Electronic and Molecular Structure Changes of Excited Polypyridyl Complexes from Picosecond X-Ray Absorption Spectroscopy

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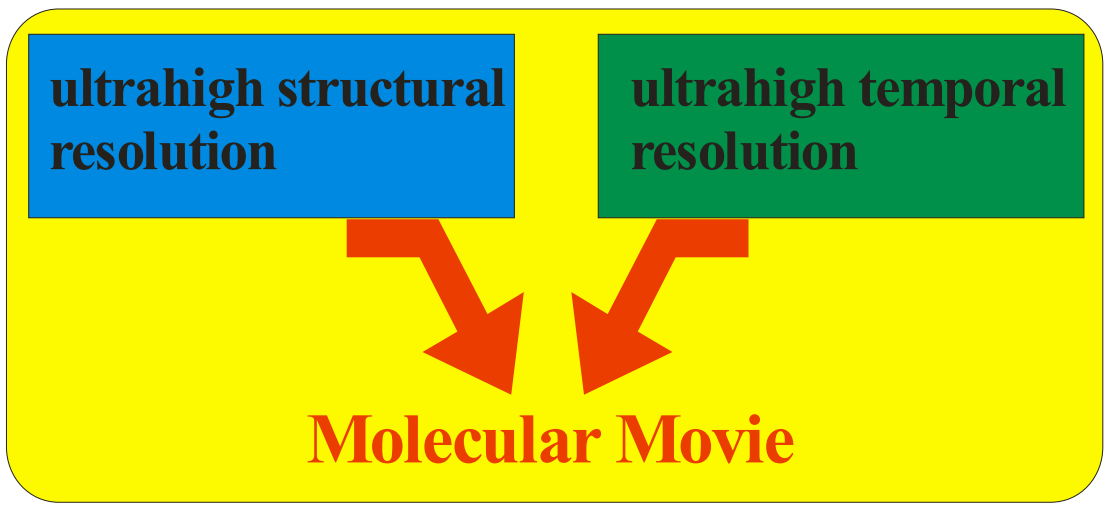
Electron transfer reactions

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

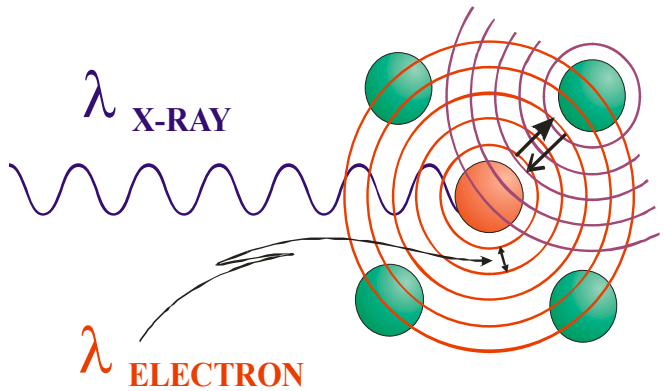
GOAL:

→ Create a molecular movie of the chemical reaction including the transition state(s) (need structural tools)

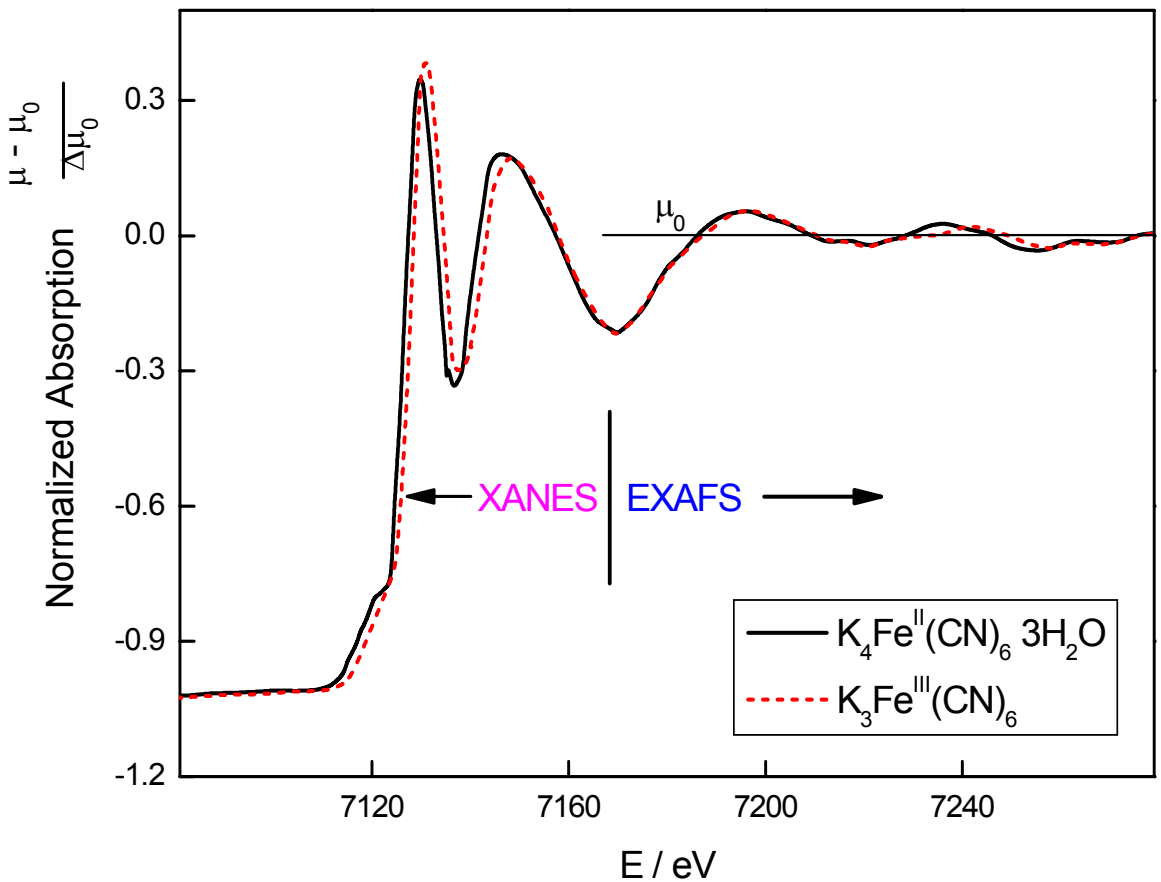


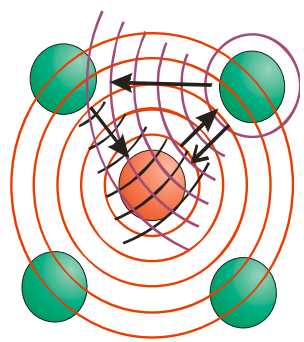
XAFS: X-Ray Absorption Fine Structure

- **Element Specific**
  Symmetry Specific
  Electronic Structure
  Geometric Structure



