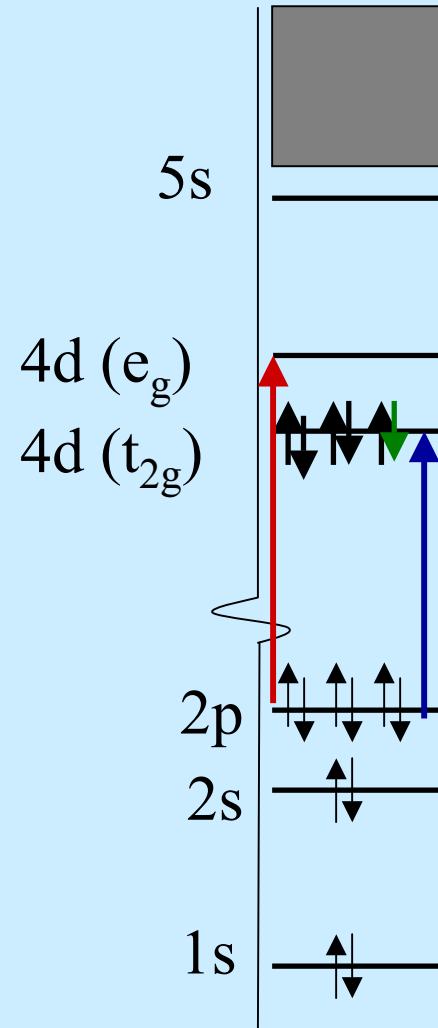
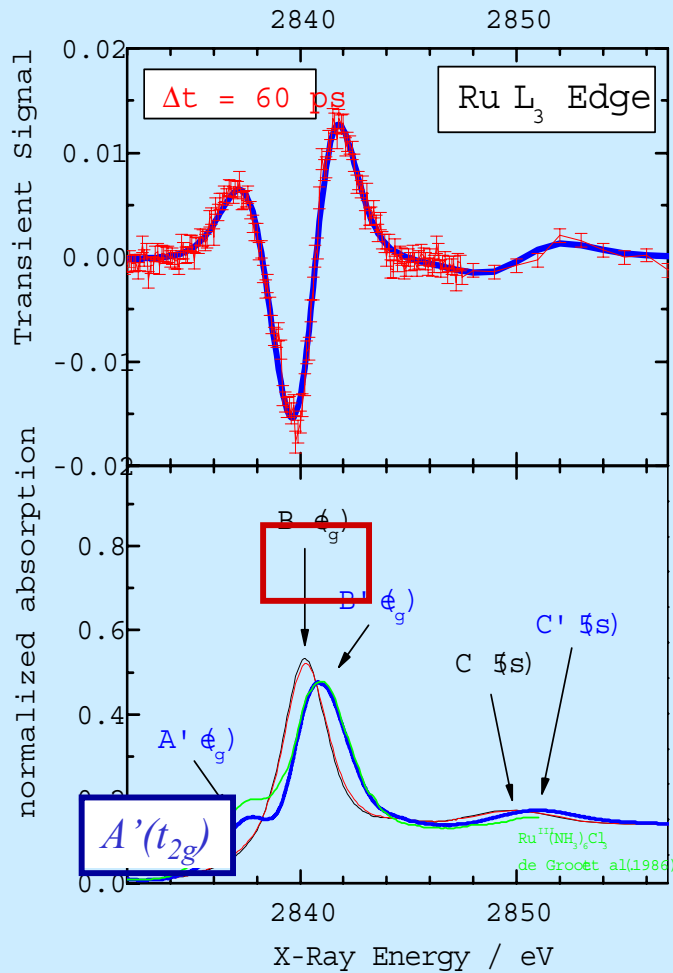
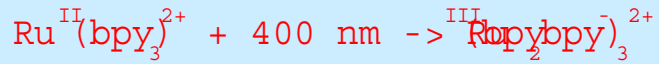
Real-Time Laser/X-Ray Cross-Correlator



