Ultrafast X-Ray Absorption Spectroscopy at an ERL X-ray Source

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Christian Bressler

ETH Lausanne

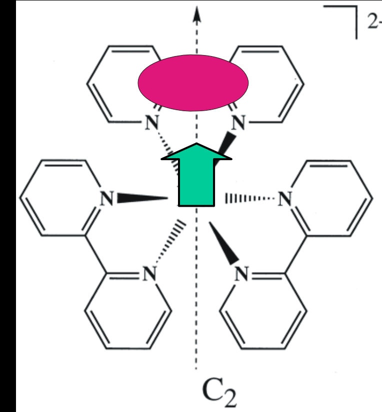
Why ultrafast X-ray Spectroscopy ?

- **Element specific**
- **Applicable to all media (gas, liquids, solids, biological samples)**
- **Probes the electronic structure via XANES (in particular valence orbitals)**
- **Probes the local geometric structure**

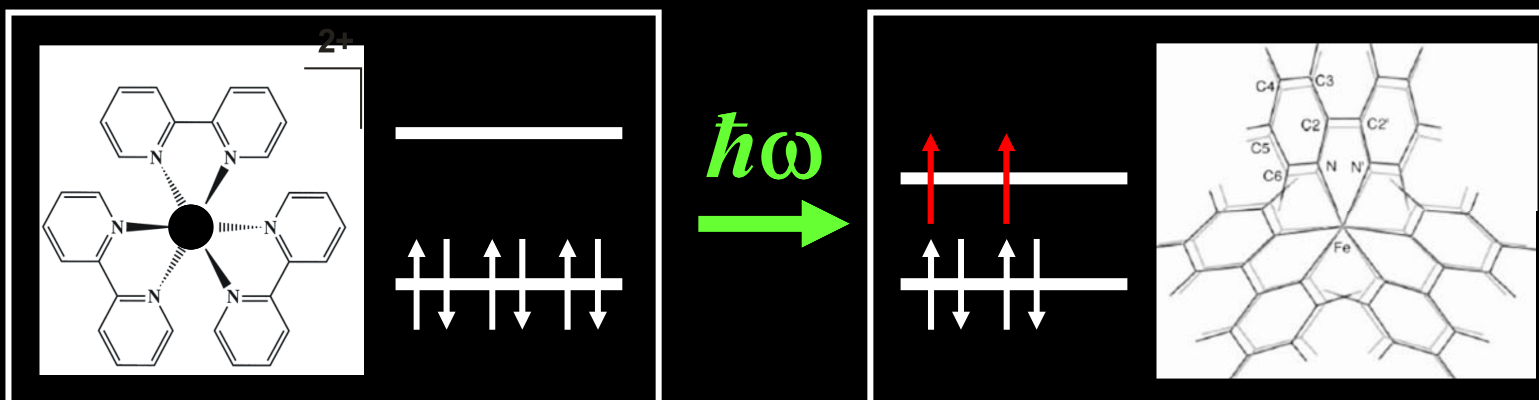
Short time scales ↔ short distance scales

- **Precision! (< 10 % of typical bond lengths)**

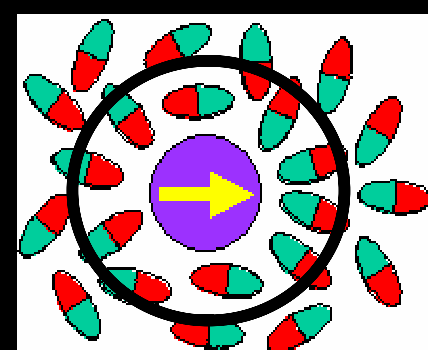
1. Intramolecular Charge Transfer



2. Light-Induced Spin Crossover

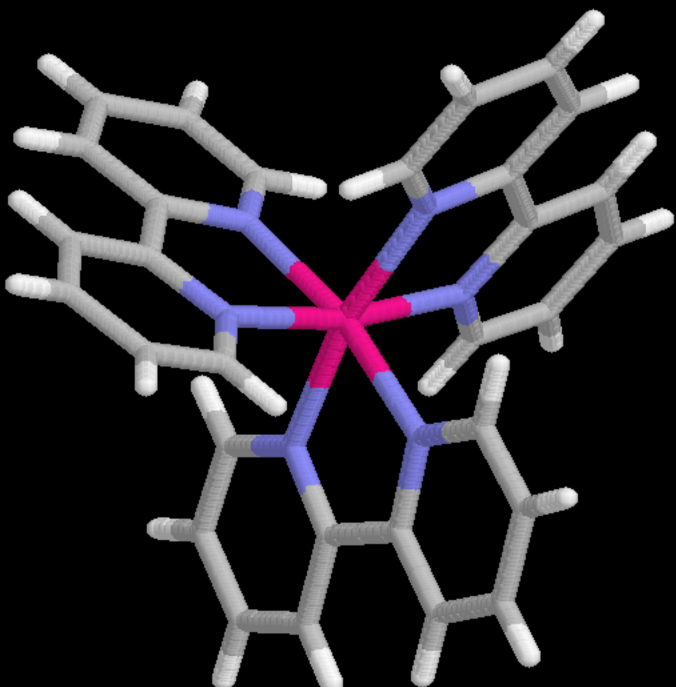


3. Solvation Dynamics in Liquids



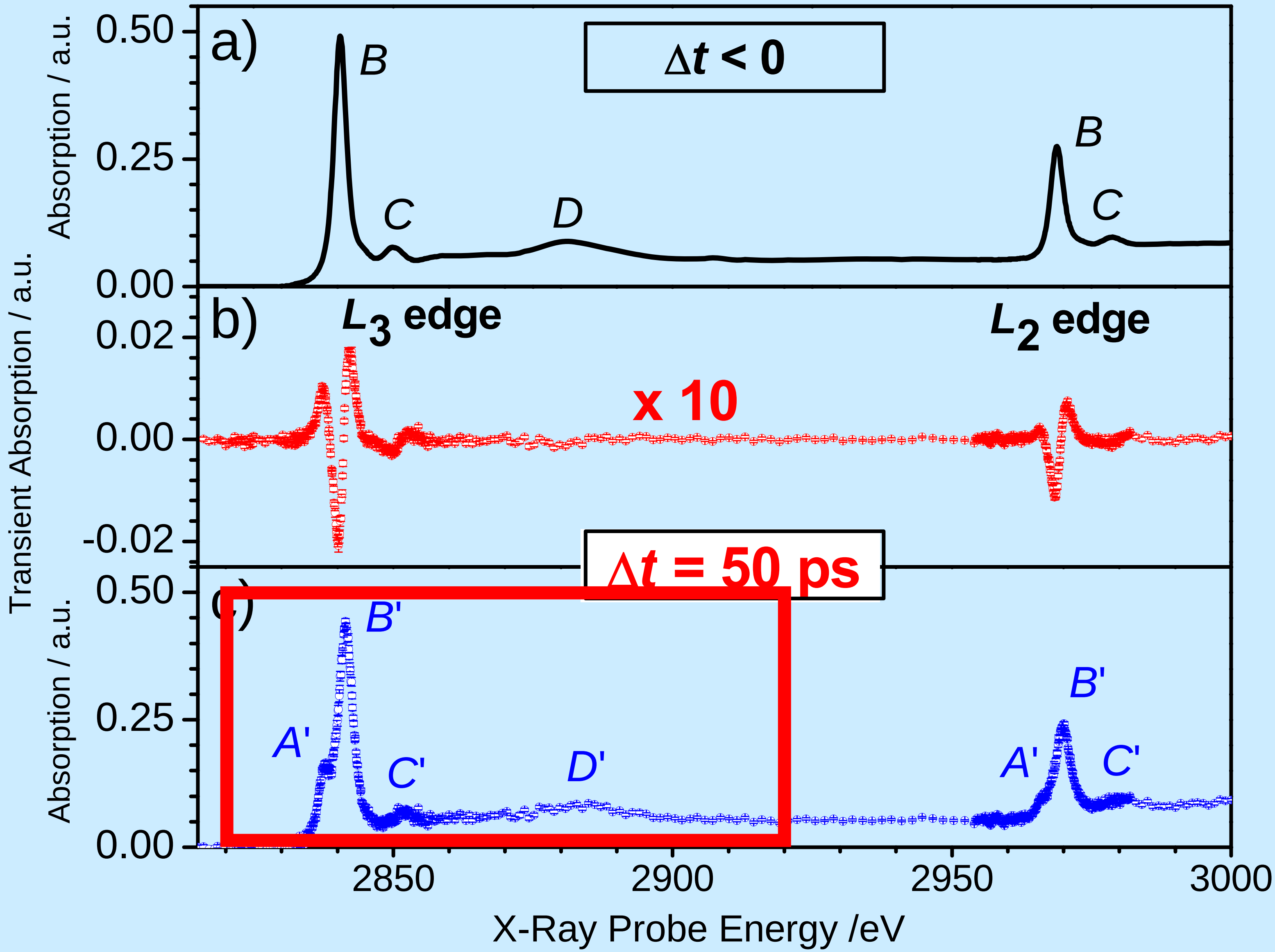
I. Electron Transfer Reactions

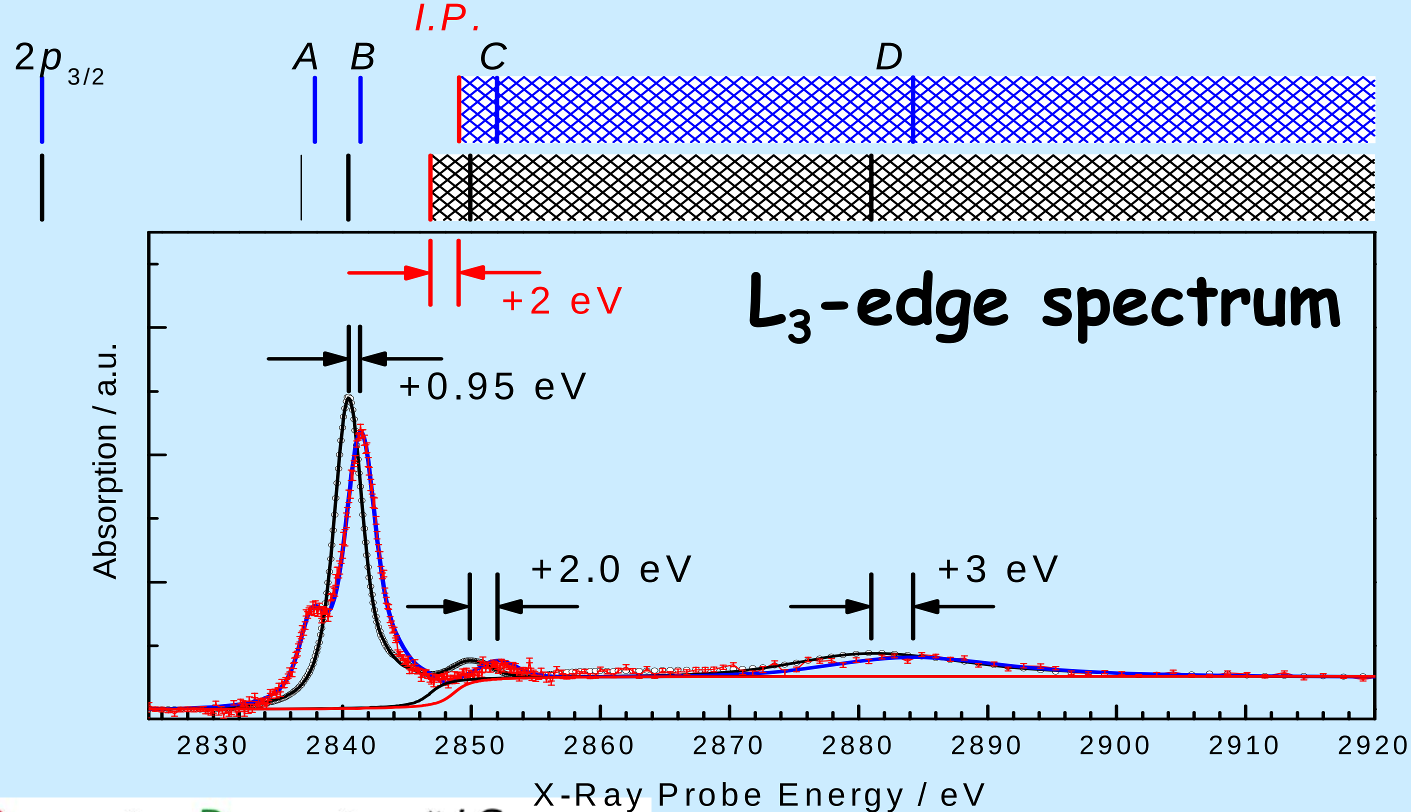
Aqueous $[Ru(bpy)_3]^{2+}$

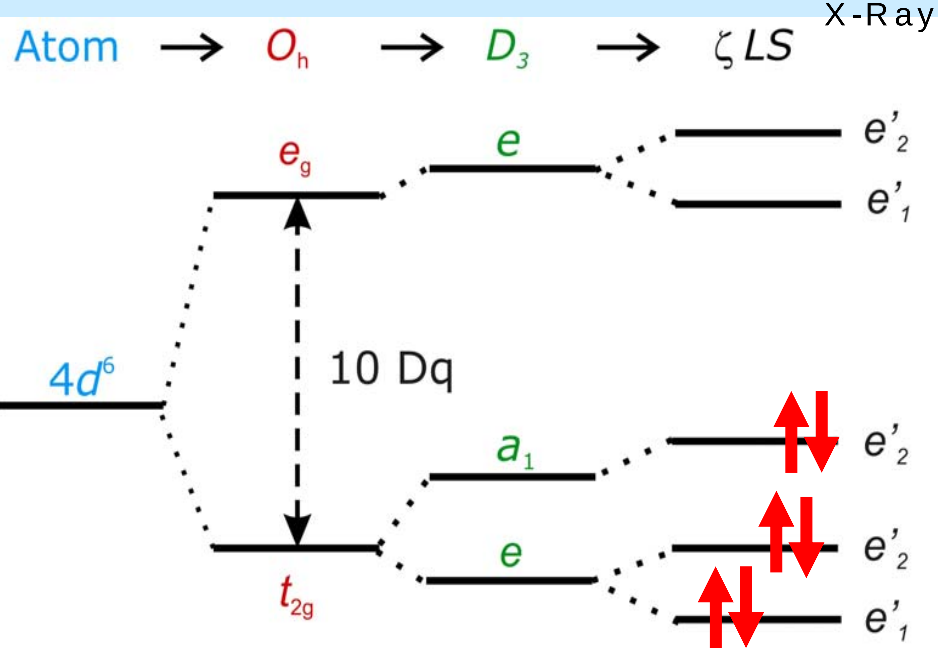


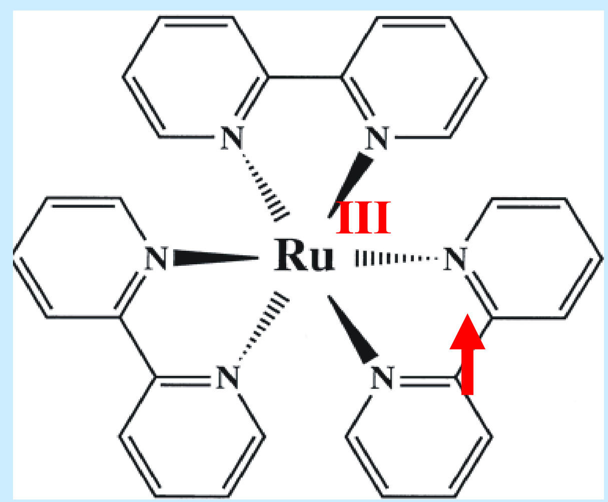
- H-atom of coordination chemistry
- Photosensitizer
- Solar Cells
- Catalyst in Redox-Reactions
- Model for metalloproteins
- Marker in Biology,...