Single Scattering

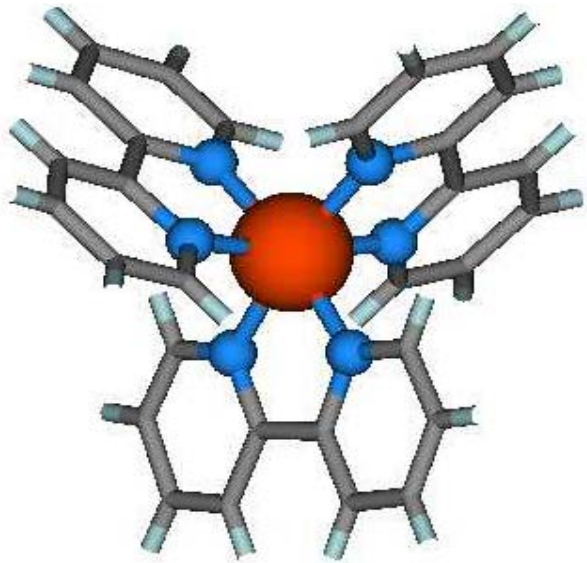


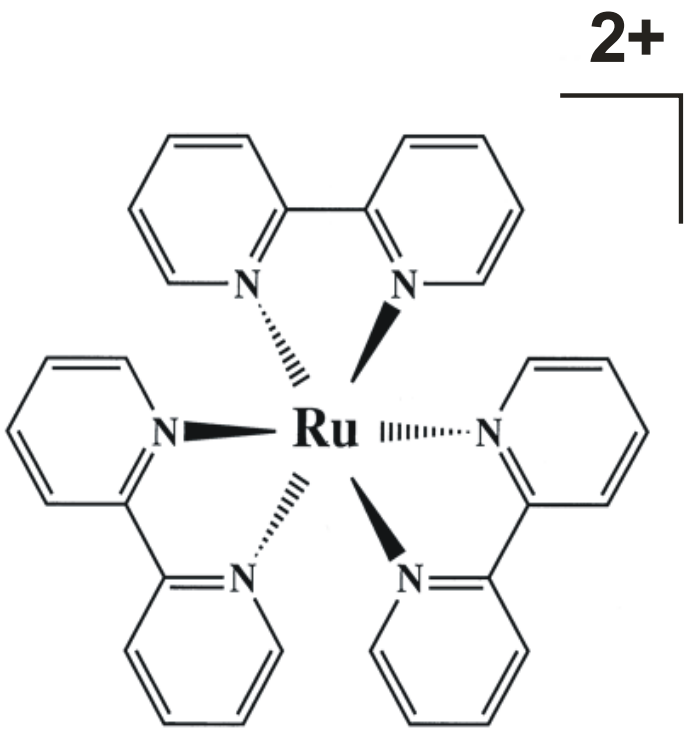


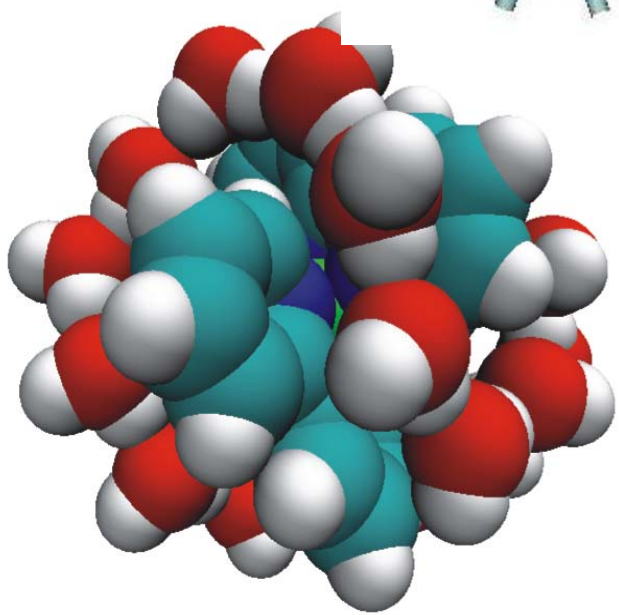
Multiple Scattering

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

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



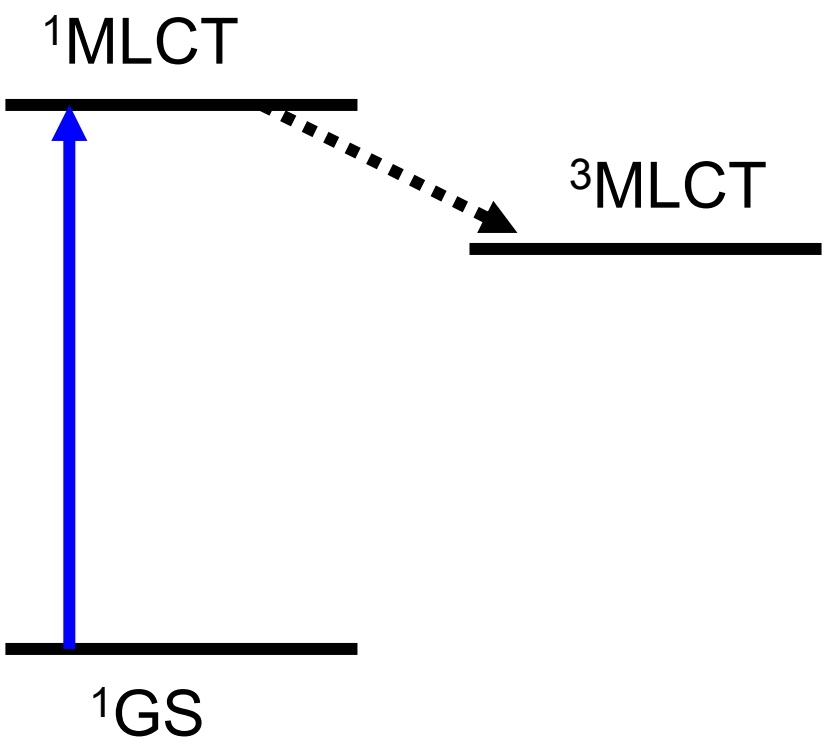


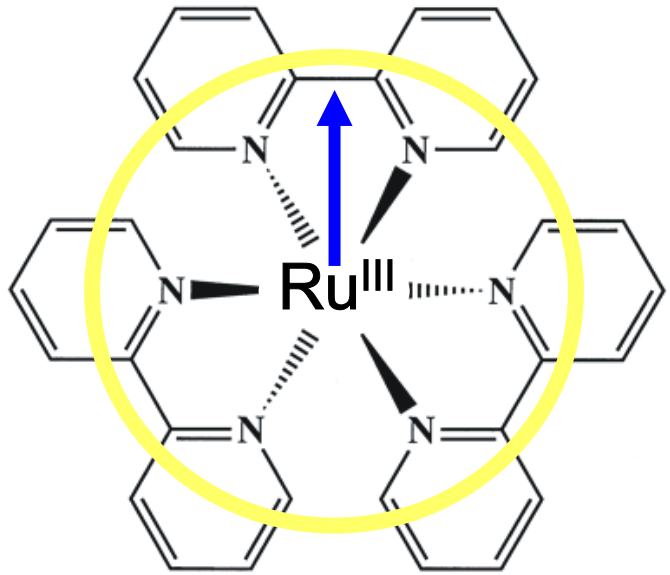


Photochemical Cycle of $[Ru^{II}(bpy)_3]^{2+}$

ISC Time

ca. 40 fs (Bhasikuttan *et al.*, 2002)





D_3

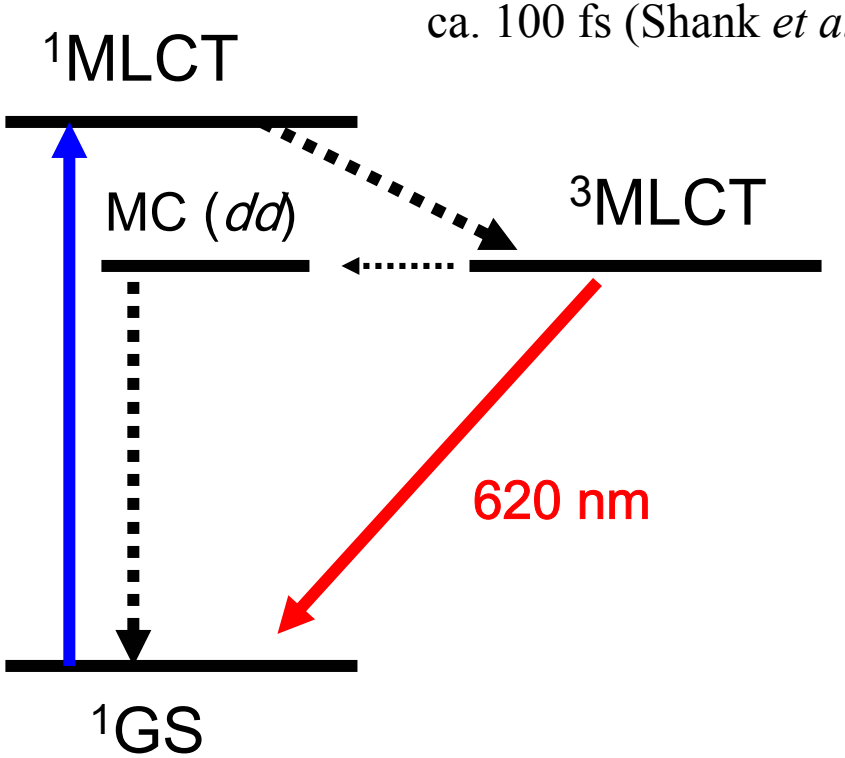
Photochemical Cycle of $[Ru^{II}(bpy)_3]^{2+}$

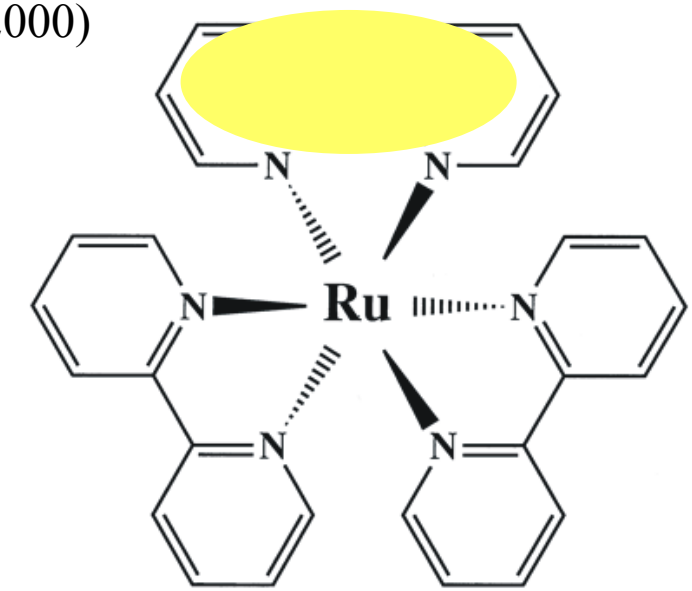
ISC Time

ca. 40 fs (Bhasikuttan *et al.*, 2002)

e^- Localization Time(s):