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

Timing jitter ≤ 10 ps accuracy

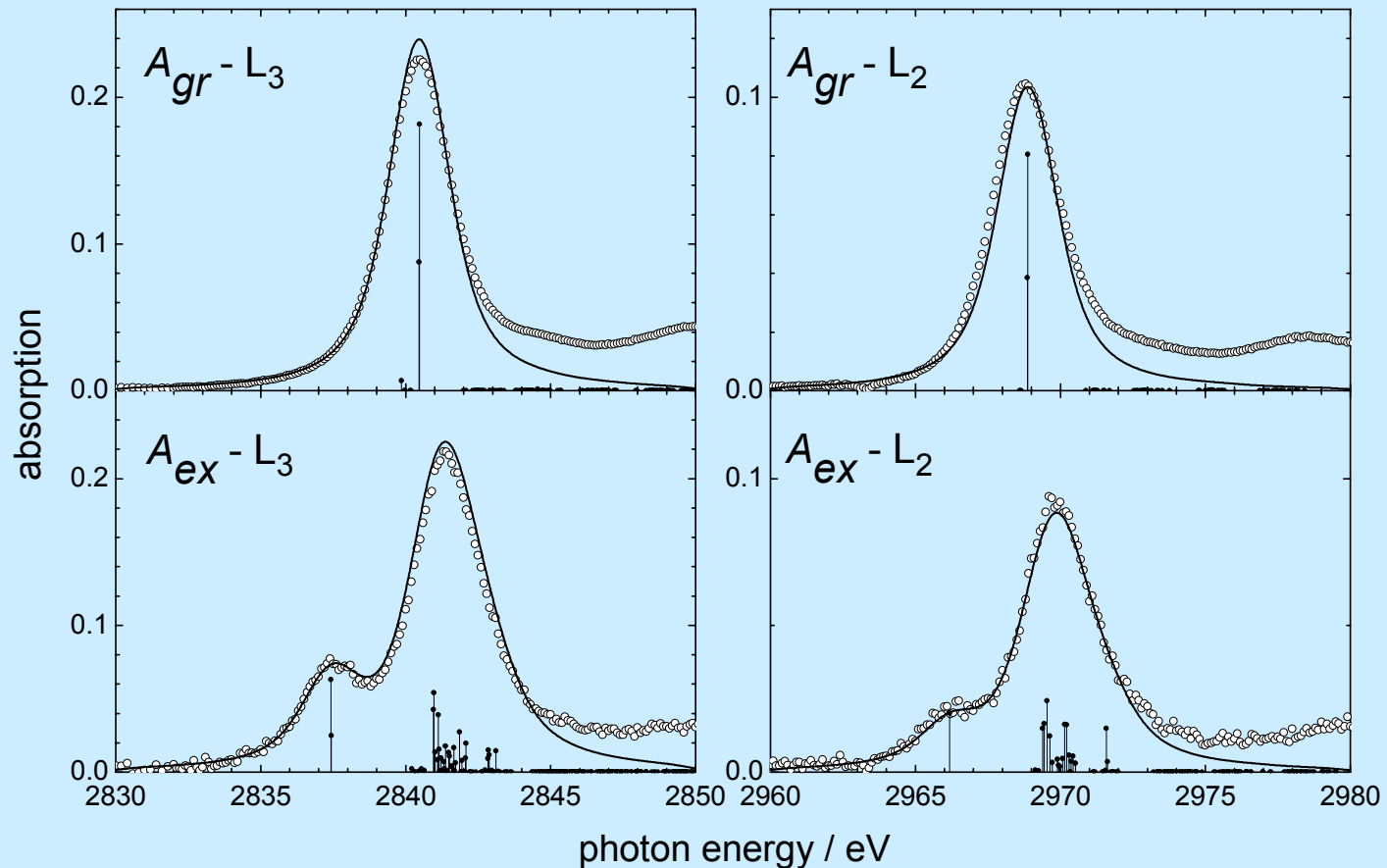