Ground, Transient and Excited State XAFS of Ru(bpy)$_3$ (aq)



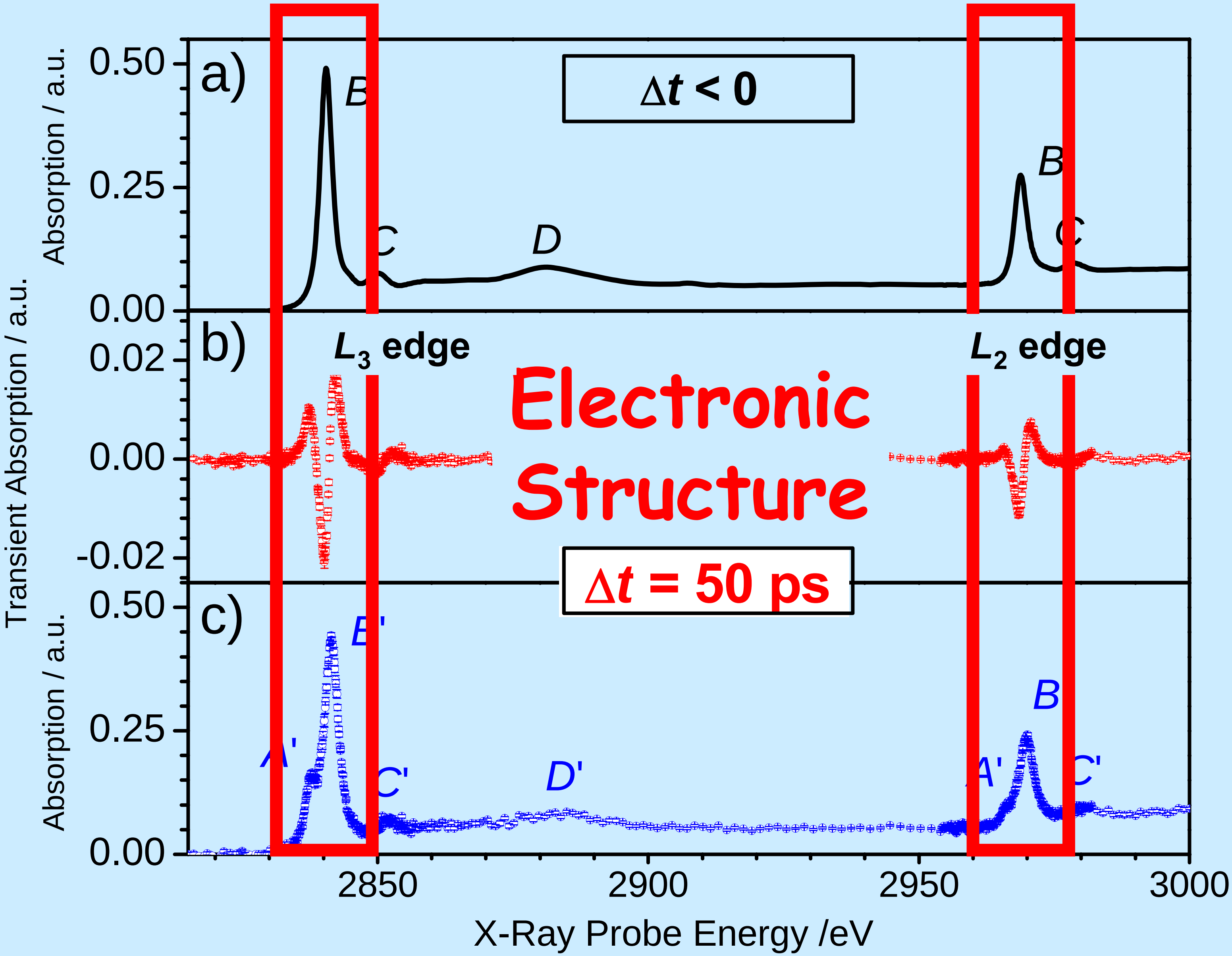




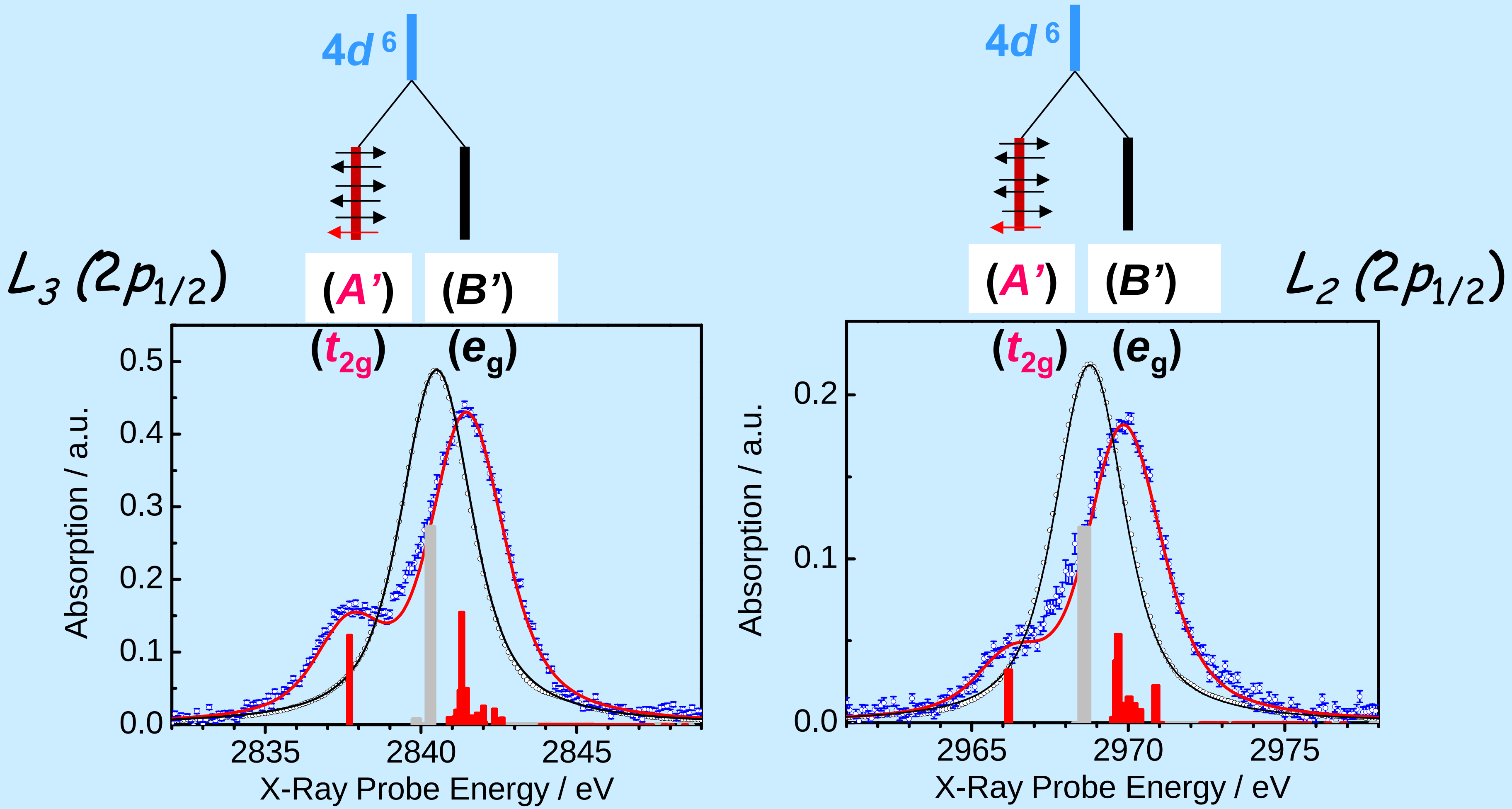


Saes *et al*, Phys. Rev. Lett. 90 (2003) 47403

Ground, Transient and Excited State XAFS of Ru(bpy)$_3$ (aq)



Comparison of experimental and simulated line shapes



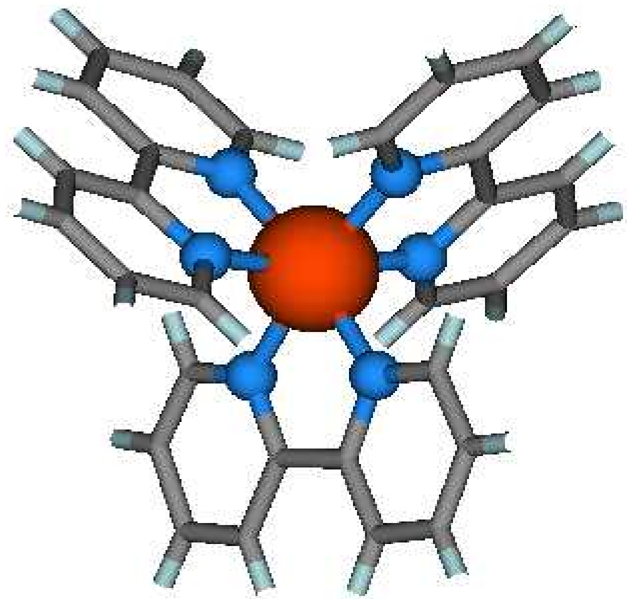
ΔE (10Dq) (ground - excited) = -0.15 eV

→ ΔR (Ru-N)= -0.02 Å

W. Gawelda *et al.*, submitted to JACS (2005)

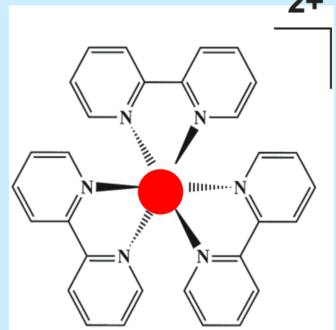
II. Light-induced spin cross-over compounds

$[Fe^{II}(bpy)_3]^{2+}$



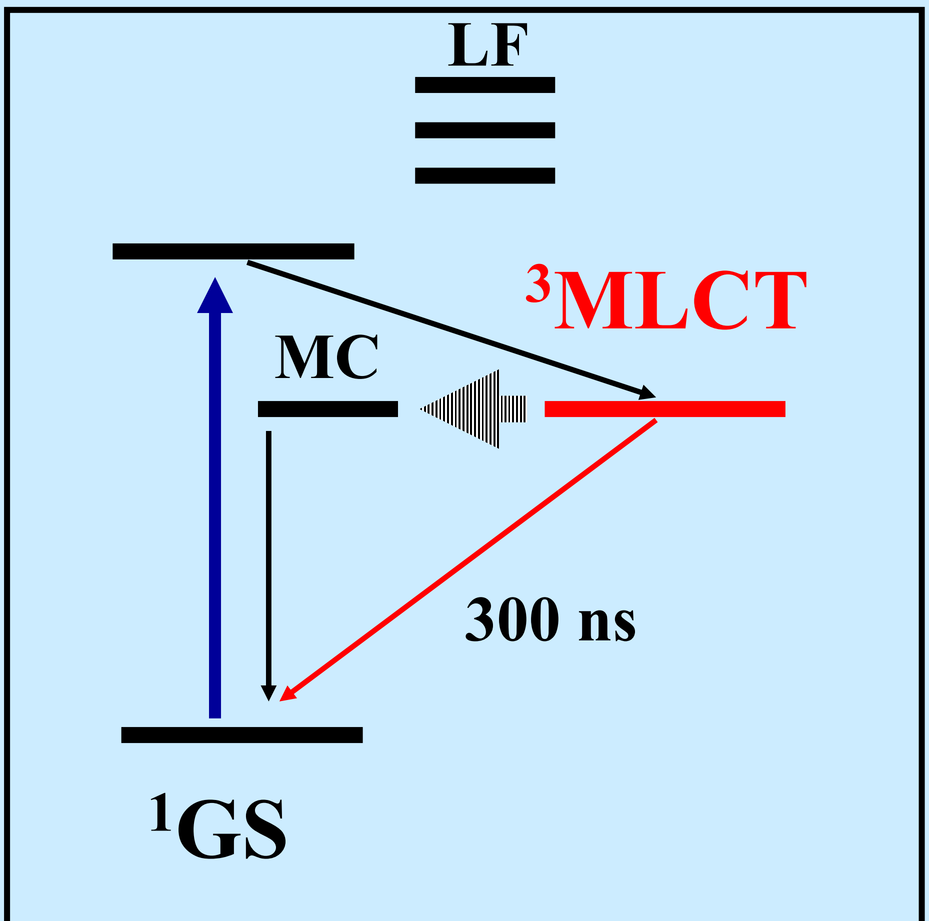
Photoinduced Low Spin (S=0) → High Spin (S=2) transition

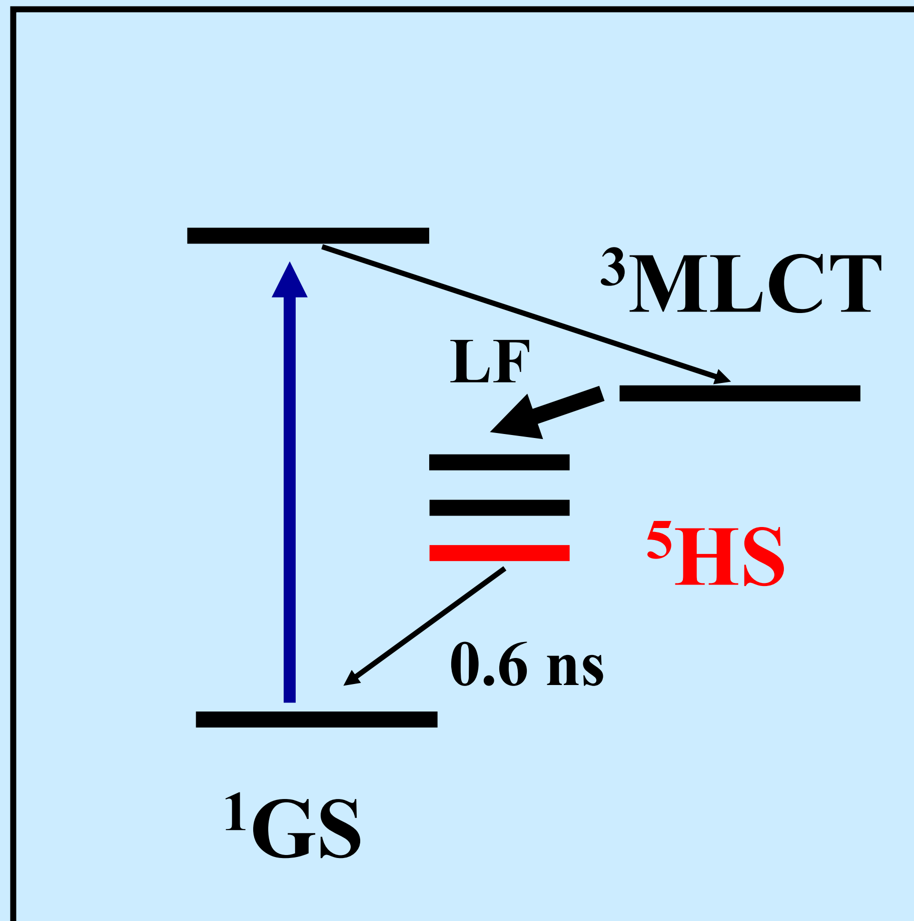
Aqueous $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$