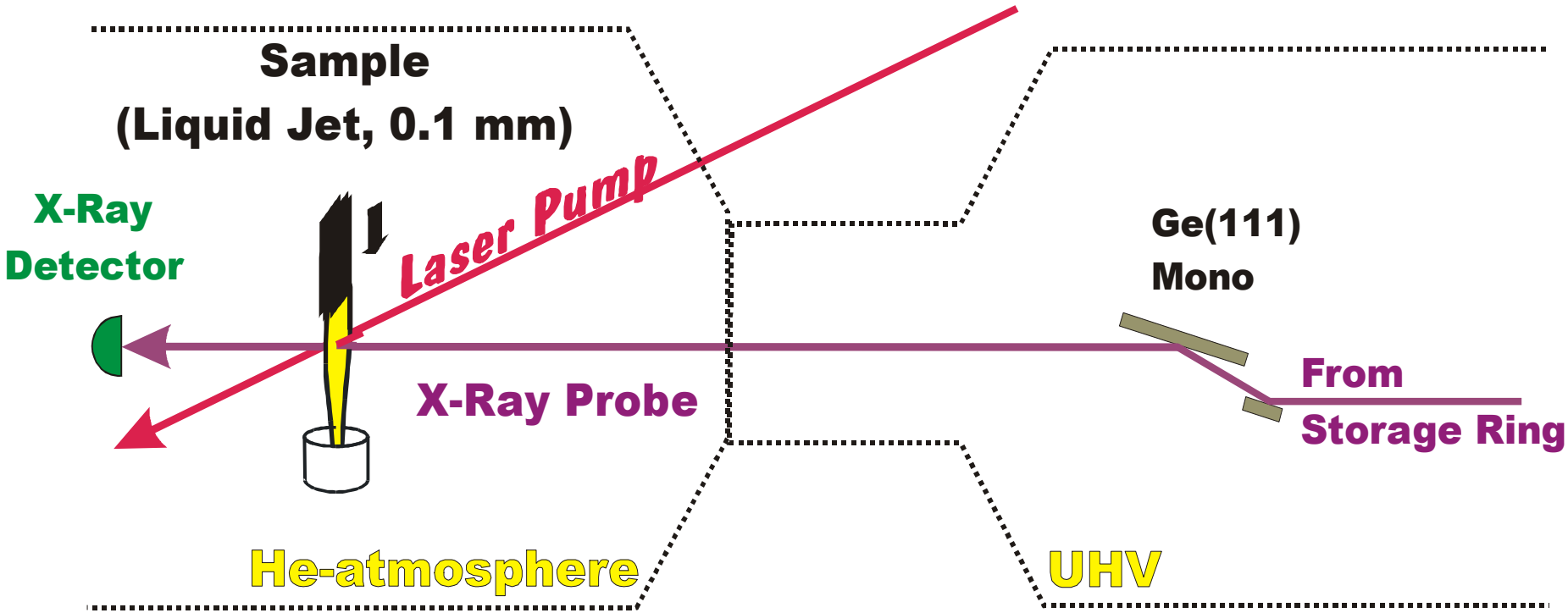
ca. 100 fs (Shank *et al.*, 2000)





C_2

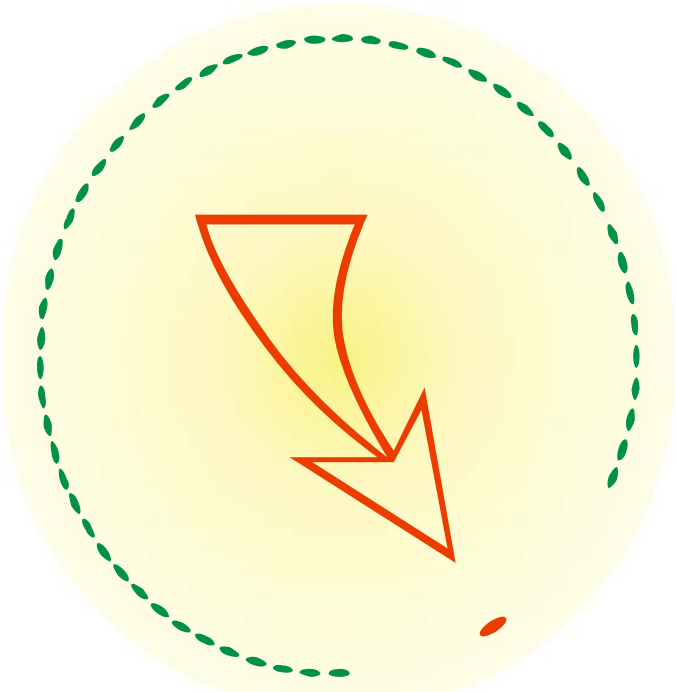
EXPERIMENTAL SETUP AT BEAMLINE 5.3.1 (ADVANCED LIGHT SOURCE)

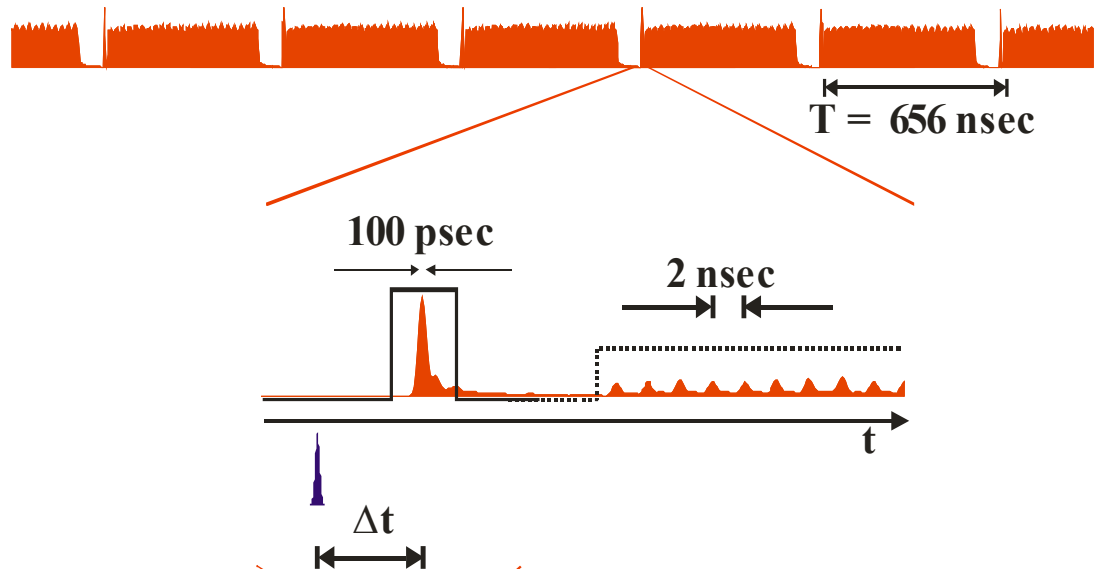


→ work in *disordered/dilute* systems

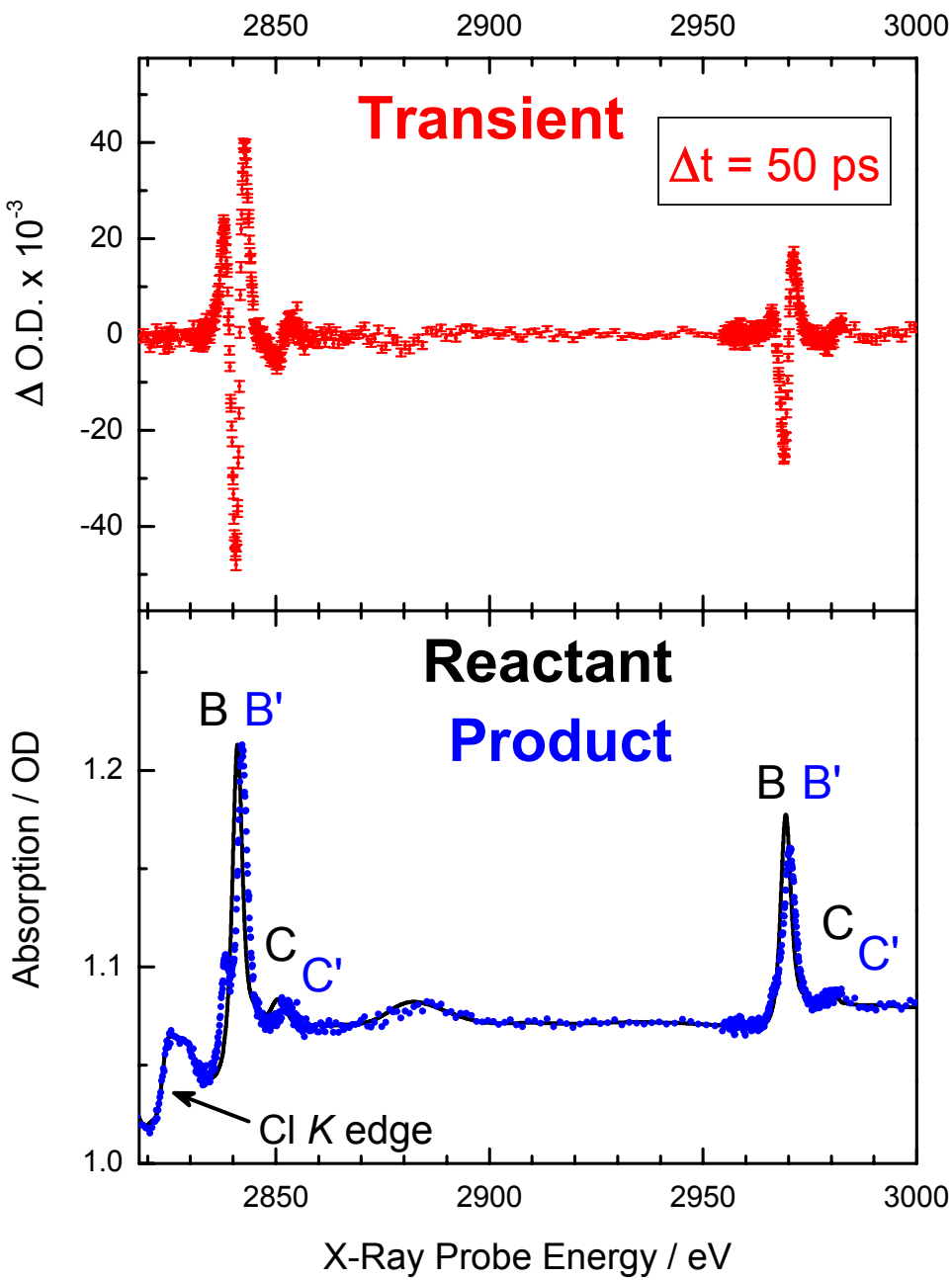
→ sample refreshed every shot → non-reversible systems