Ru^{III}



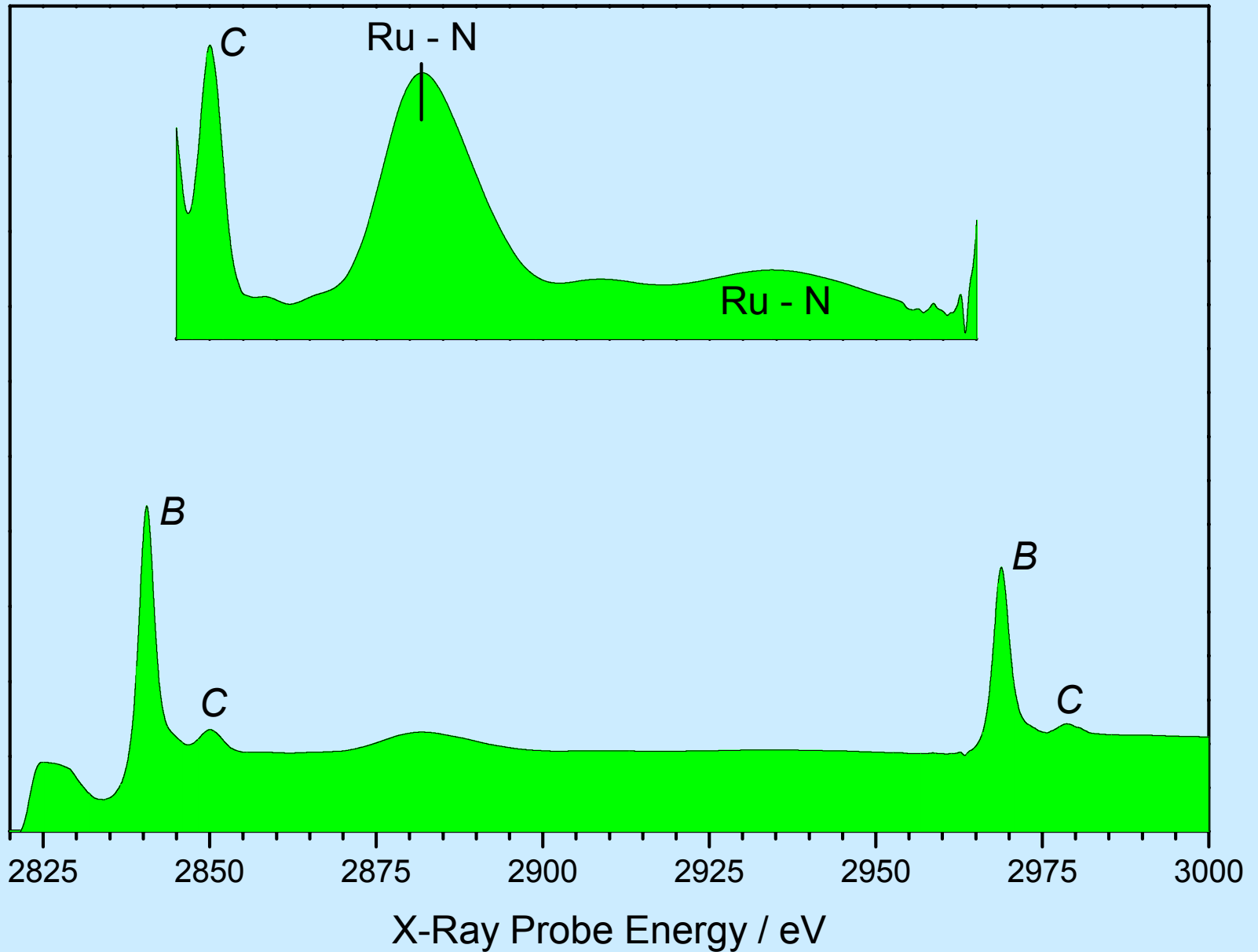
$$H = H_{atom} + H_{Cryst.}$$

H_{atom} includes e-e correlations, spin-orbit coupling