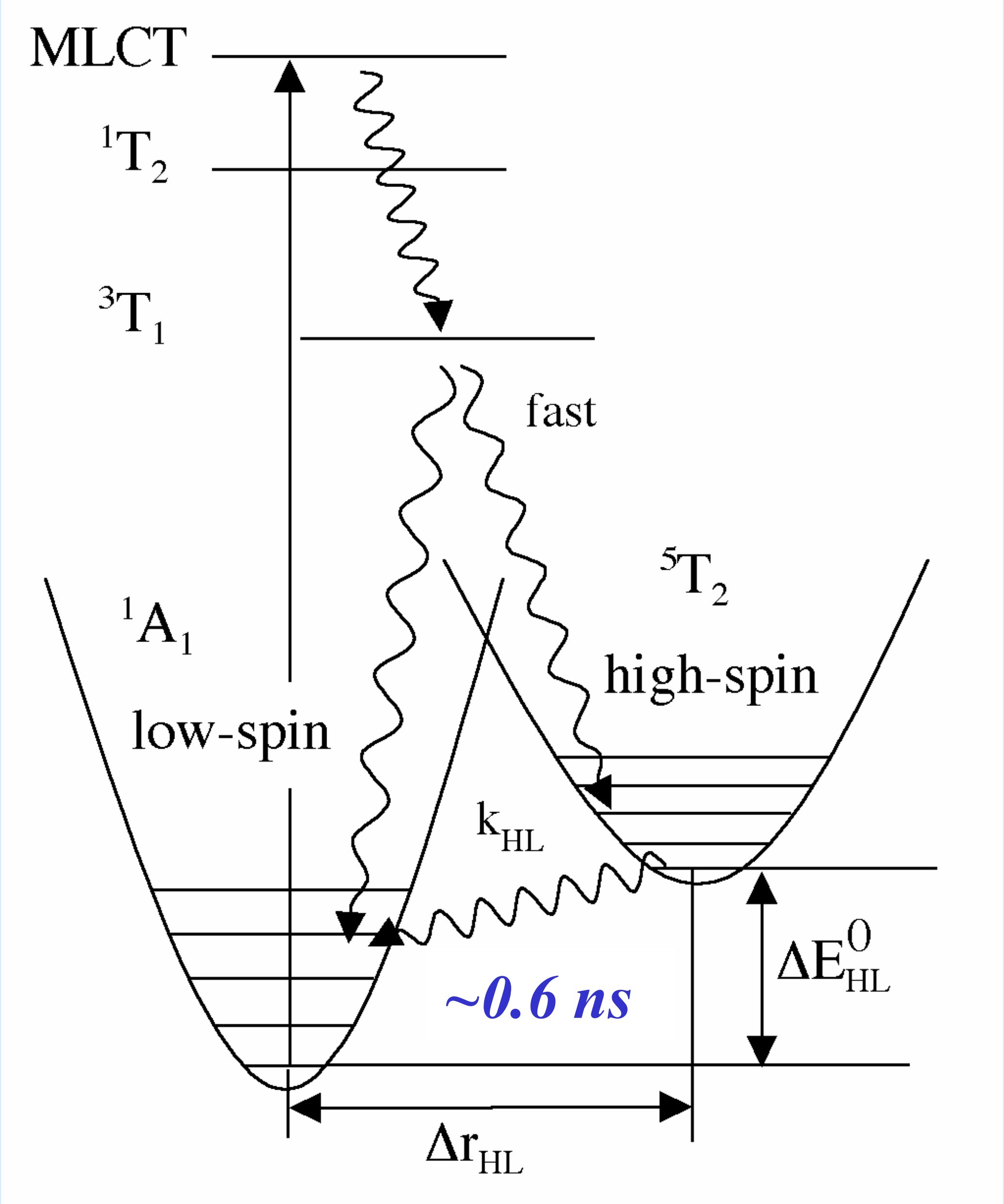
$Ru(bpy)_3]^{2+}$:

$Fe(bpy)_3]^{2+}$:





Photocycle

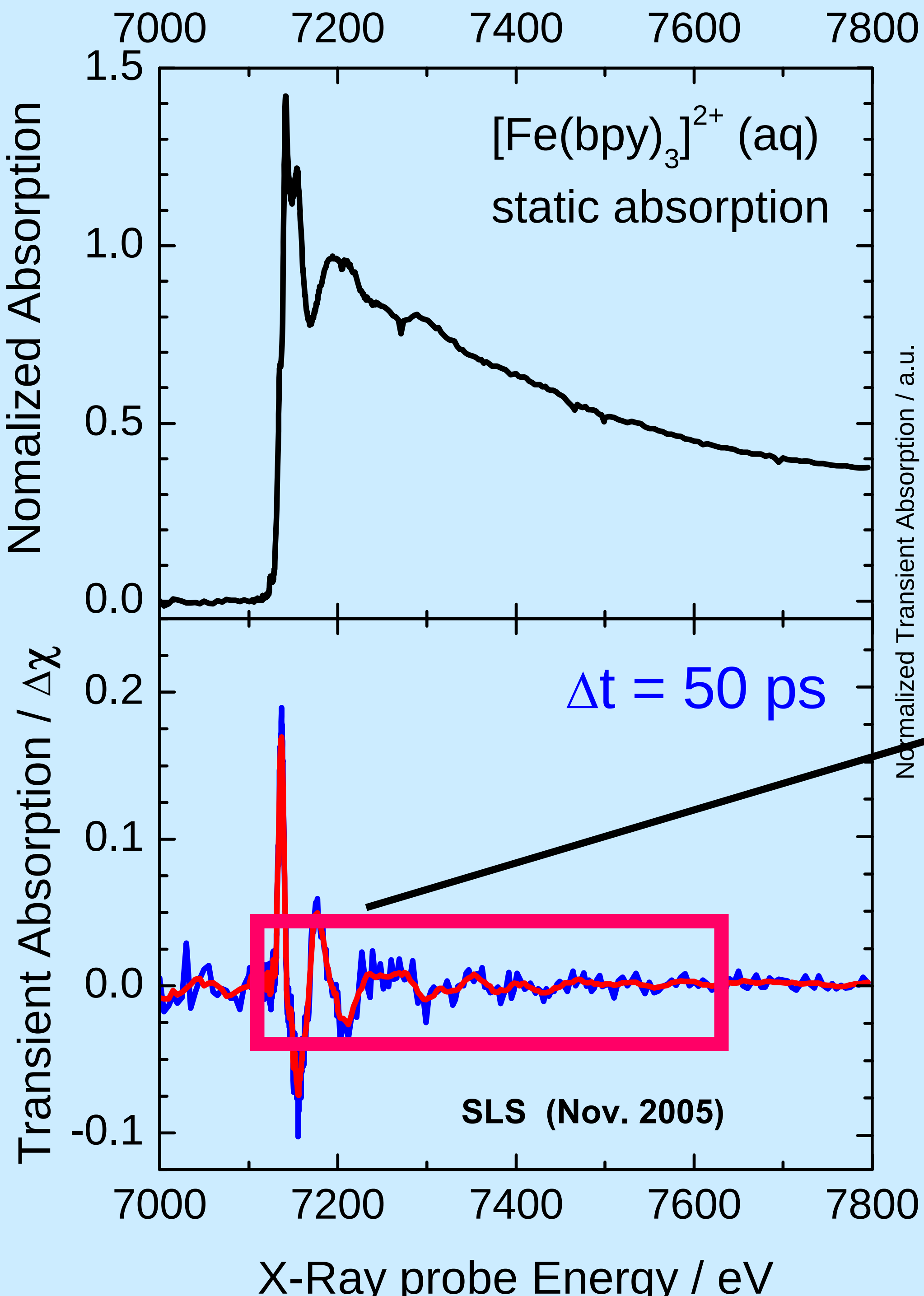


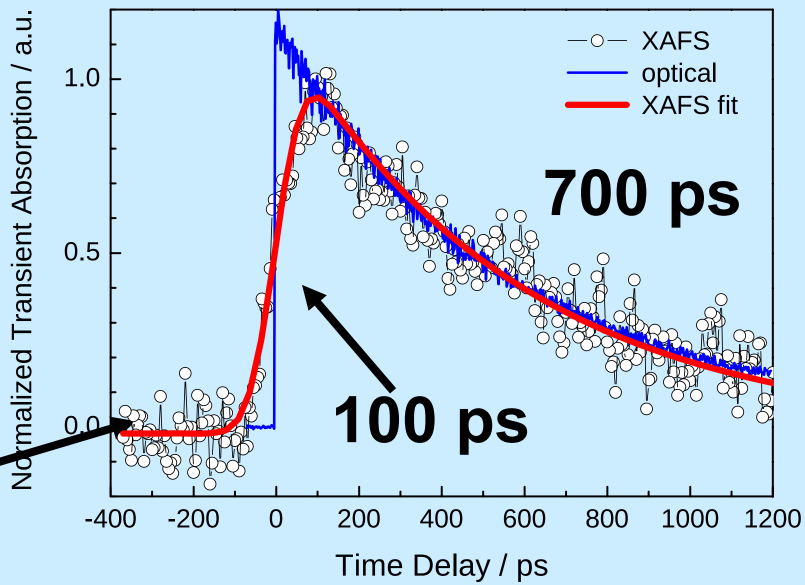
Fe(bpy)$_3$]$^{2+}$(aq):

(LS) → (HS) (<1ps)

(HS) → (LS) (700 ps)