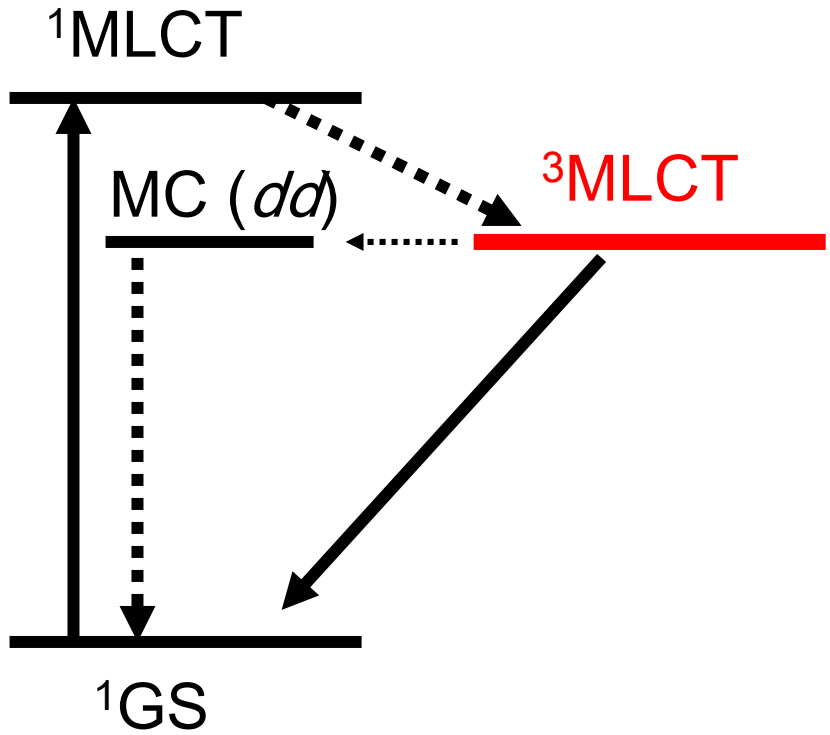
Data Acquisition Strategy





- synchronize two independent sources
- maintain control of chosen time delay

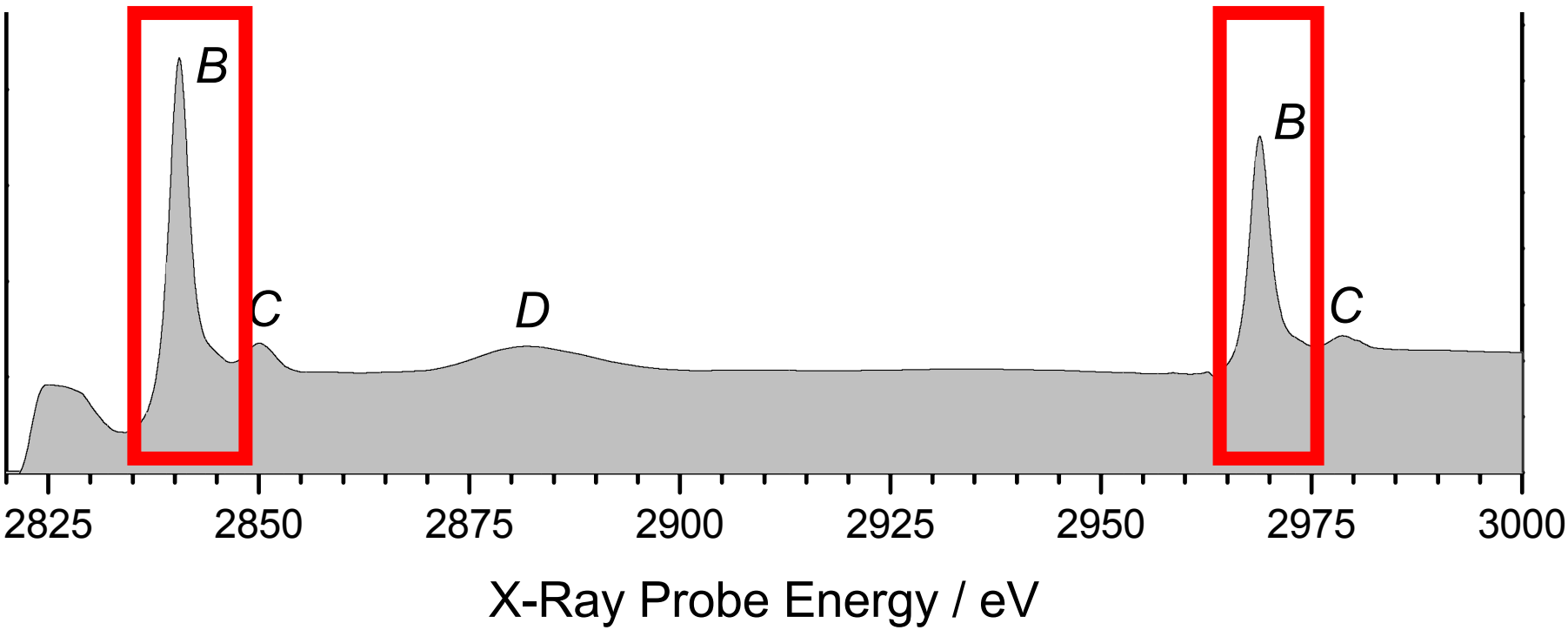

Transient
Δt = 50 ps
Δ O.D. x 10^-3
Reactant
Product
B B'
C C'
B B'
C C'
Cl K edge
Absorption / OD
X-Ray Probe Energy / eV


1MLCT
MC (dd)
3MLCT
1GS

Information about the Electronic Structure
XANES - Region

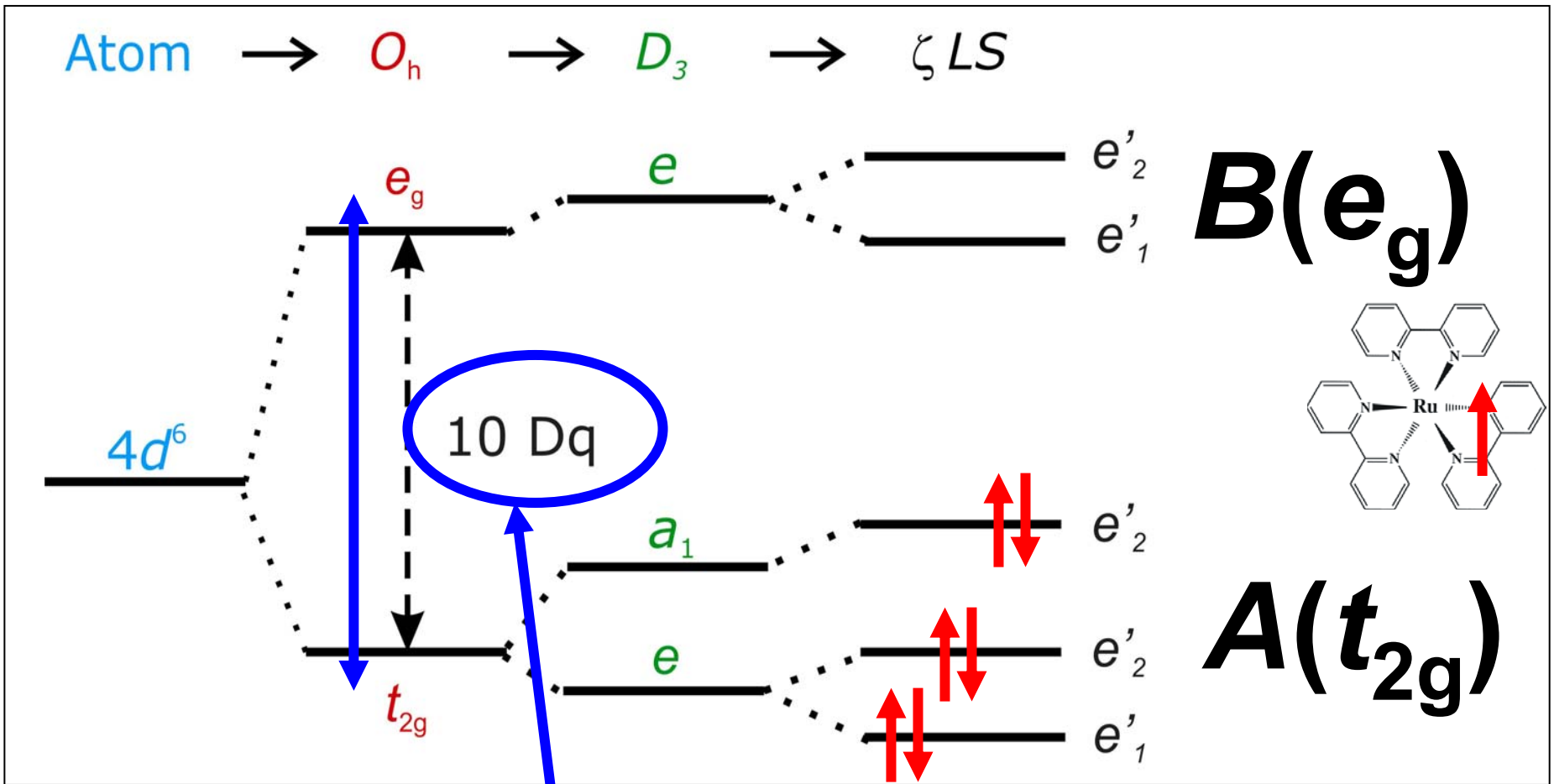
L_3-edge ($2p_{3/2}$ → ..)

L_2-edge ($2p_{1/2}$ → ..)