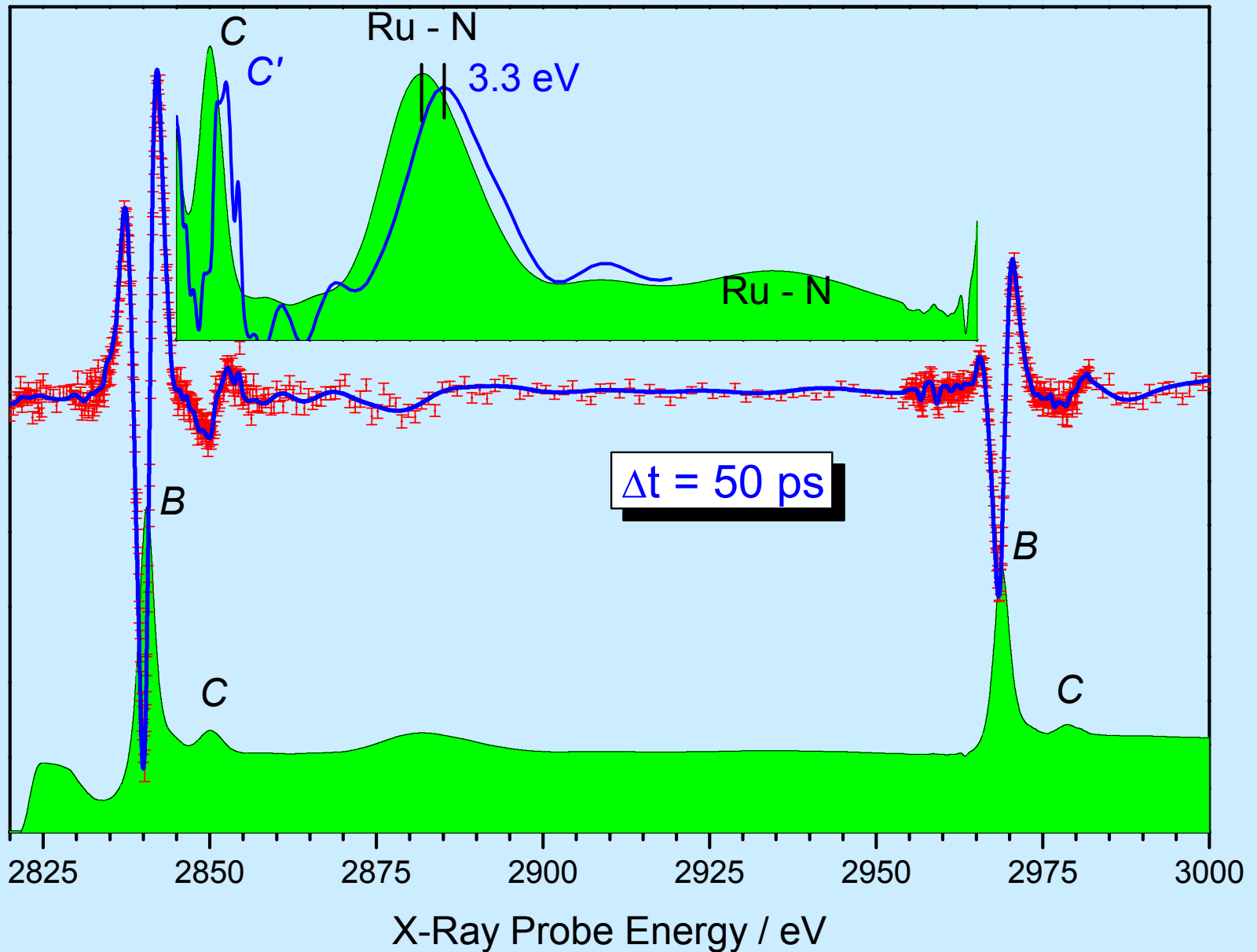
H_{Cryst} includes octahedral and trigonal field contributions