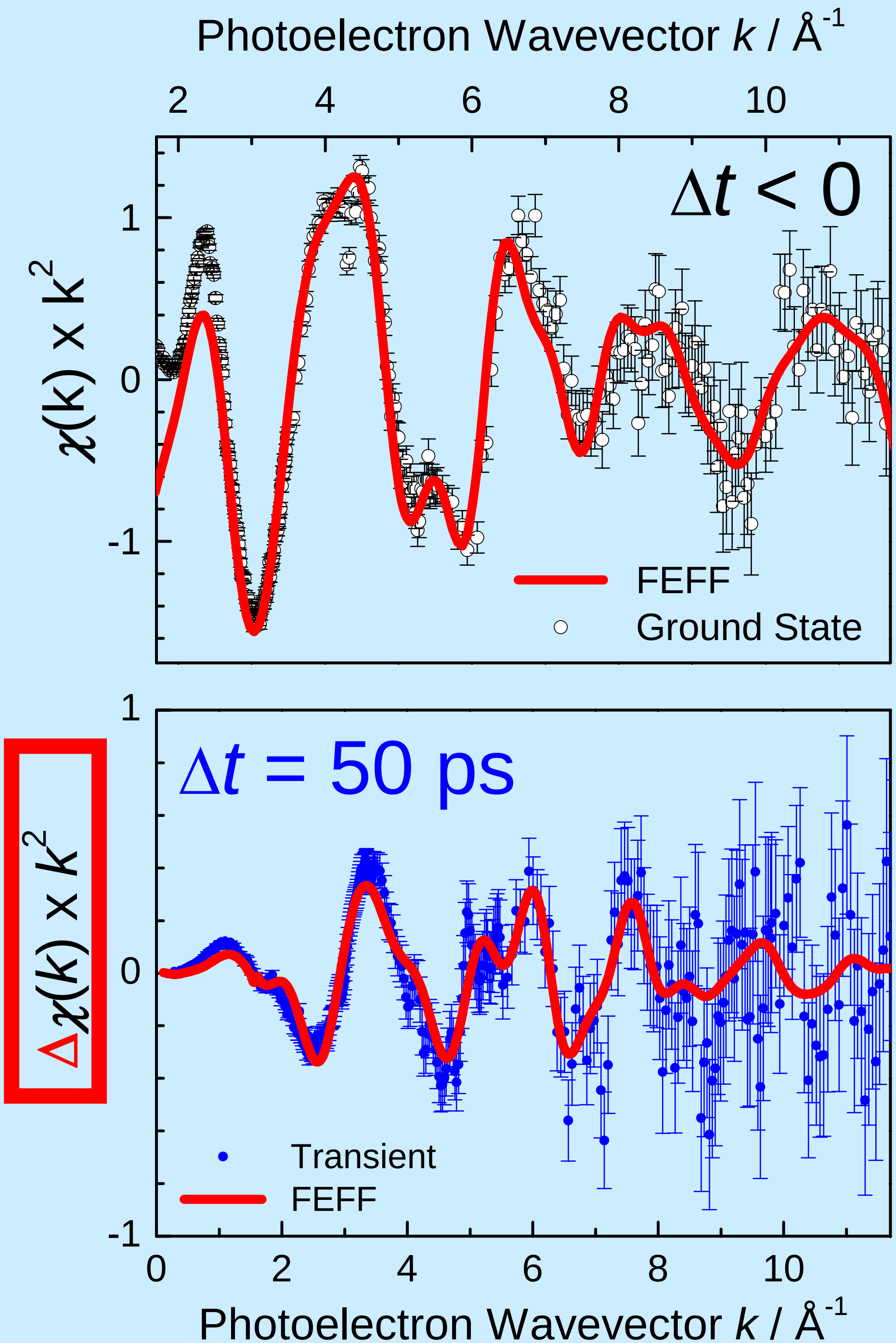
Fe K-edge XAS





c = 1-100 mMol/l

→ Fluorescence Detection



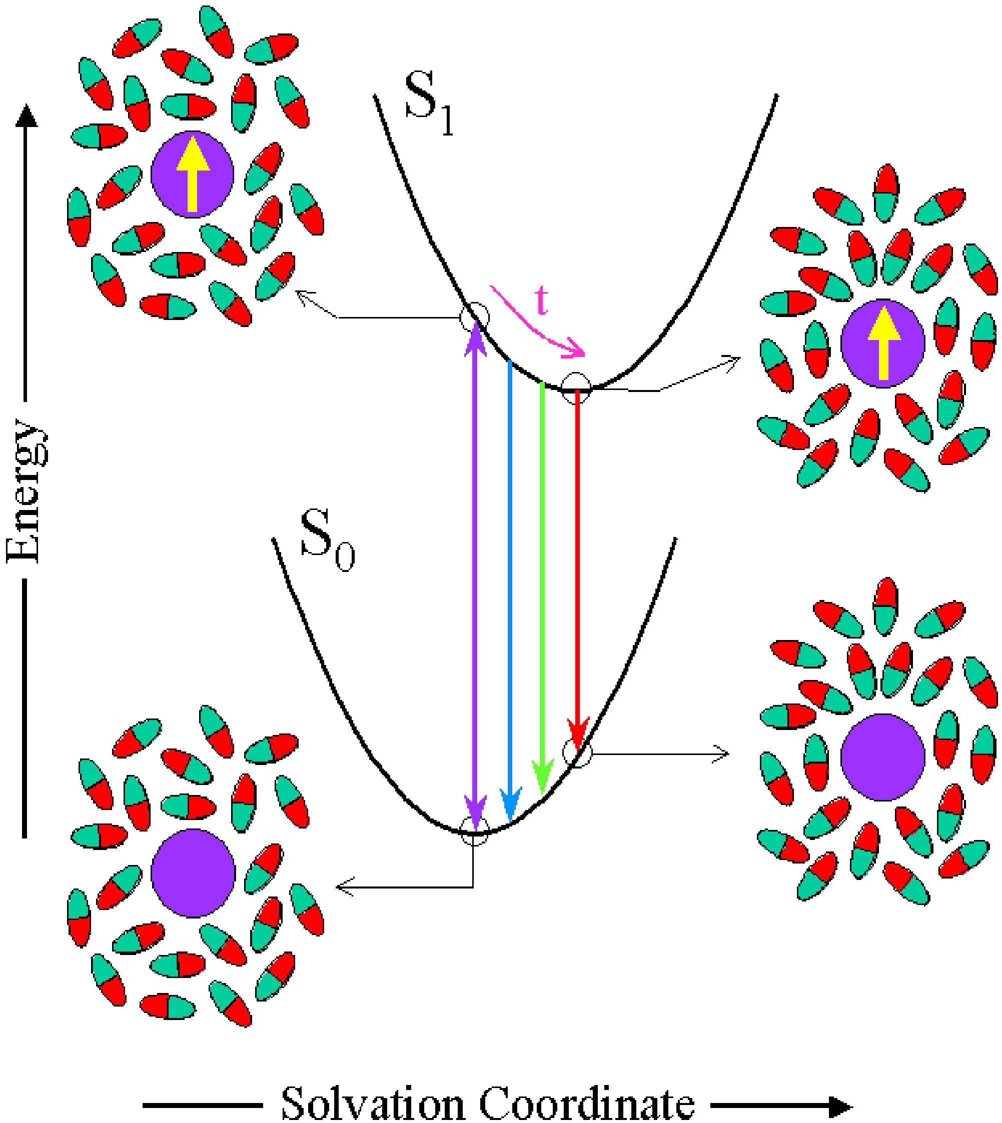
Ground state spectrum

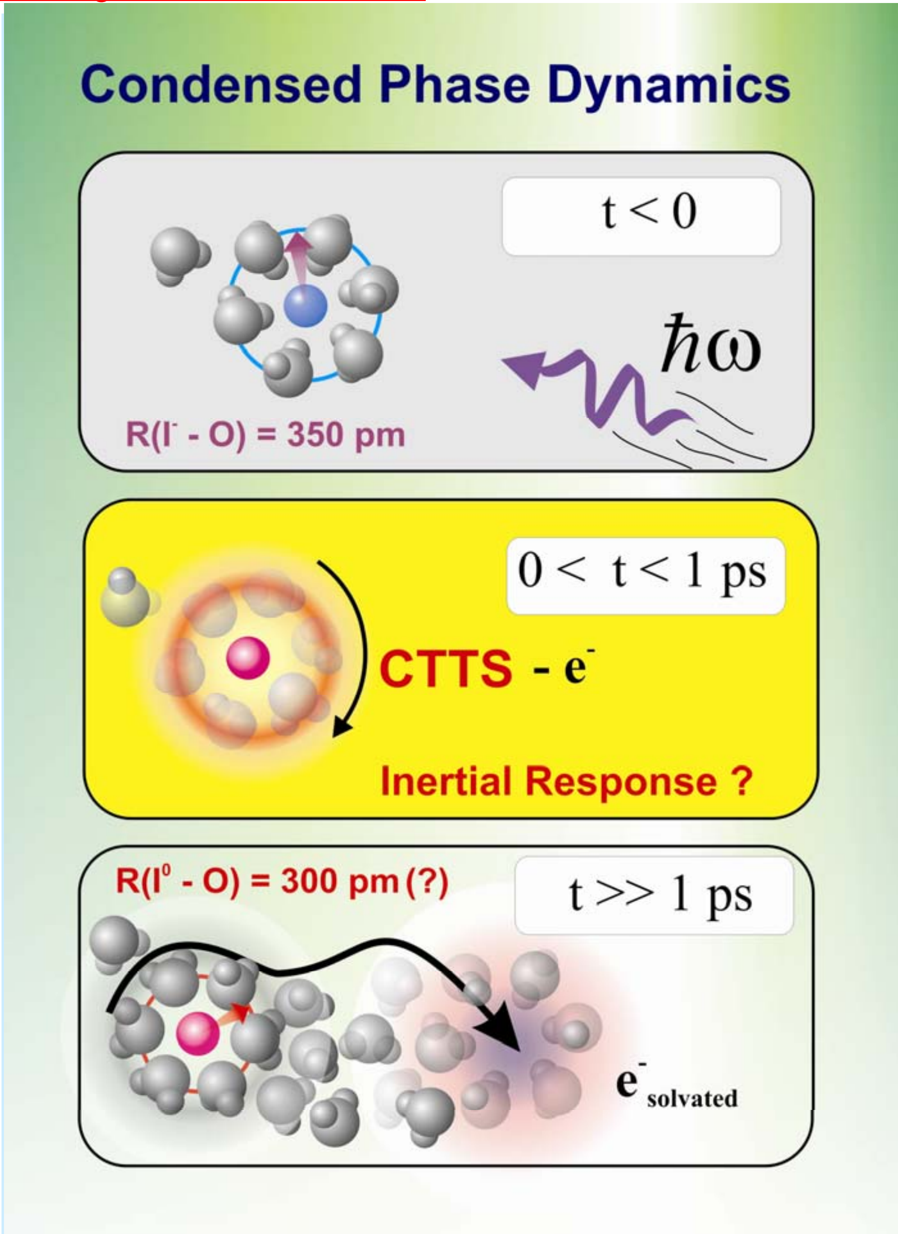
Transient spectrum

Fe-N Bond increase:

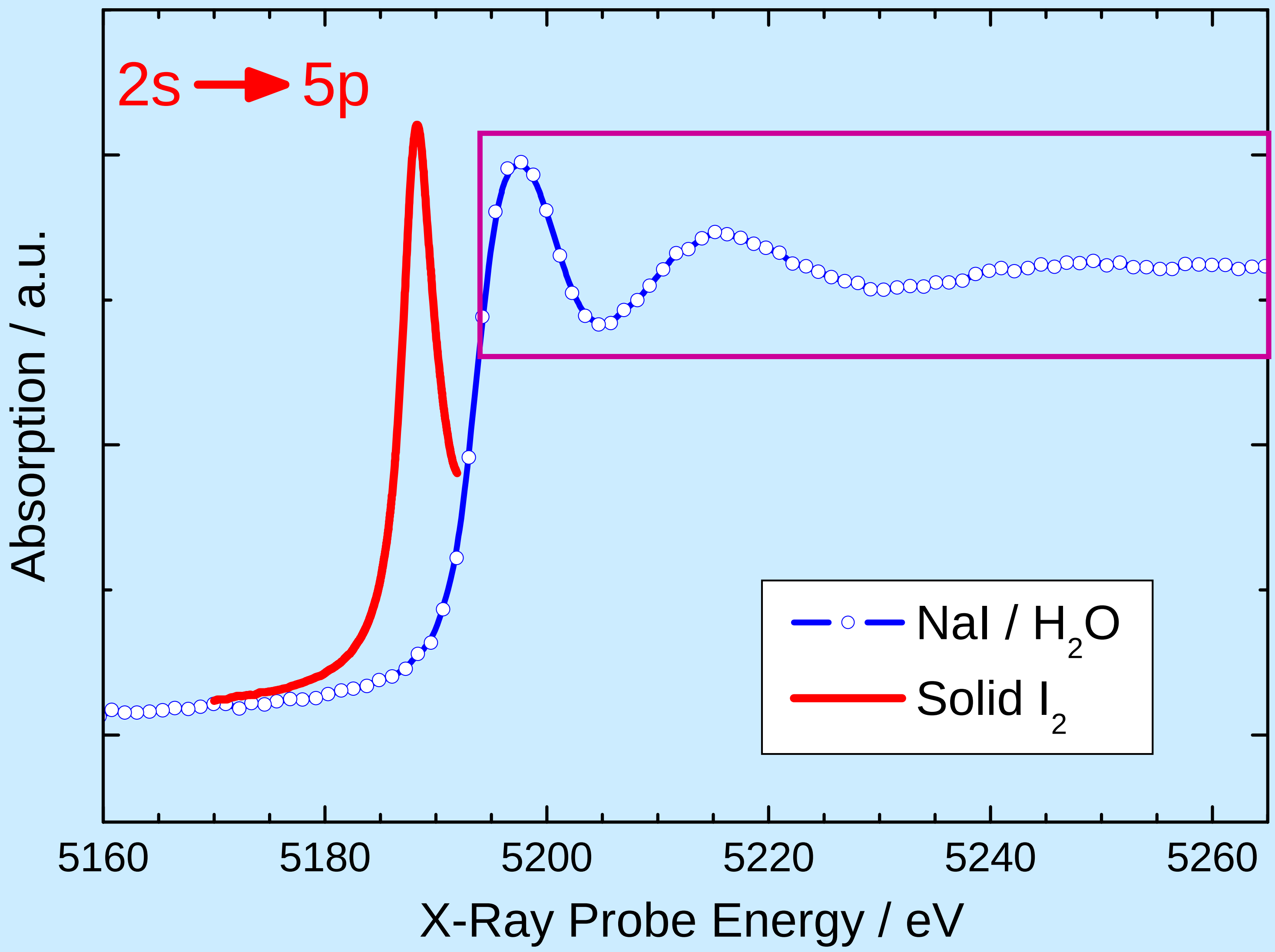
ΔR = 0.2 ± 0.015 Å

III. Solvation Dynamics

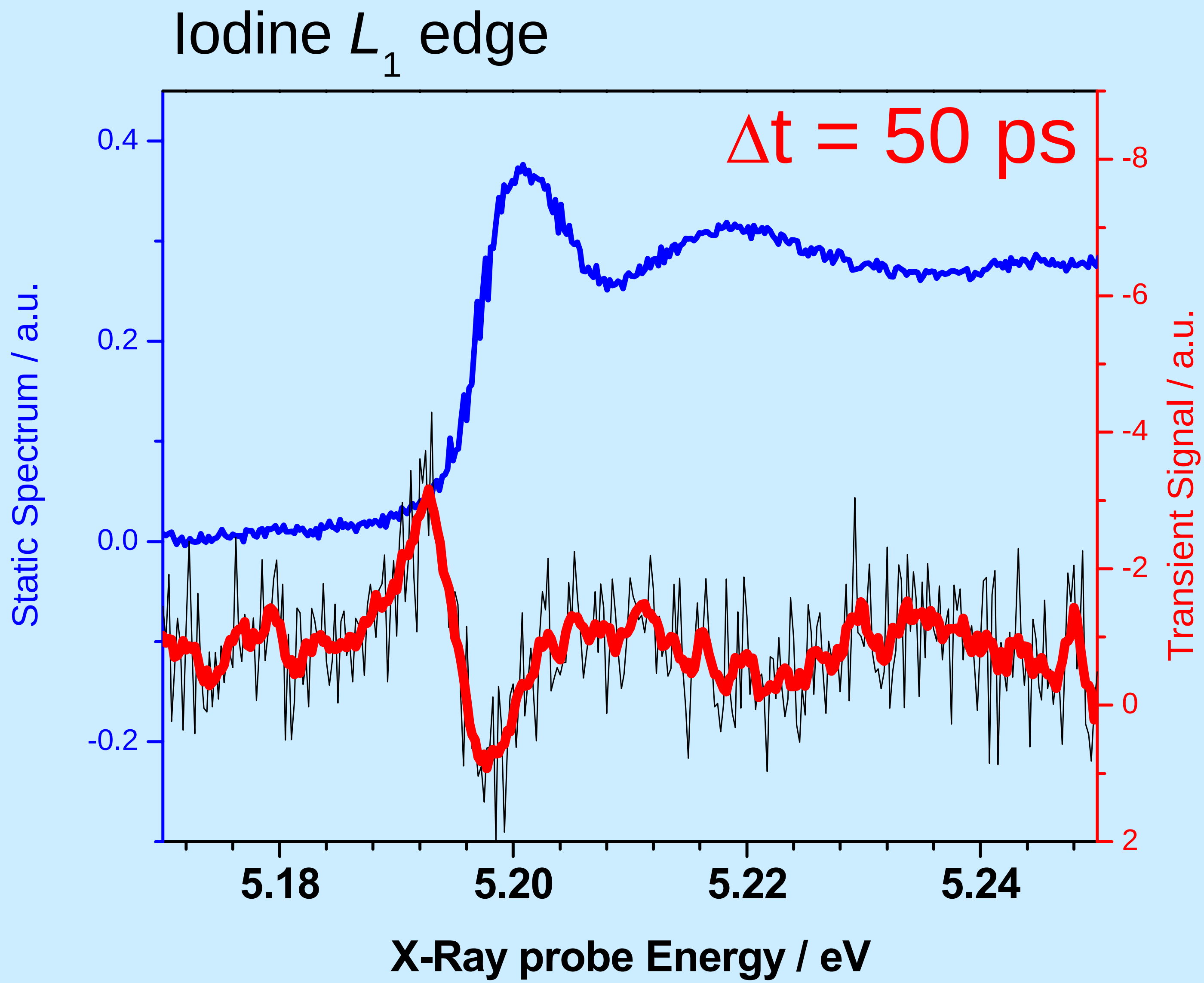


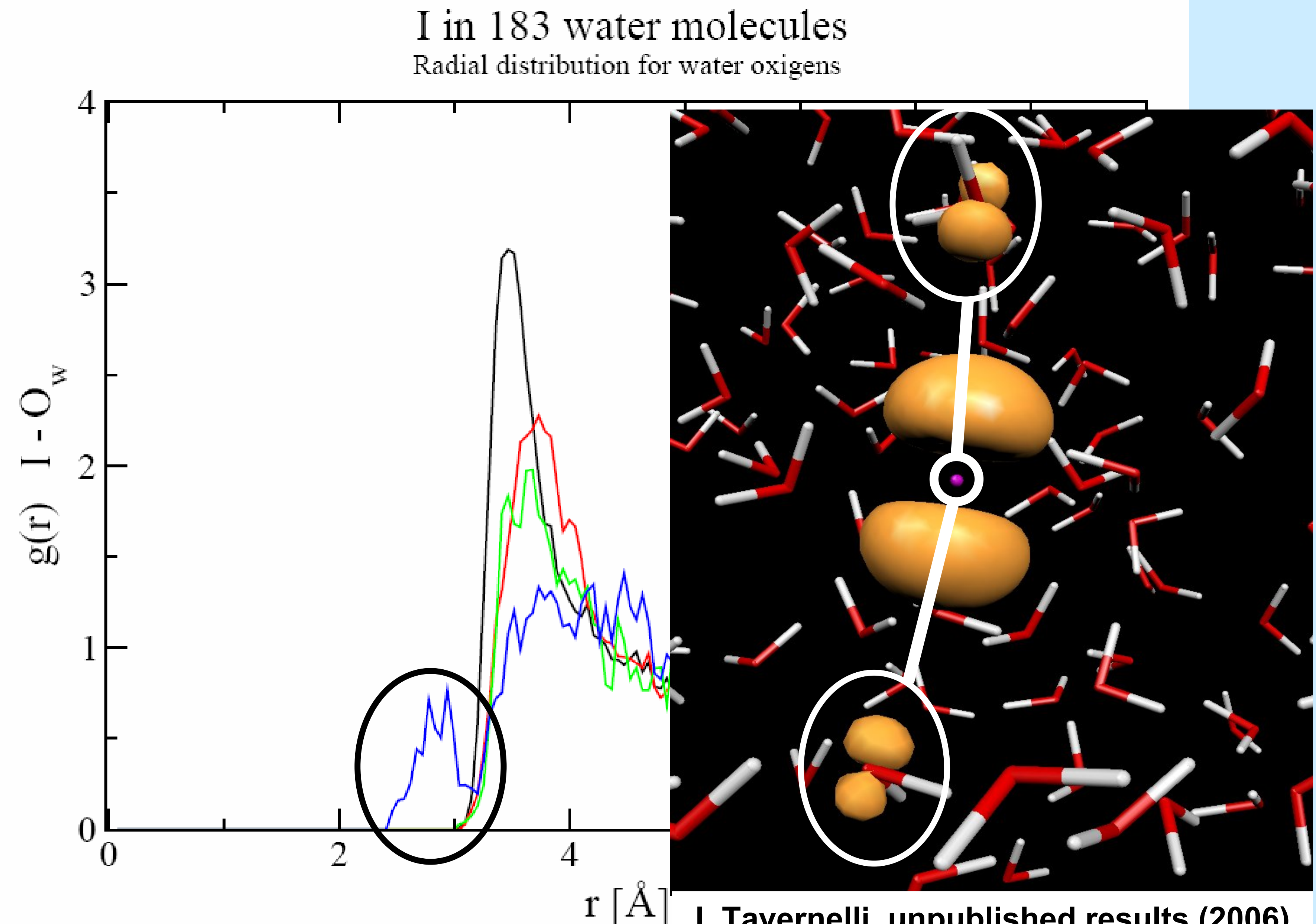


$$I^- (5p^6) + (H_2O)_n + h\nu \rightarrow I^0 (5p^5) + (H_2O)_m + e^- (aq)$$

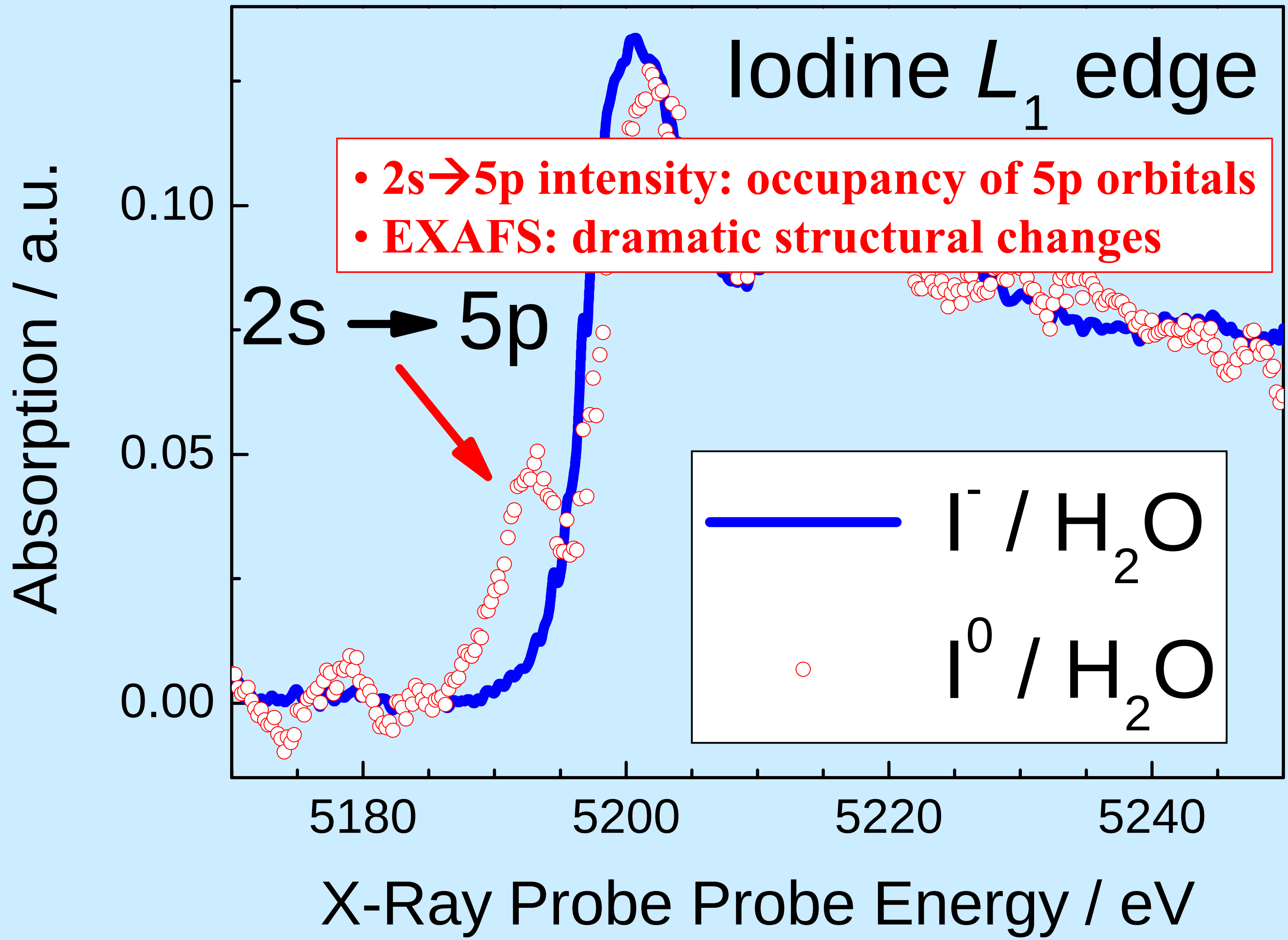


Time-Resolved XANES of aqueous Iodide





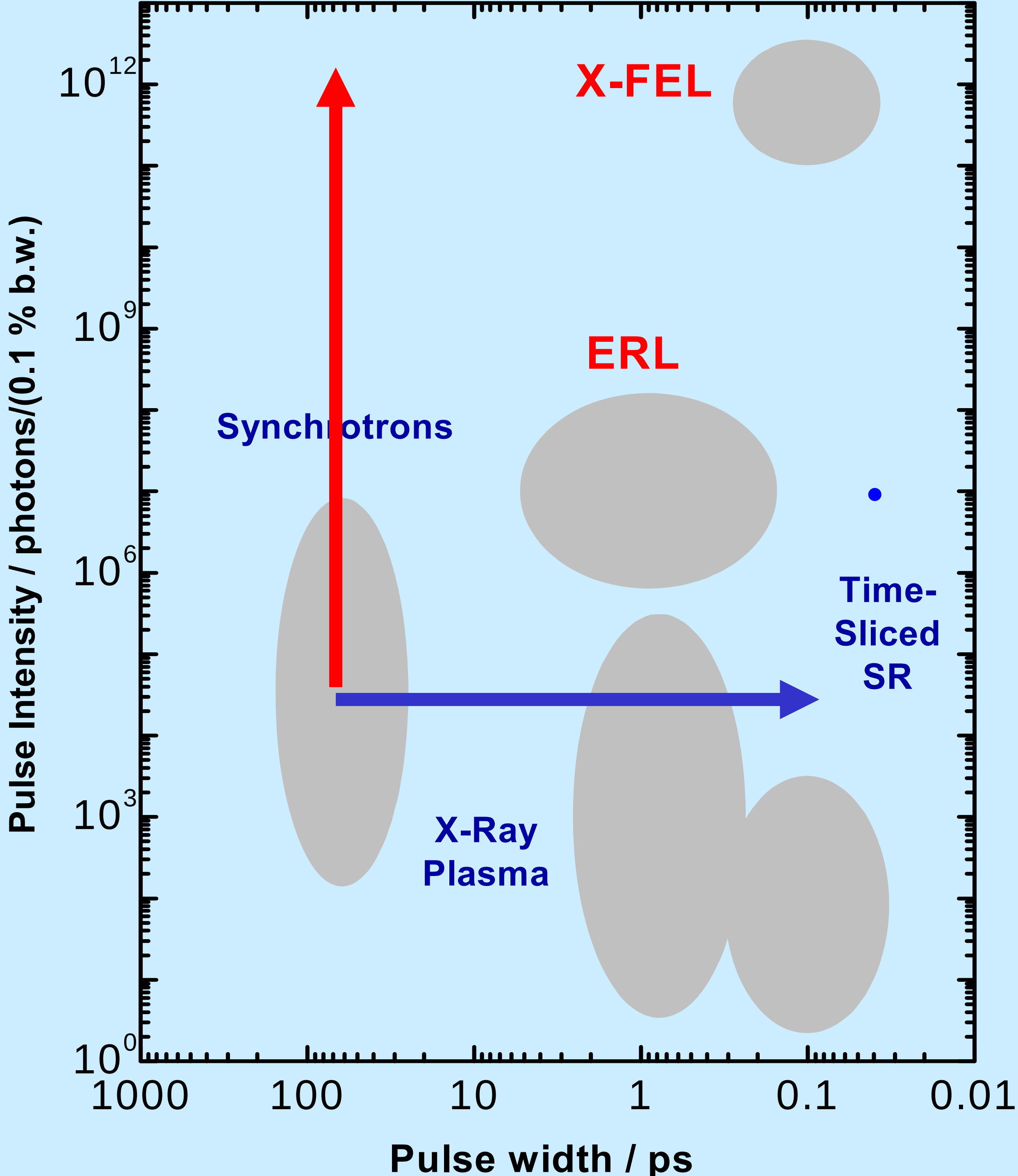
I. Tavernelli, unpublished results (2006)



Iodine L_1 edge
• 2s→5p intensity: occupancy of 5p orbitals
• EXAFS: dramatic structural changes
2s → 5p
Absorption / a.u.
0.10
0.05
0.00
5180
5200
5220
5240
X-Ray Probe Probe Energy / eV
I^- / H_2O
I^0 / H_2O

