New Developments in Hard X-Ray Spectroscopy

Pieter Glatzel

Four Techniques Using Hard X-Rays

1. K Fluorescence Emission, K Capture
2. Site-Selective EXAFS in Mixed-Valent Compounds
3. Non-Resonant Inelastic X-Ray (Raman) Scattering
4. Resonant Inelastic X-Ray Scattering

Inner-Shell Spectroscopies

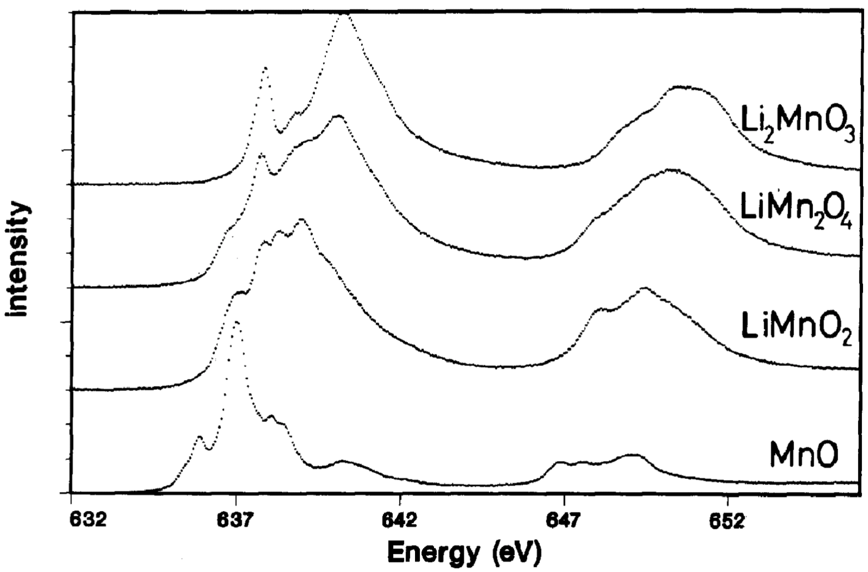
1) Soft x-rays (0.2 - 2.0 keV):

Transition Metal L-edges

→ dipole allowed 2p to 3d transition

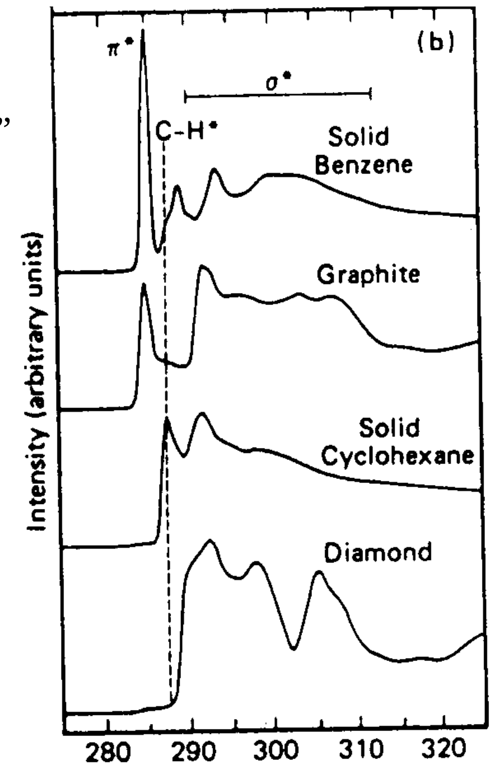
O and C K-edges

→ dipole allowed 1s to 2p transition



Frank De Groot, J. Elec. Spec. Rel. Phen., 519 (1994)

Joachim Stöhr, "NEXAFS Spectroscopy"