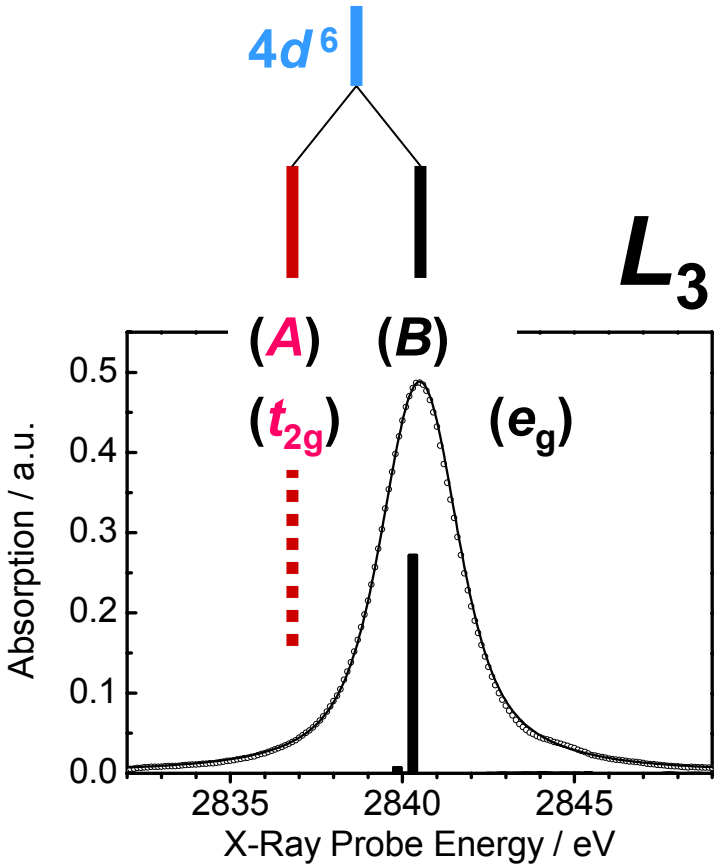
Static Electronic Structure (DOS, Symmetry)

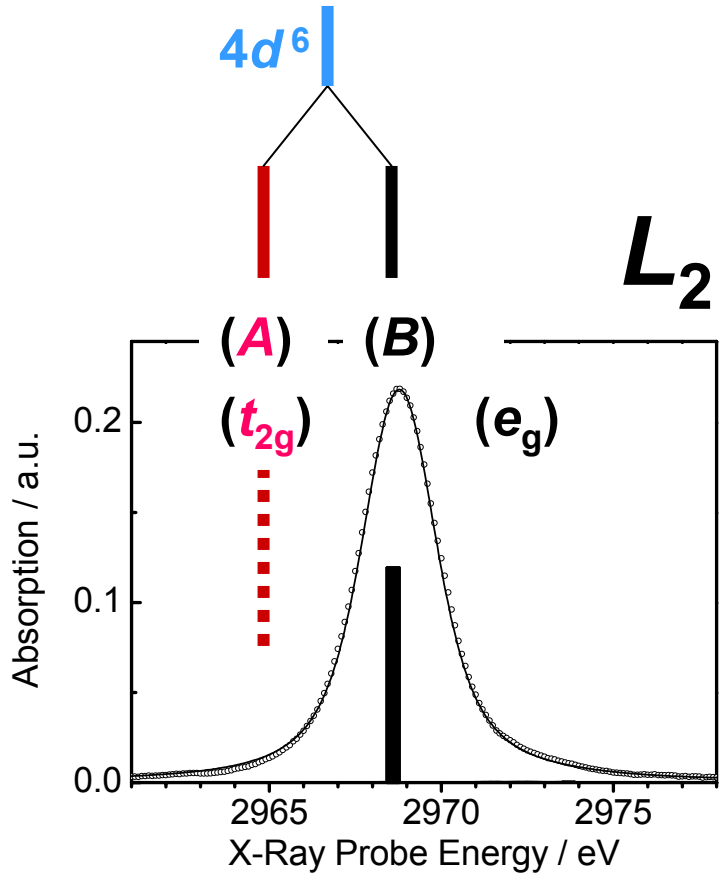
$$H_{total} = H_{atom} + H_{Oh} + H_{D3} + H_{\zeta LS}$$

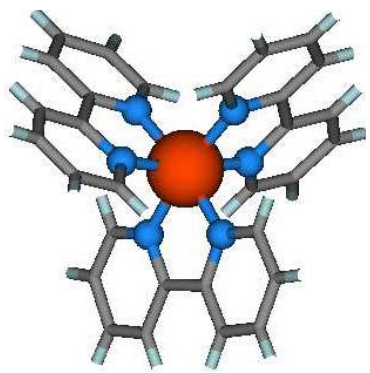


depends on Ru-N distance !!

Static Electronic Structure (DOS, Symmetry)

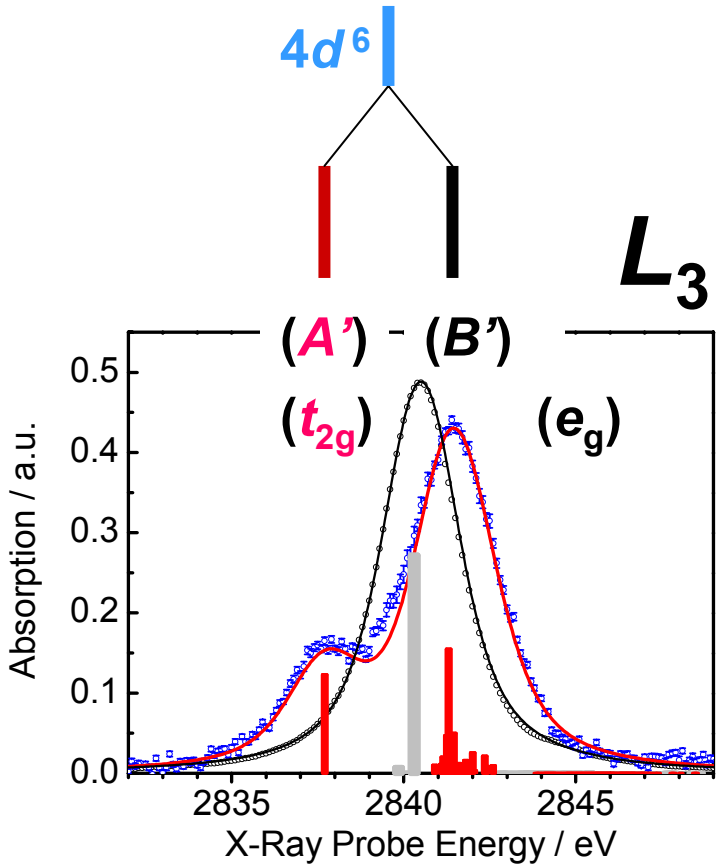


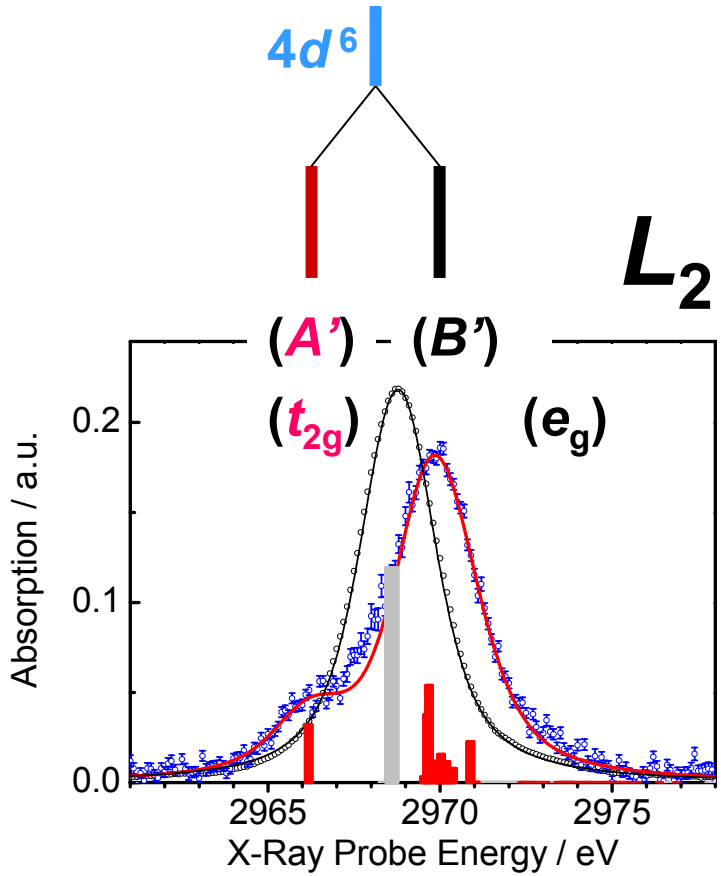


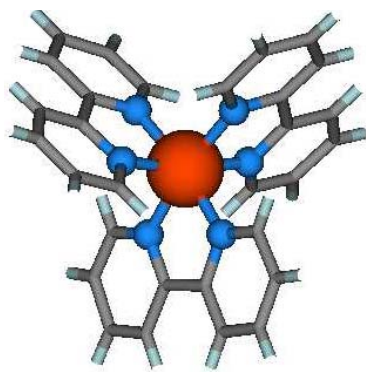


W. Gawelda *et al.*, submitted (2005)

Transient Electronic Structure (DOS, Symmetry)