Using an ERL Hard X-Ray Source

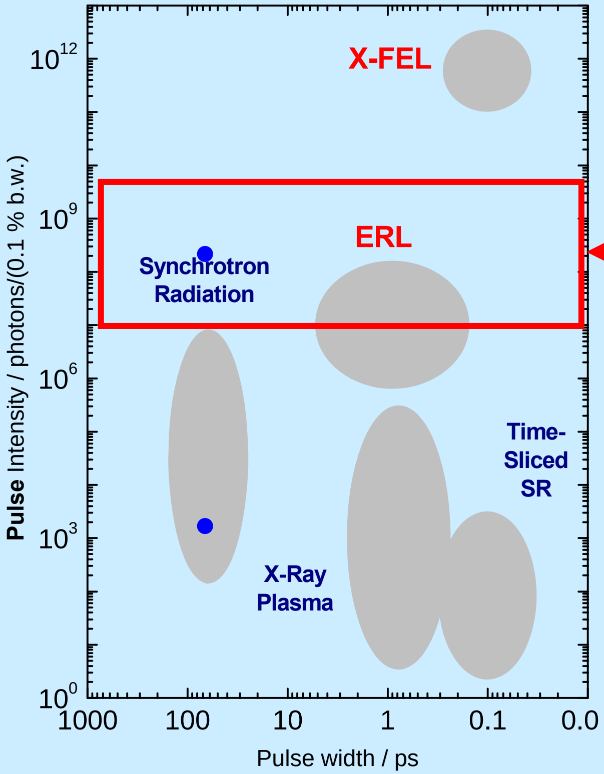
- Flux (Photons/pulse)
- Pulse Width

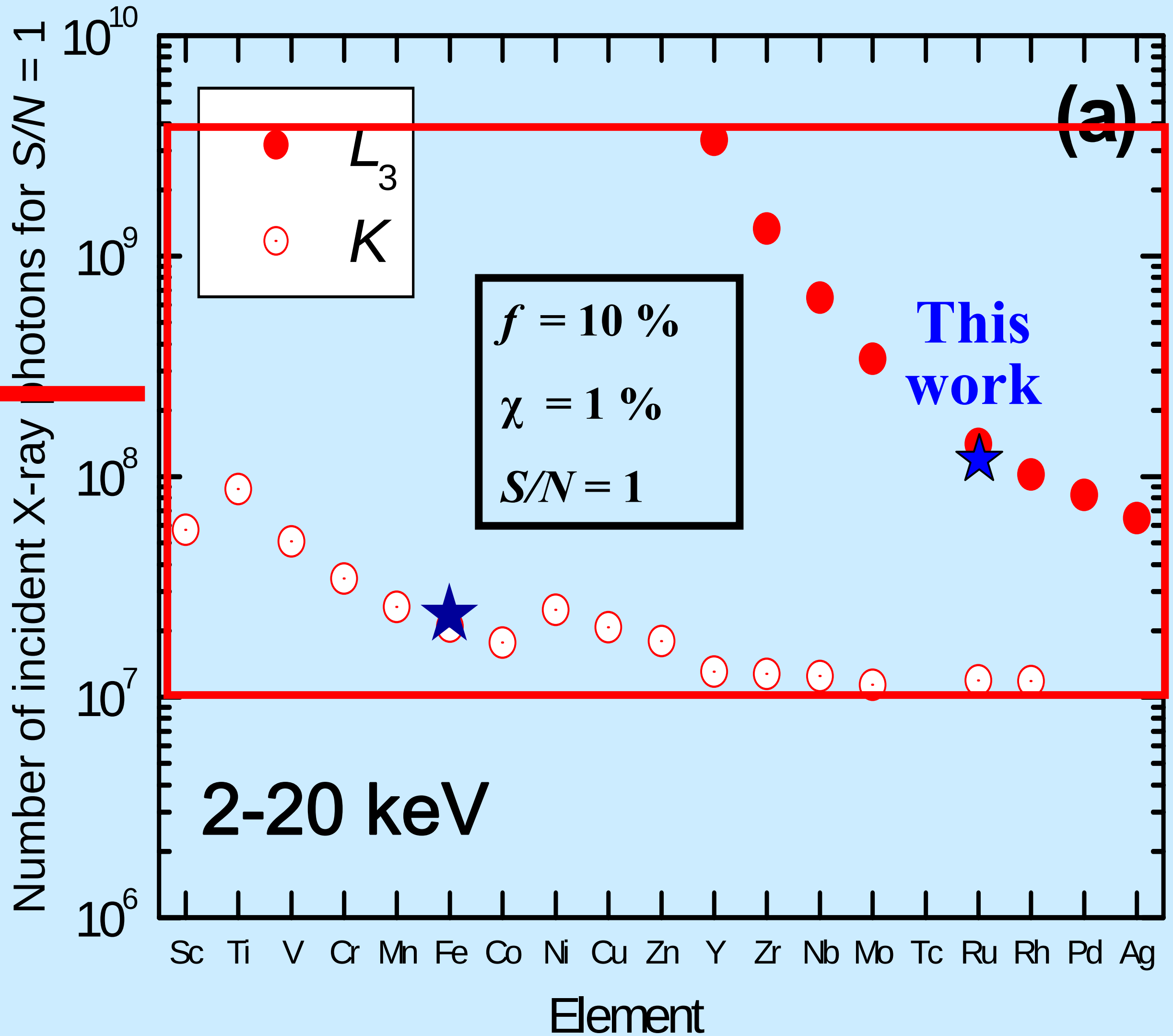


X-FEL
ERL
Synchrotrons
Time-
Sliced
SR
X-Ray
Plasma
10^12
10^9
10^6
10^3
10^0
1000
100
10
1
0.1
0.01
Pulse Intensity / photons/(0.1 % b.w.)
Pulse width / ps

Ultrafast *EXAFS* on Transition Metal Compounds

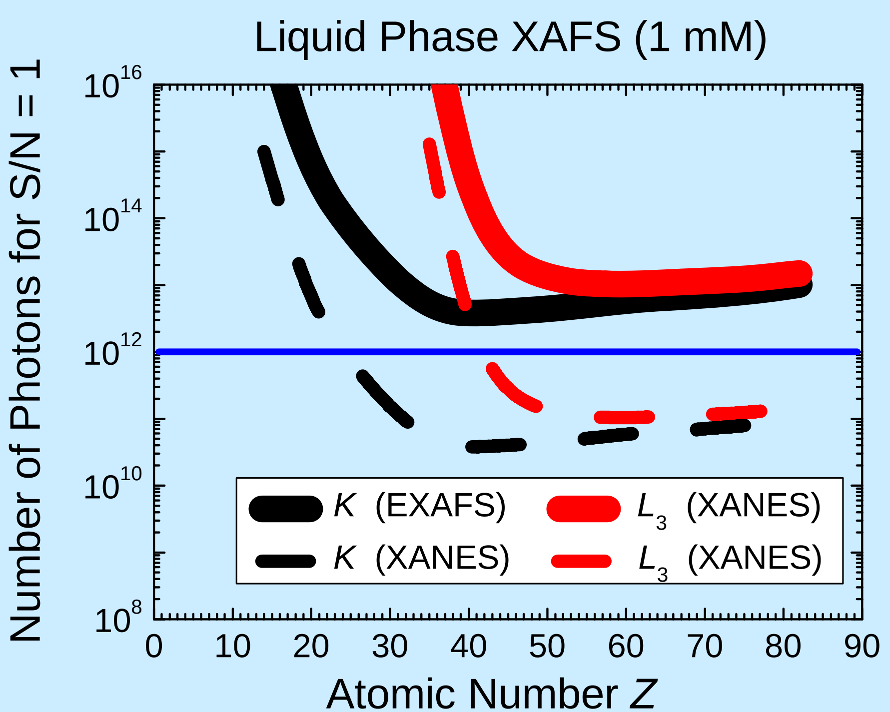
Pulsed X-Ray Sources

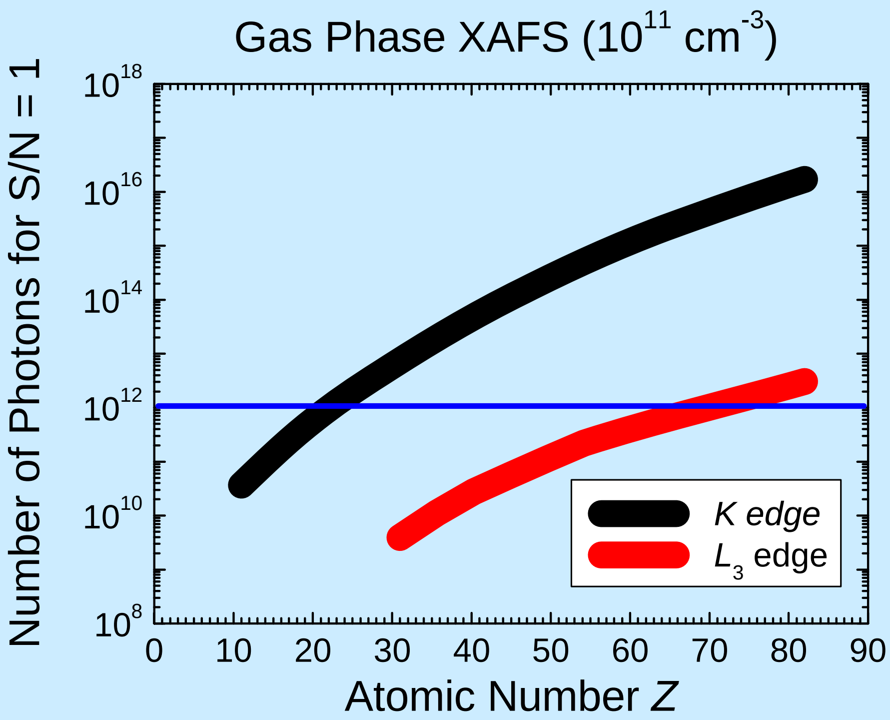




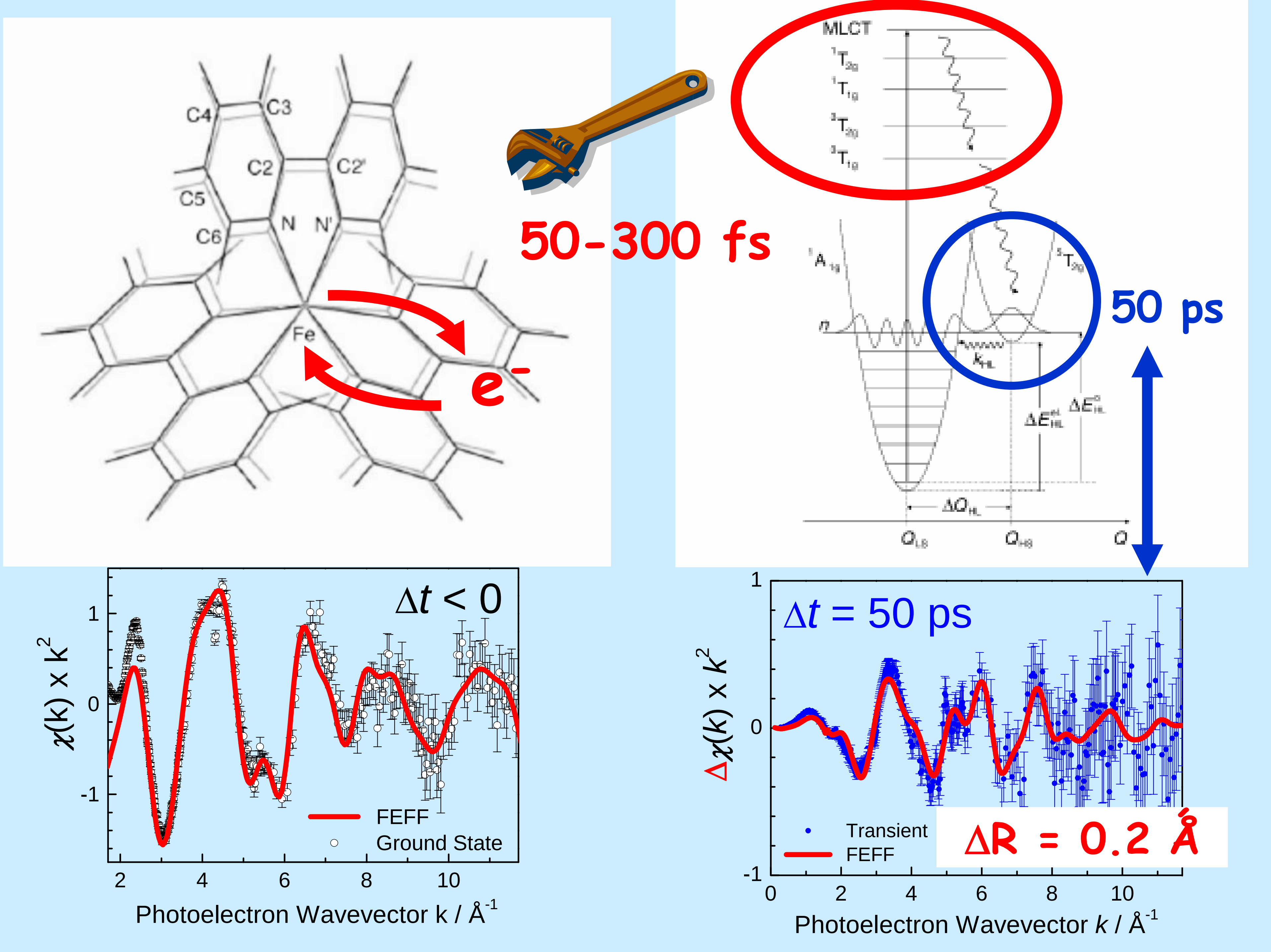
Bressler and Chergui, Chem. Rev. (2004)

Feasibility Range of Possible Experiments





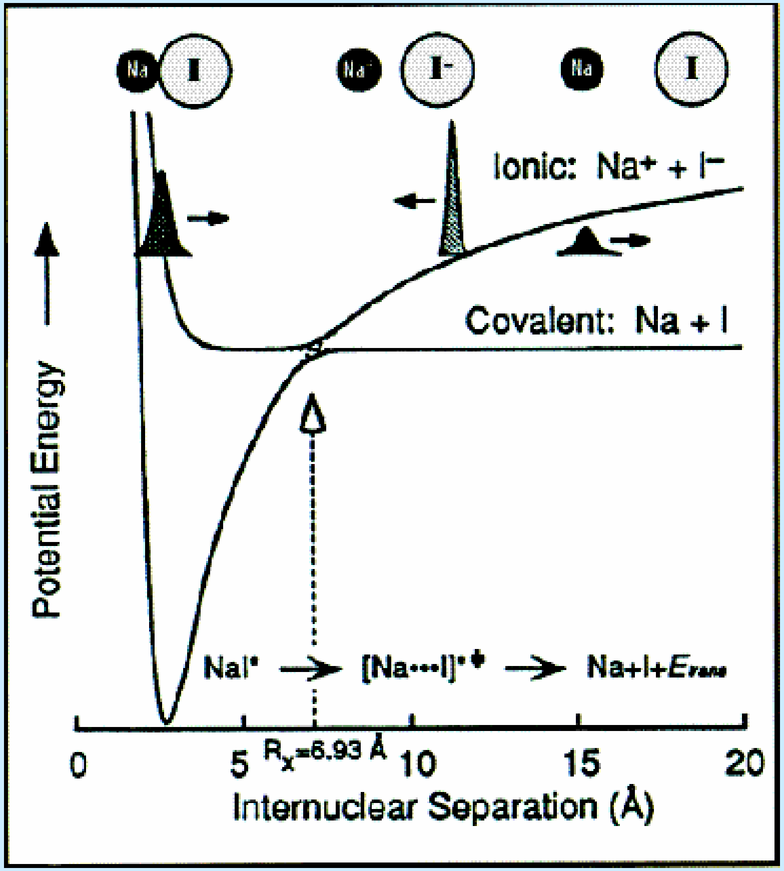
One Possible ERL Experiment

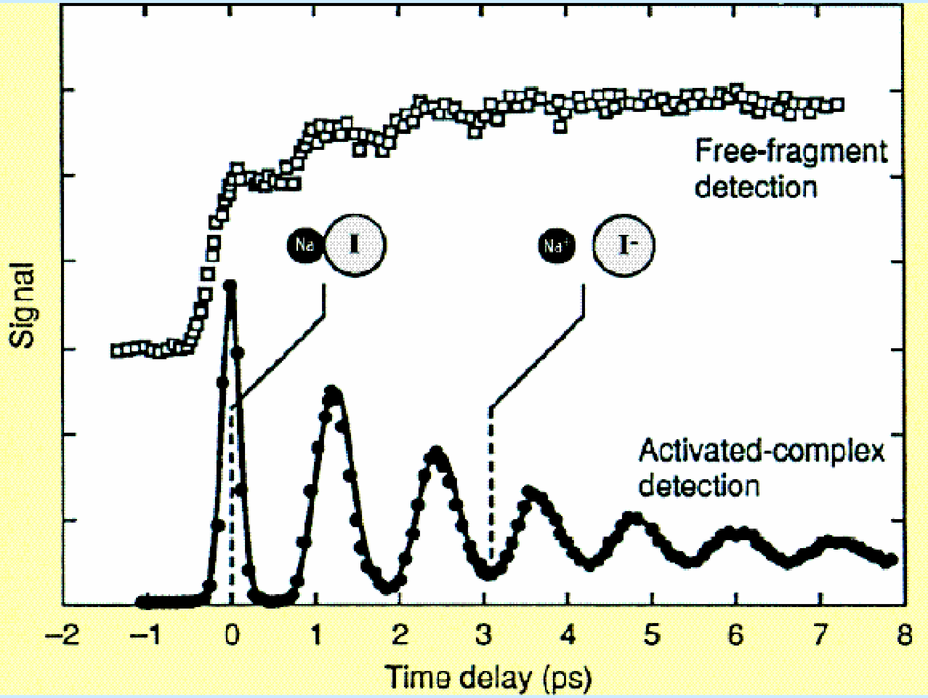


C4
C3
C2
C2'
C5
C6
N
N'
Fe
e⁻
50-300 fs
MLCT
¹T2g
¹T1g
³T2g
³T1g
¹A1g
⁵T2g
50 ps
ΔQHL
QLS
QHS
Q
Δt < 0
FEFF
Ground State
χ(k) x k²
Photoelectron Wavevector k / Å⁻¹
Δt = 50 ps
Transient
FEFF
Δχ(k) x k²
Photoelectron Wavevector k / Å⁻¹
ΔR = 0.2 Å