Structure from transient EXAFS



Structure from transient EXAFS

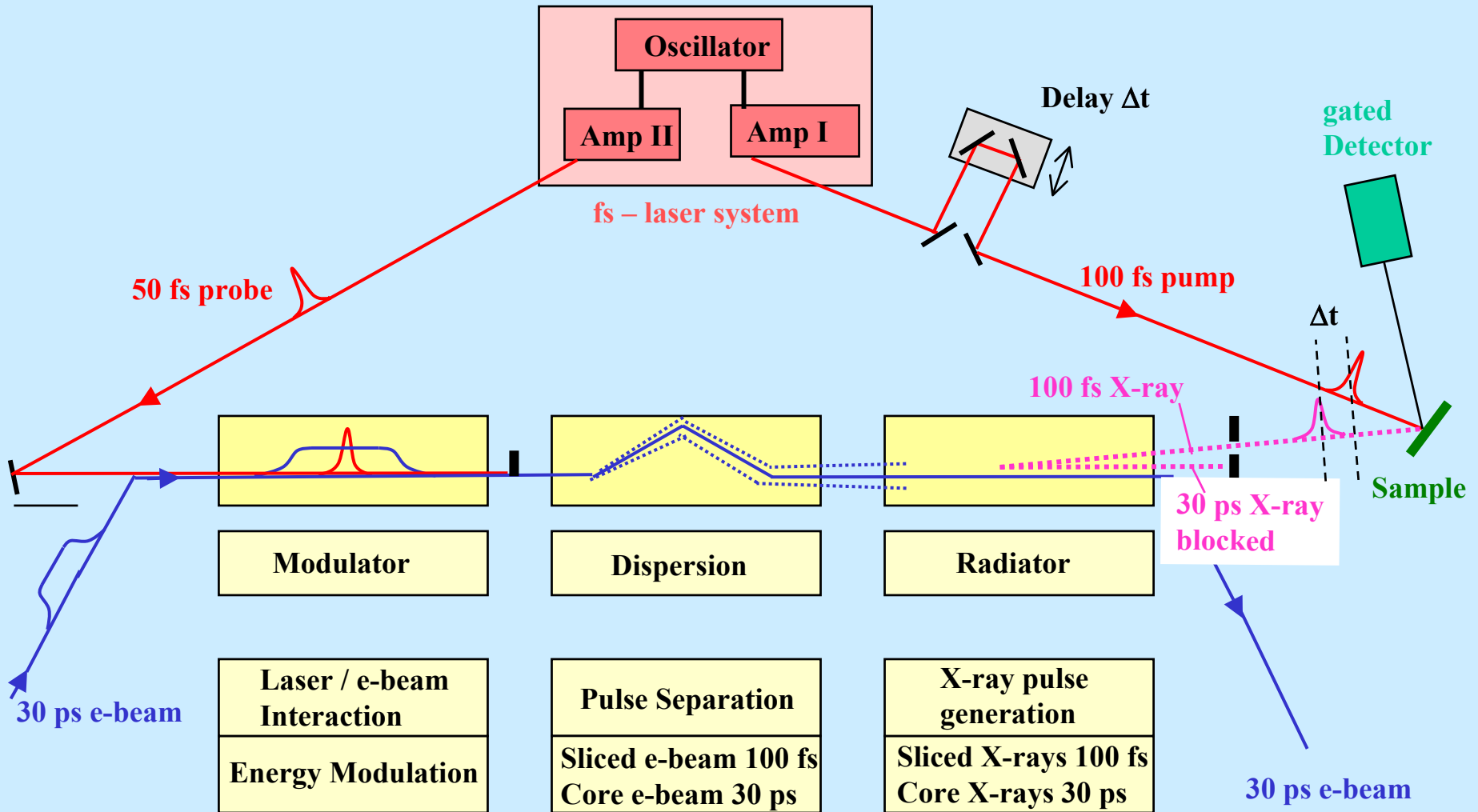


Summary

- Picosecond X-ray absorption spectra: both electronic and geometric structure
- Fsec resolution not a problem (only 10^6 x-ray photons on the sample/data point !)
- Dilute systems (chemistry and biology)
- Optical-X-ray cross-correlator down to fsec

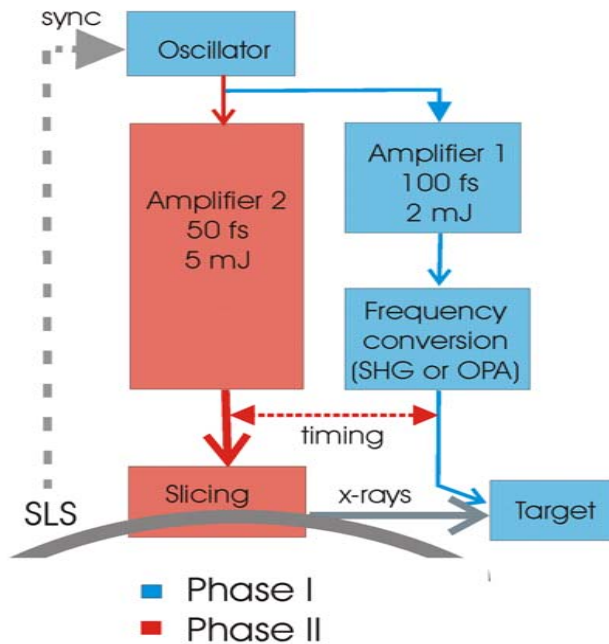
*Universal method for detecting ultrafast
(non) reversible structural and electronic changes*

Principle 'slicing source'



Laser: fs Ti:sapphire

Configuration



Specification

Oscillator

(Femtsource 20 seed, Femtolaser Vienna)

pulse duration	20 fs
bandwidth	> 45 nm
repetition rate	100 MHz
power	400 – 600 mW
jitter to SLS	< 2 ps

Amplifiers

	Phase I	Phase II
pulse duration	80 – 100 fs	< 50 fs
pulse energy	1 – 2 mJ	5 mJ
wavelength	~ 800 nm	
M ²	< 1.5	
time-bandwidth product	< 0.6	
stability	< 2% rms	
repetition rate	1 kHz	

Phase I: end 2003 / early 2004

**pump/probe experiments
100 fs pump / 20 ps x-ray probe**

Phase II: end 2004 / early 2005

**fs pump/probe experiments
100 fs pump / ~100fs x-ray probe**

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CHF: Swiss NSF and SLS