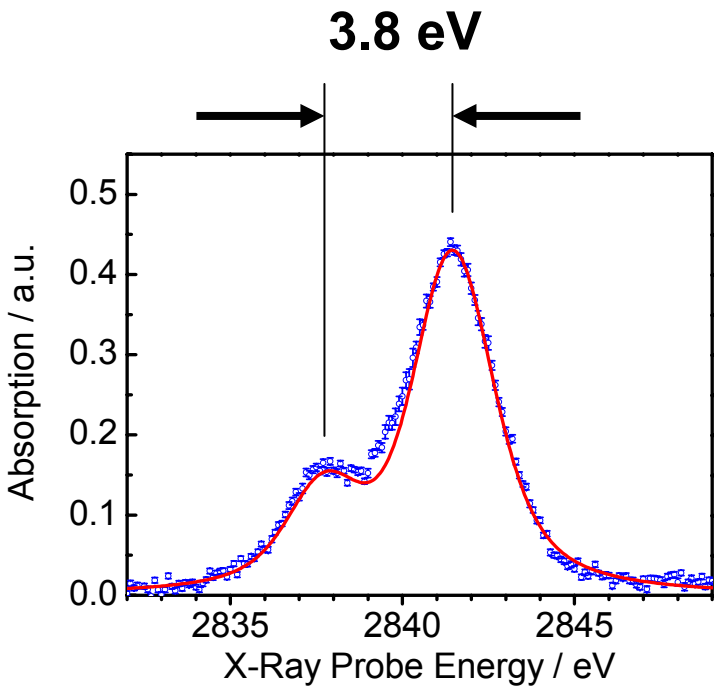


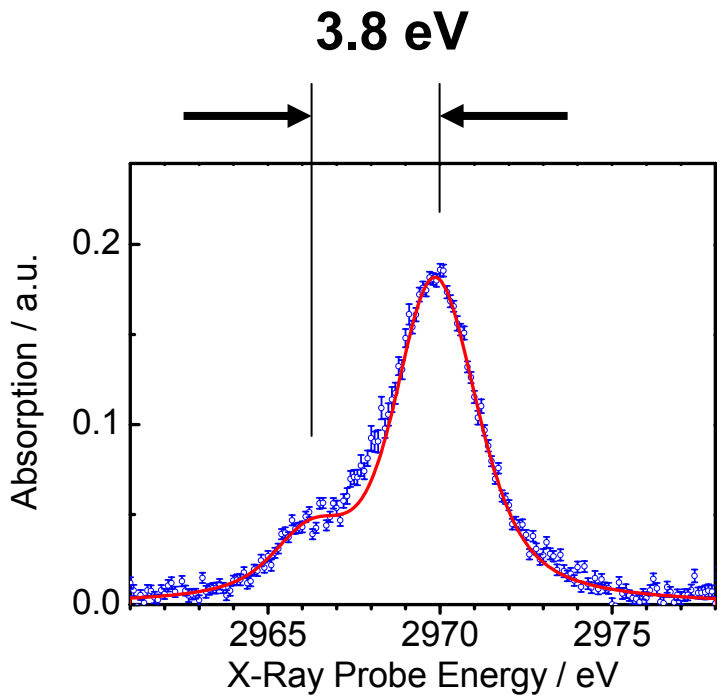
W. Gawelda *et al.*, submitted (2005)

Information about the Transient *Structure*

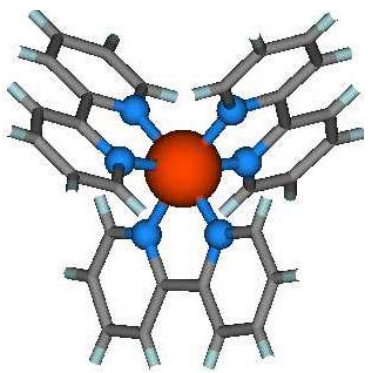
ΔE (10Dq) (ground - excited) = -0.15 eV

→ ΔR = -0.02 Å





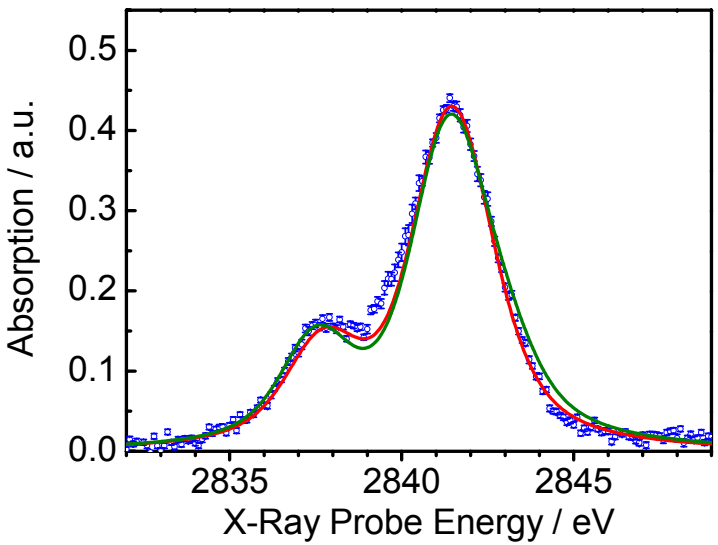
D_3 (C_2):
$Ru(bpy)_3$

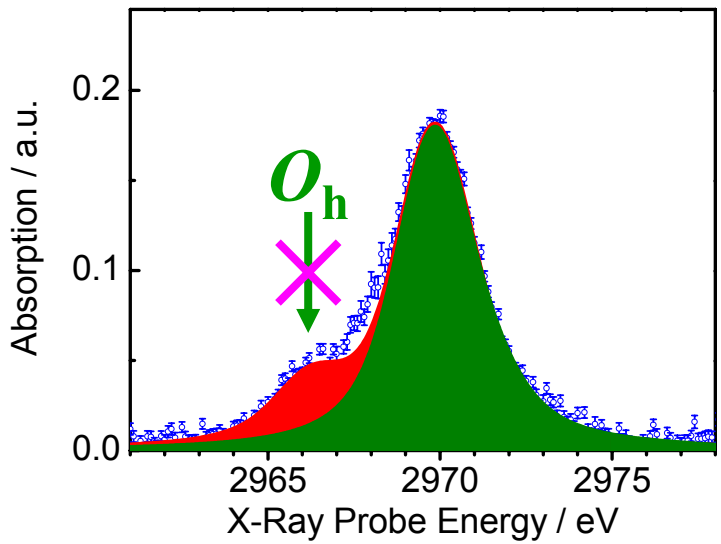


…more on local *symmetry* (O_h)…

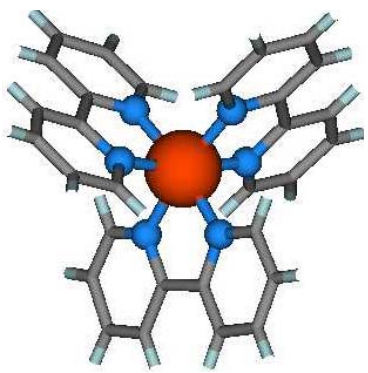
Information about the Transient *Symmetry*