Molecular Physics

Non-adiabatic dynamics in Molecules

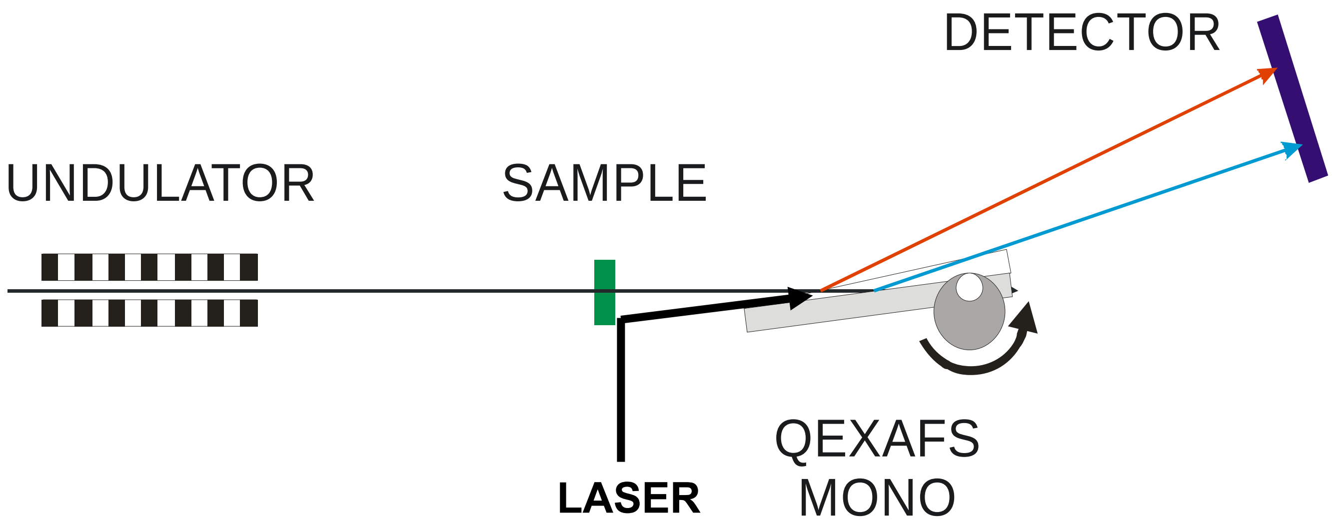


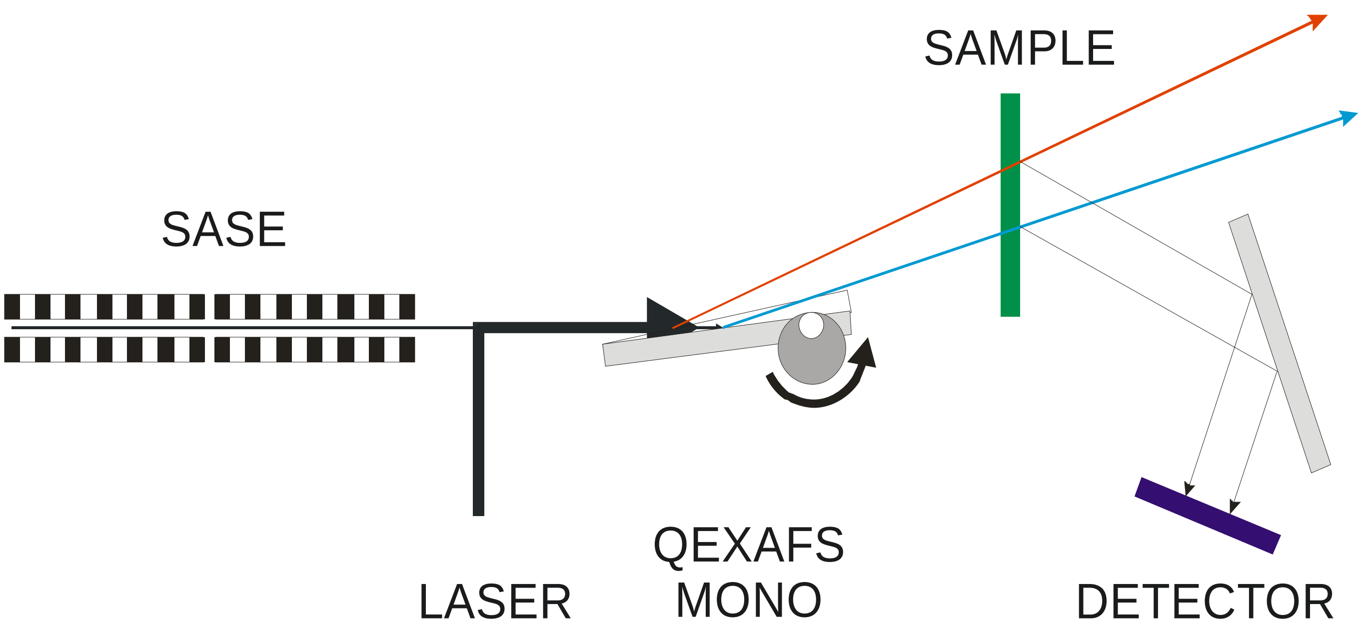


Applications

Atomic and Plasma Physics
Molecular Physics
Condensed Phase Chemical Dynamics
Coordination Chemistry
Biological systems
Solid state physics
Nanosystems
Magnetic systems
Material science,…

Possible experimental lay-outs





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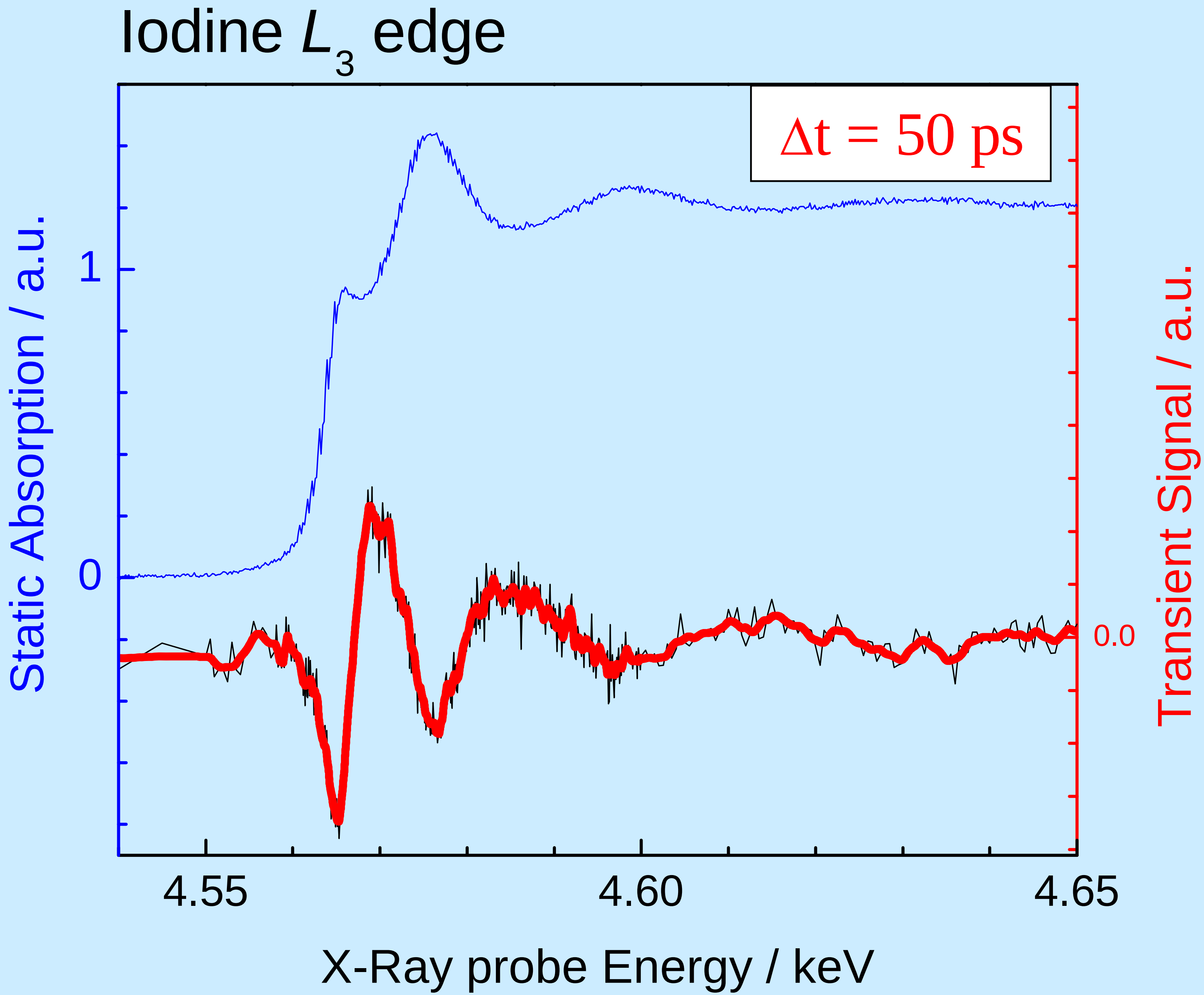
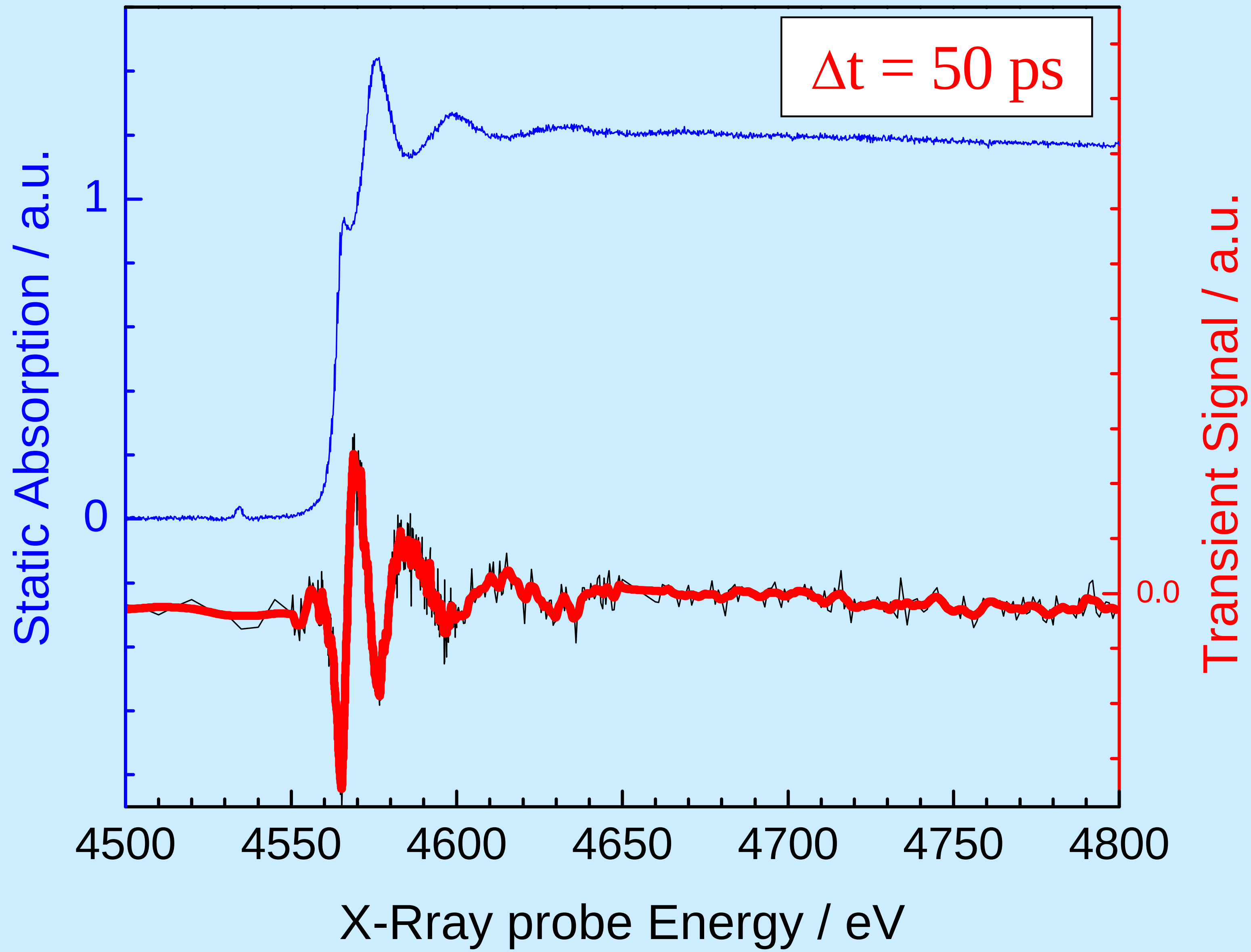
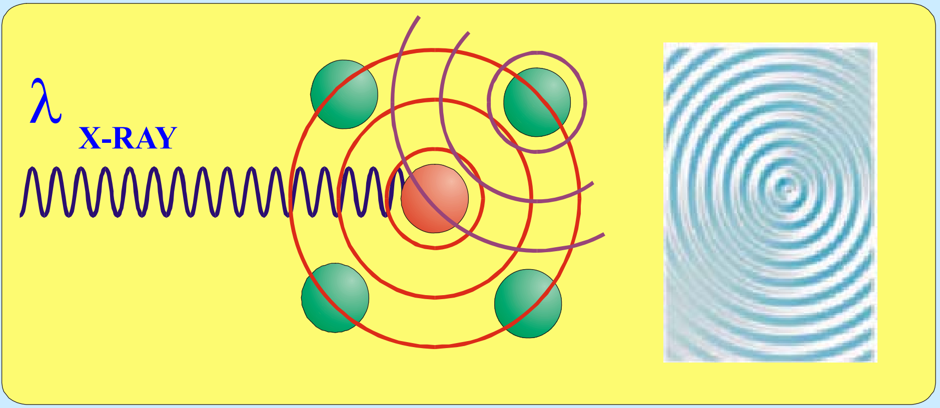
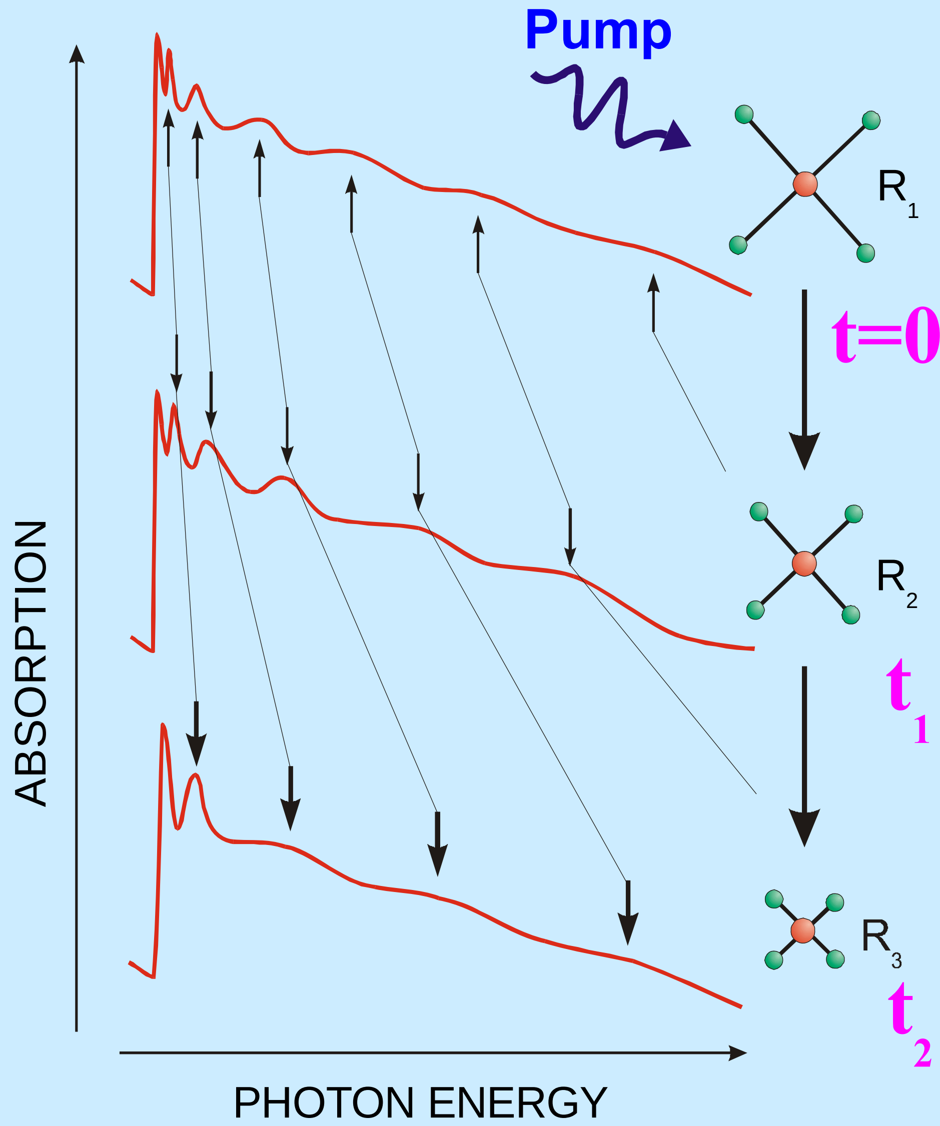