D_3 : N – Ru - N angle: 79°

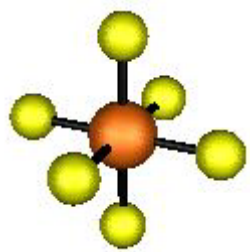




D_3 :
$Ru(bpy)_3$



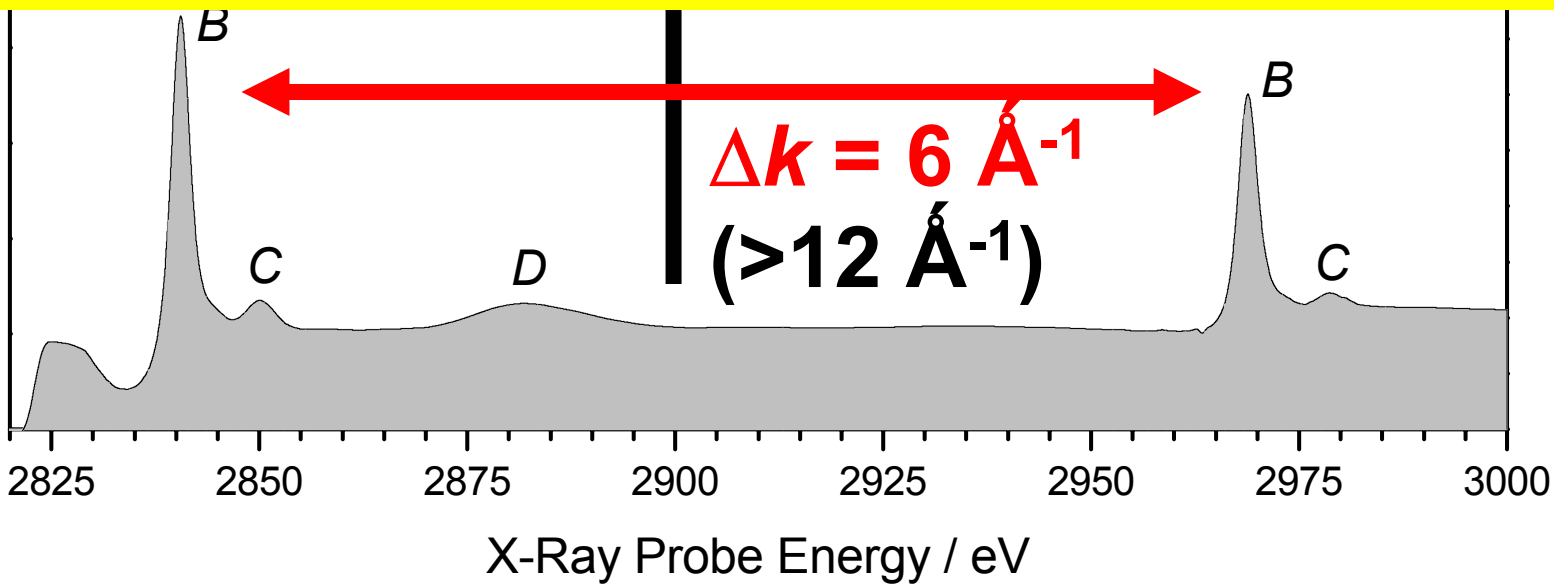
O_h :
$Ru(NH_3)_6$



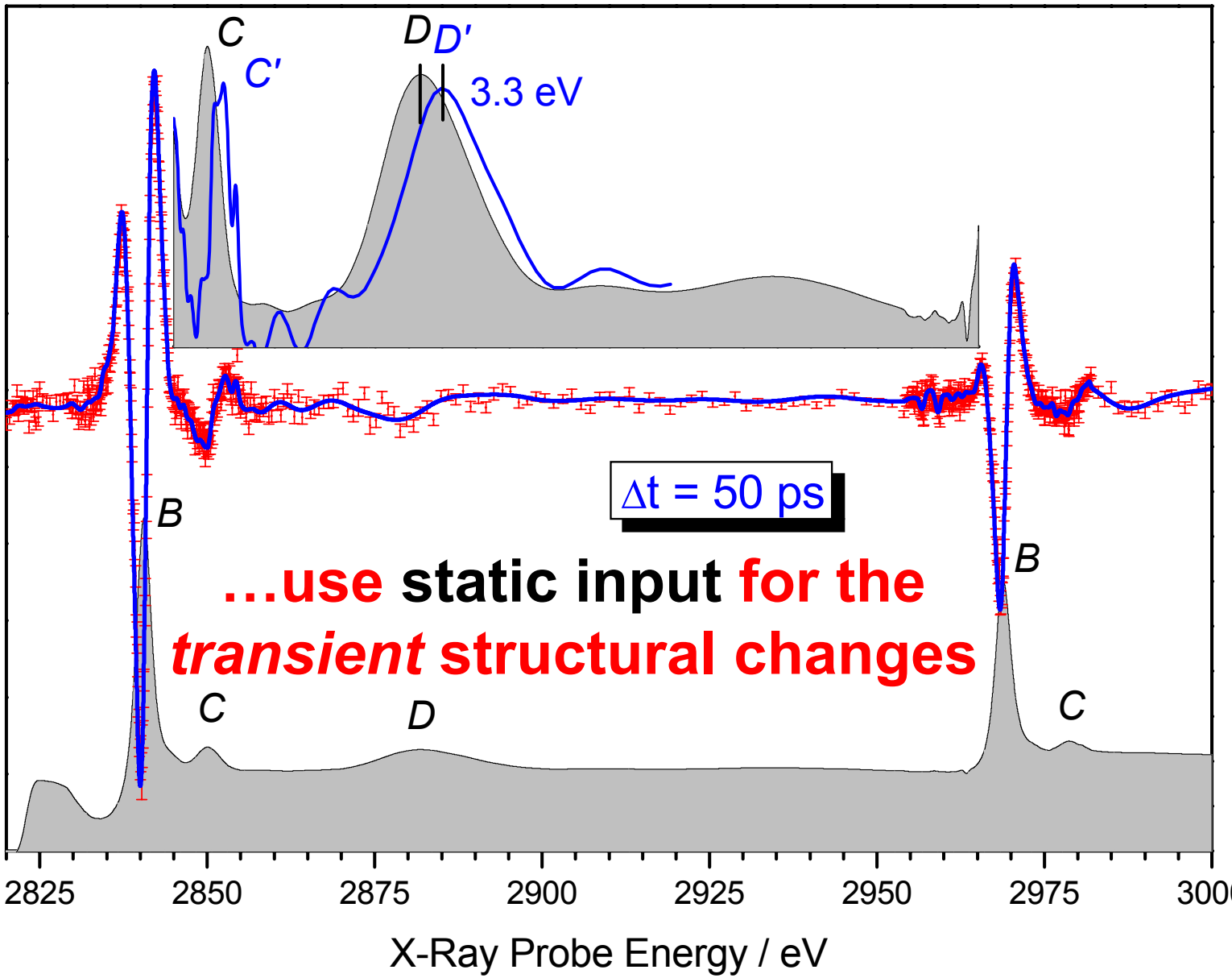
Static Structure from EXAFS

…better rely on x-ray diffraction data…

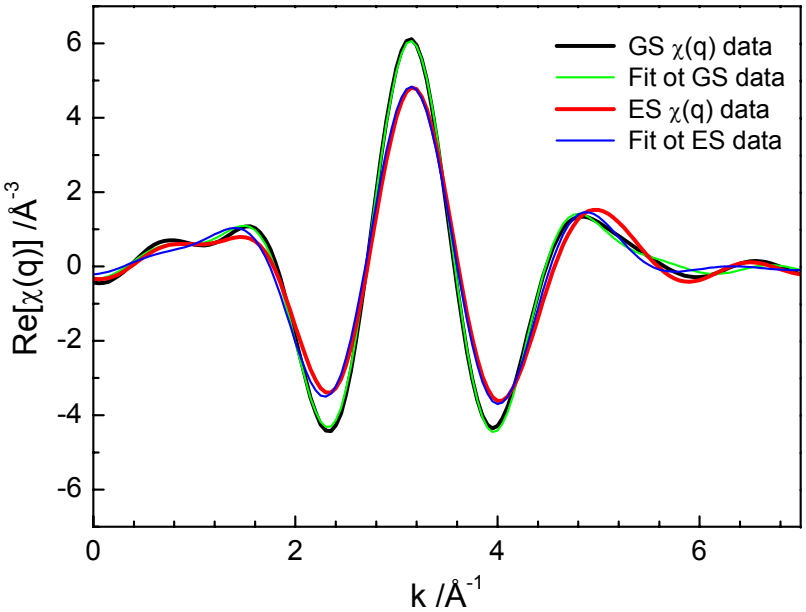
(for static spectra)

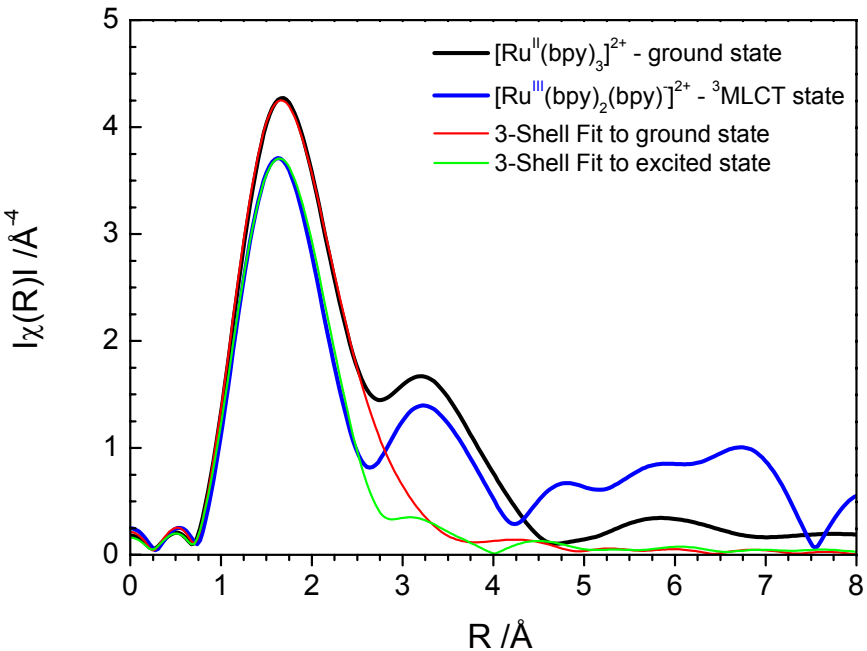


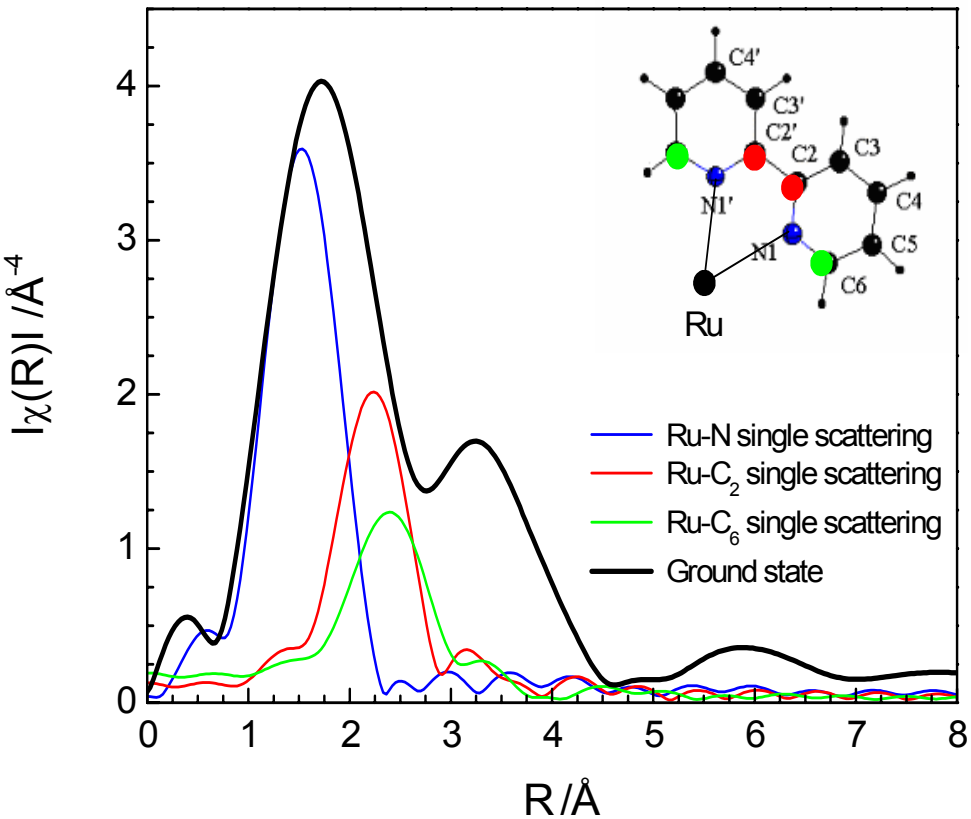
Transient Structure from EXAFS



Transient Structure from EXAFS (Δt = 50 ps)