Time-Resolved *EXAFS* of aqueous Iodide



Structural Information via X-Ray Absorption (EXAFS)



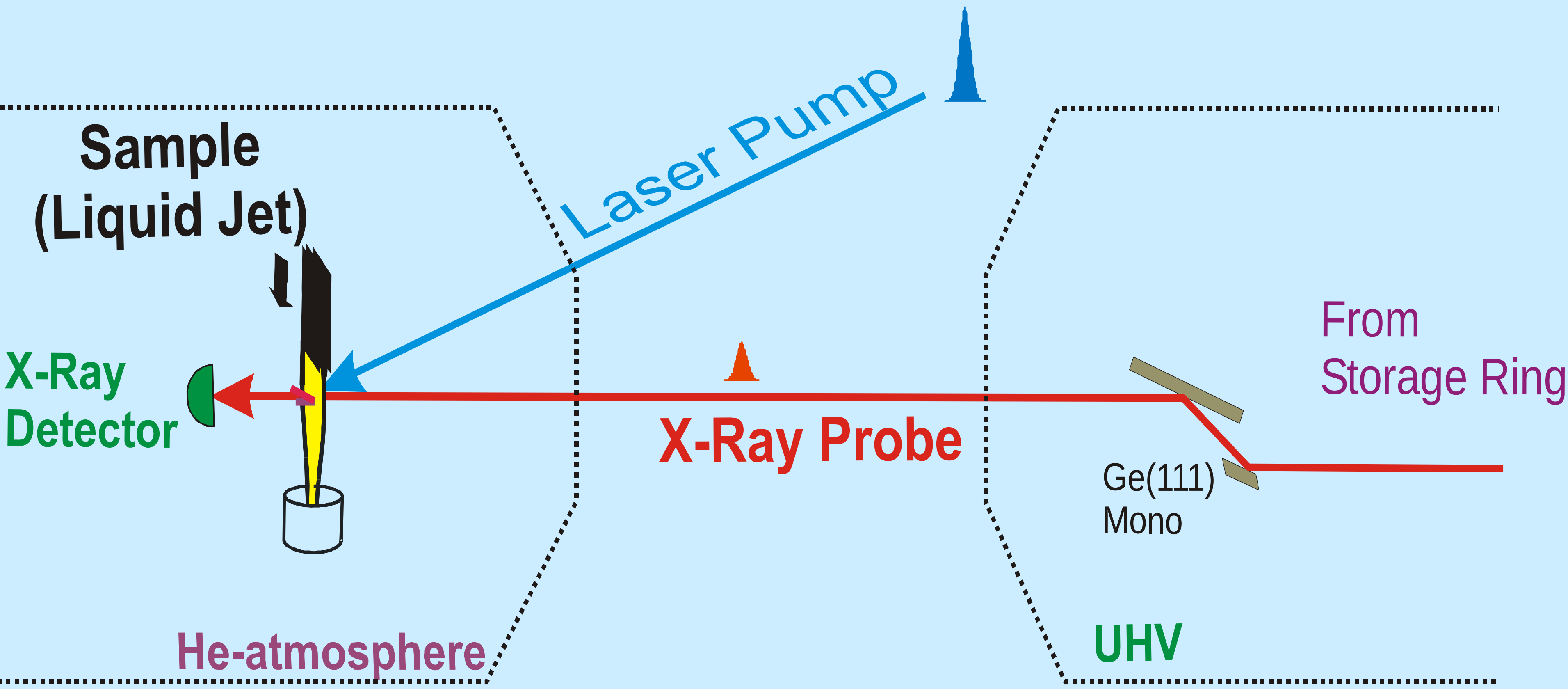


- Single scattering events due to higher energy photoelectrons

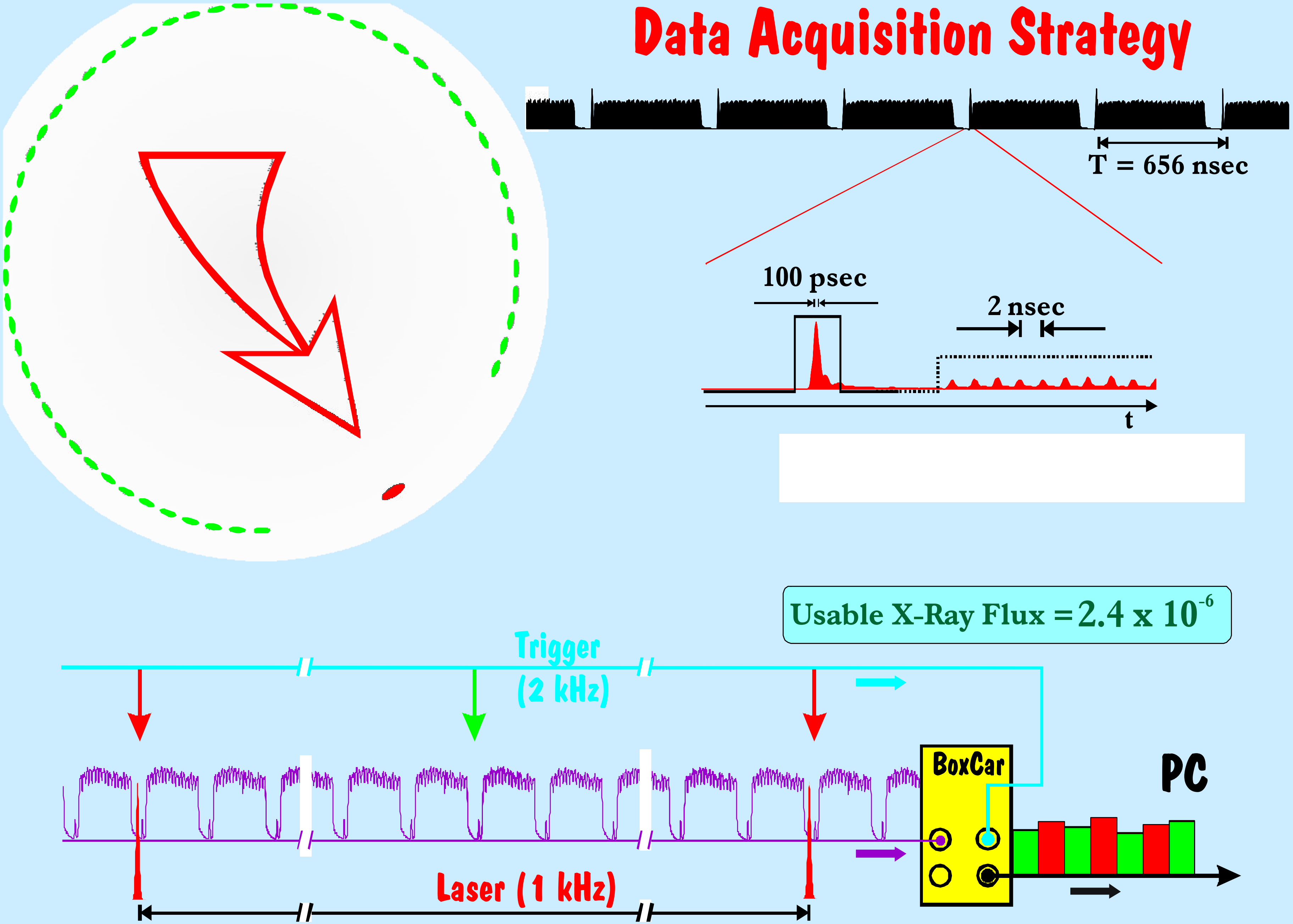
- Bond distances and coordination numbers from simple FT of energy spectrum

Laser-Pump X-ray-Probe Set-up

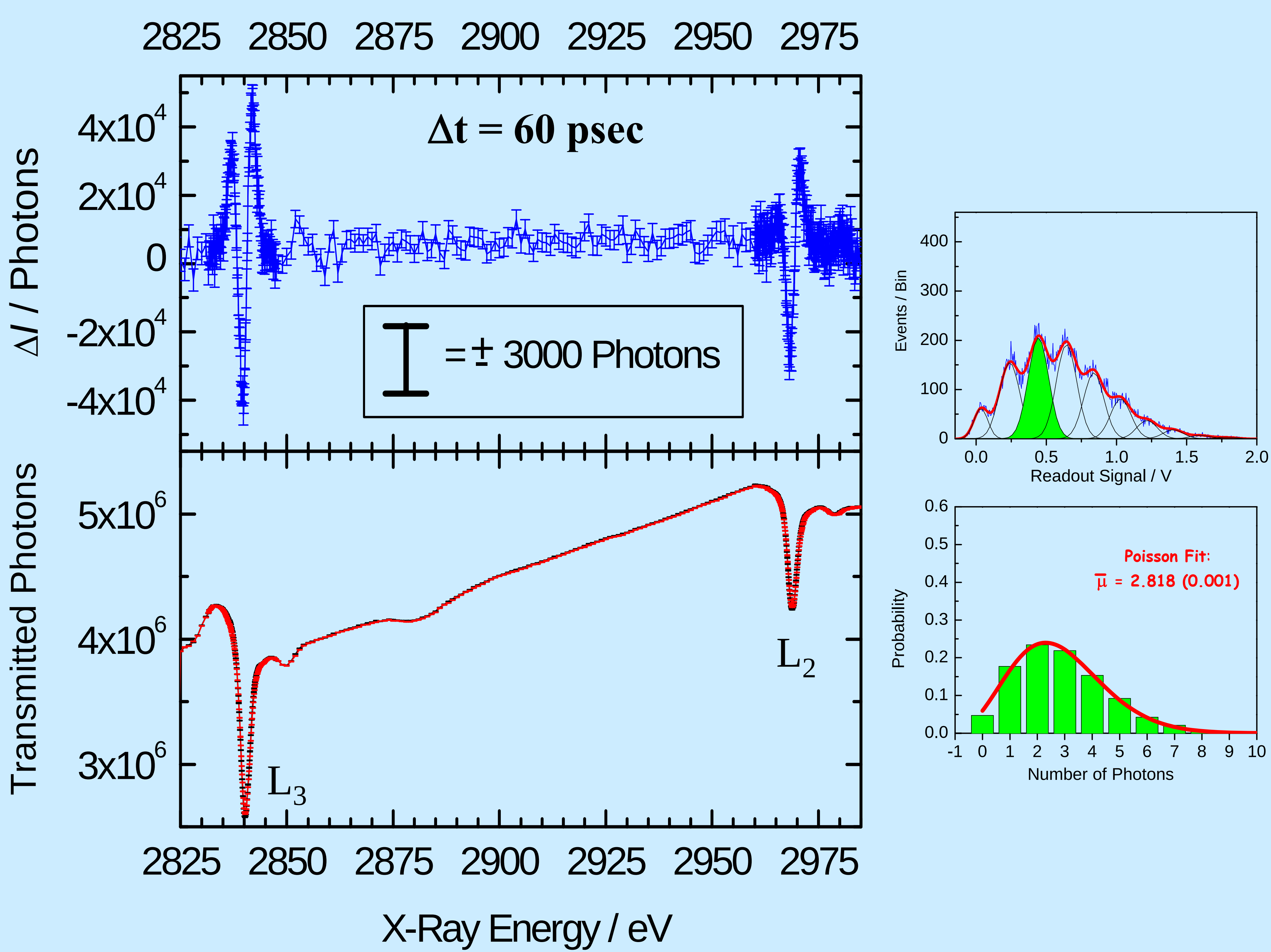
Bend Magnet Beamline 5.3.1 Advanced Light Source, Berkeley



Data Acquisition Strategy



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



2825 2850 2875 2900 2925 2950 2975
Δt = 60 psec
ΔI / Photons
4x10^4
2x10^4
0
-2x10^4
-4x10^4
= ± 3000 Photons
Transmitted Photons
5x10^6
4x10^6
3x10^6
L3
L2
X-Ray Energy / eV
Events / Bin
400
300
200
100
0
0.0 0.5 1.0 1.5 2.0
Readout Signal / V
Probability
0.6 0.5 0.4 0.3 0.2 0.1 0.0
Poisson Fit:
μ = 2.818 (0.001)
-1 0 1 2 3 4 5 6 7 8 9 10
Number of Photons