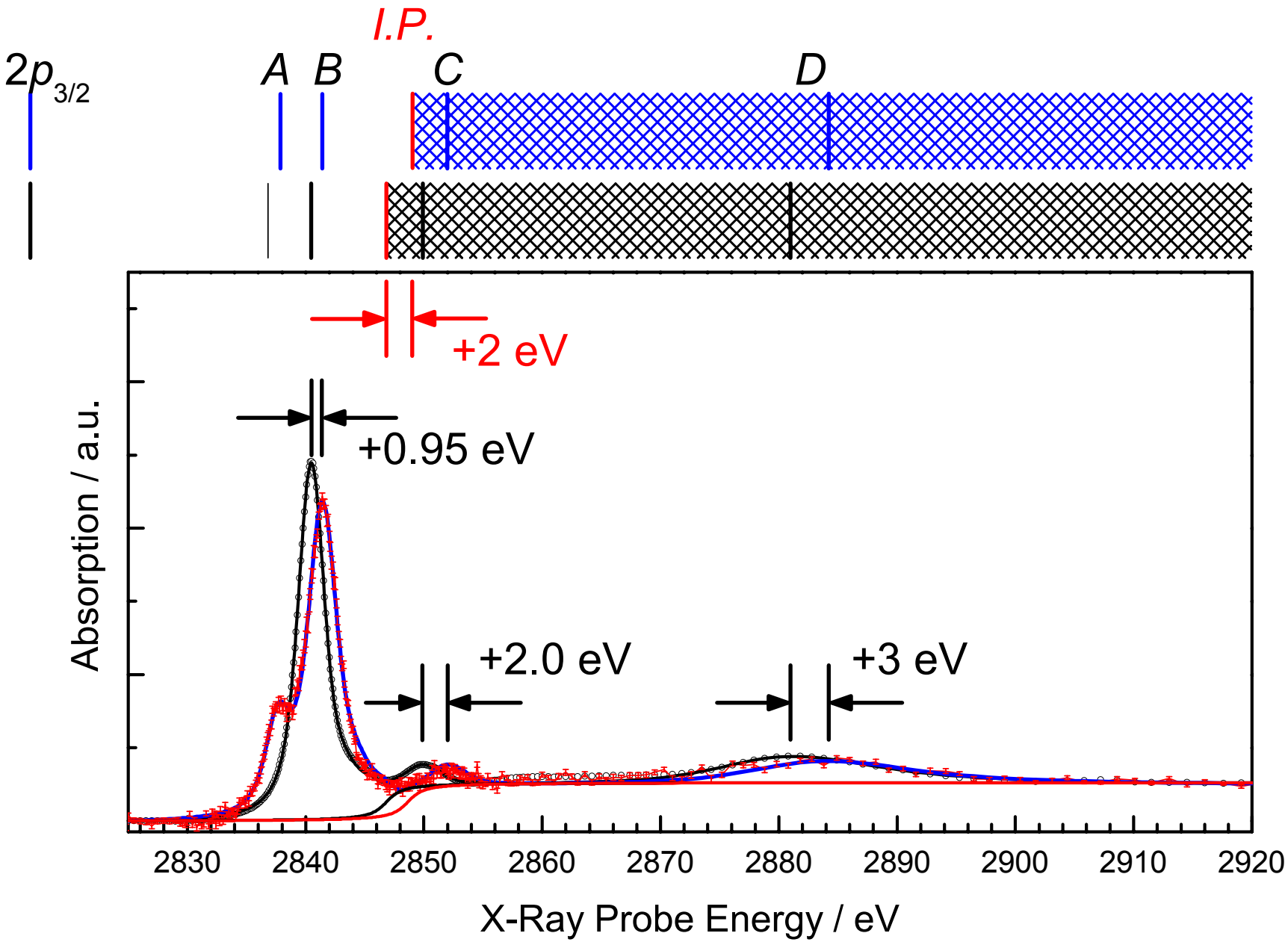


ΔR (Ru-N) = - 0.037 (0.02) Å

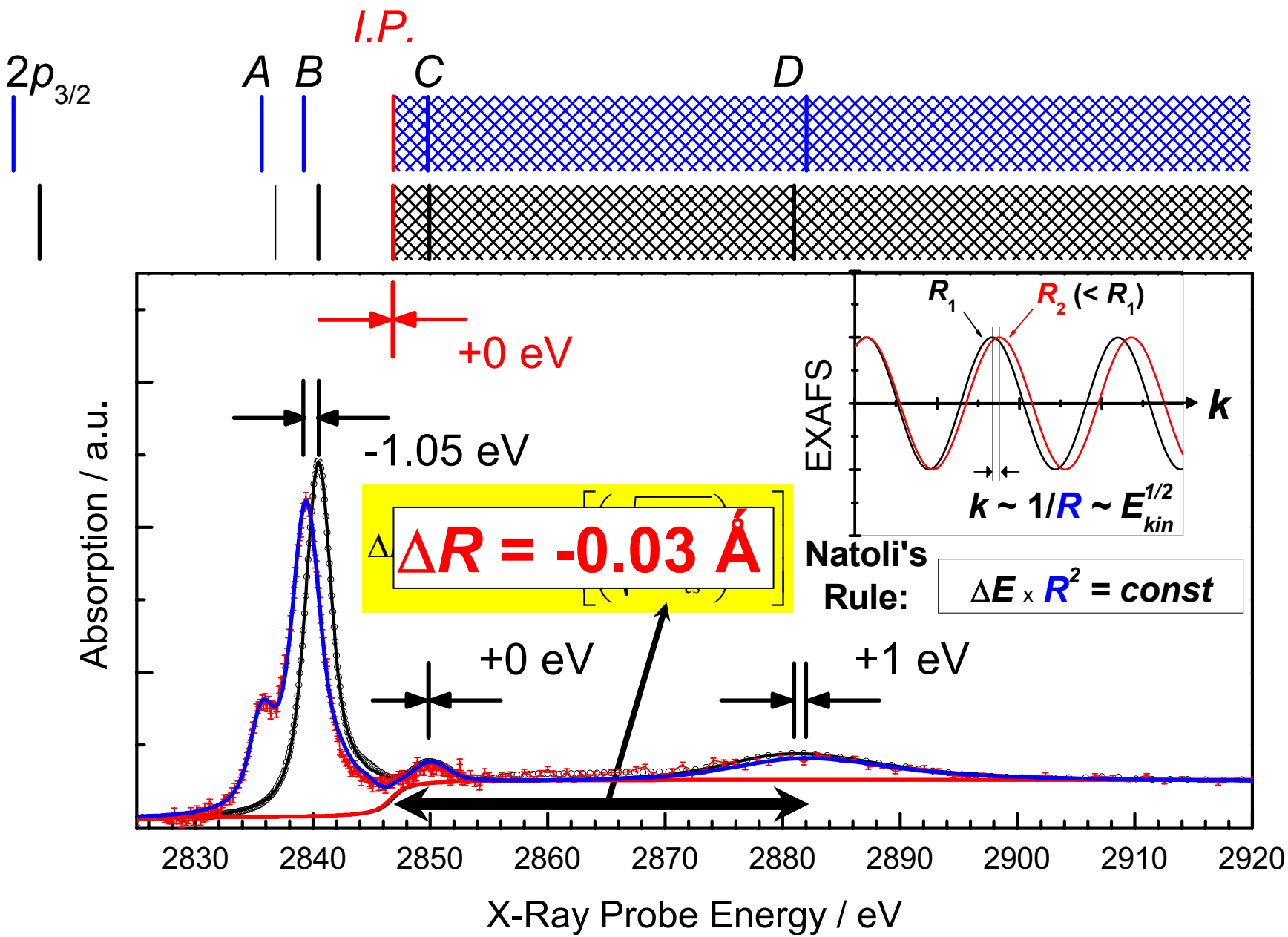
σ^2_{gr} (Ru-N) = 0.009 Å^2

σ^2_{ex} (Ru-N) = 0.01 Å^2

Structural Information via Time-Resolved XAFS



Structural Information via Time-Resolved XAFS



Summary

•*Electronic* and *Atomic* Structure of Reaction Intermediates ($\Delta t = 50$ ps)

- Precise chemical data via transient measurements

  ΔE (B-B') = 0.95 eV

  ΔE (IP_{val}) = 1.0 eV

  ΔE (IP_{2p}) = 2.0 eV

  → important input into EXAFS analysis

  ΔR (*D-D'*) = -0.03 Å

- XANES Comparison with Multiplet Calculations (DOS)

  $Ru(bpy)_3$ dominantly D_3 symmetry **ΔR (10Dq) = -0.02 Å**

- EXAFS analysis reveals nearest neighbor structural changes

  ΔR (FEFF) = -0.037 (0.02) Å

  (Δk (EXAFS) = 6 $Å^{-1}$)

Summary

- **Picosecond XAFS in the Condensed Phase !**

XANES useful for

- ***symmetry*** **(*O_h*, *D_3*, …)**
- ***structure*** **(Ligand-field)**
- ***charge transfer*** **(+1e, even fractions)**

EXAFS useful for

- ***structure***

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

Members and Collaborators:

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SWISS LIGHT SOURCE SLS

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INFN Frascati
- Maurizio Benfatto

CHF: Swiss NSF, SWISS LIGHT SOURCE SLS