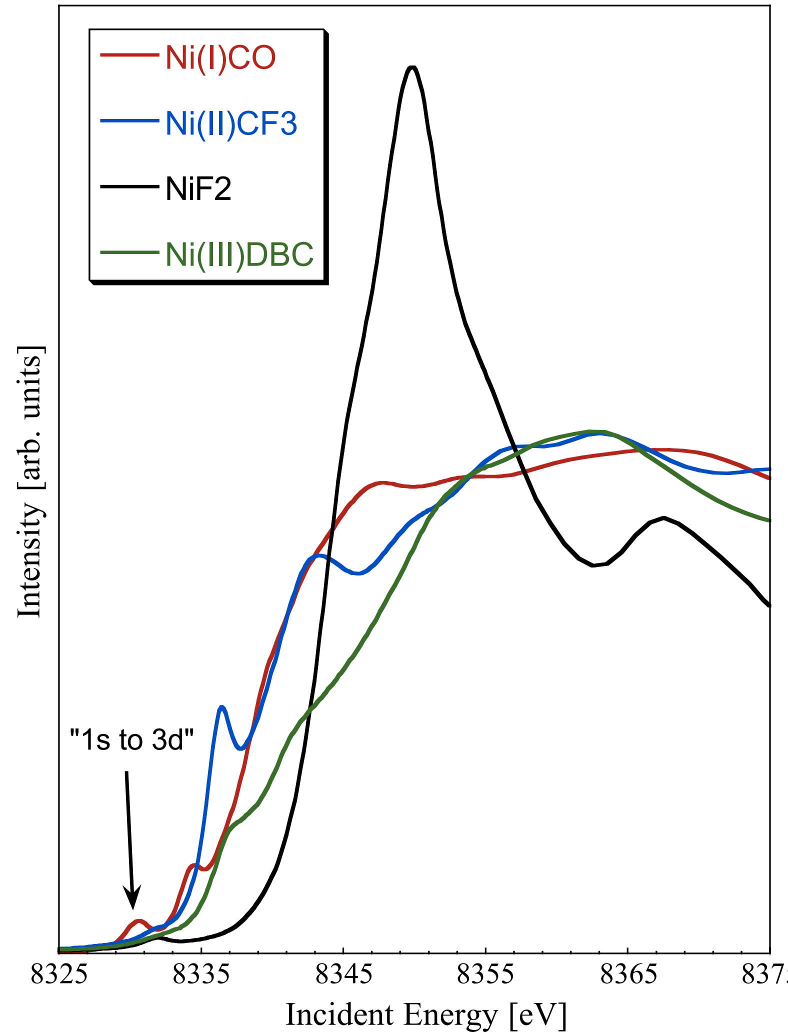
Experimental Difficulties

2) Hard x-rays (5.0 - 11.0 keV):

Transition Metal K-edges:

→ 1s to 3d transition dipole forbidden

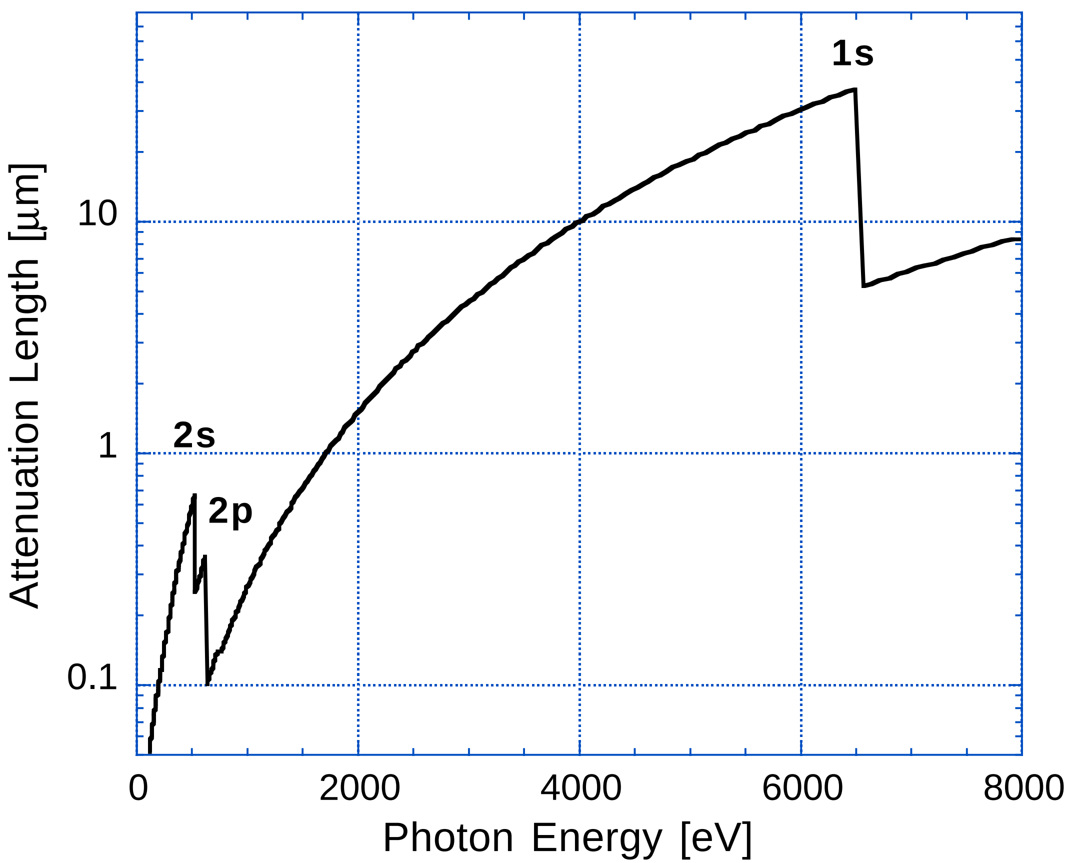
Information on local electronic structure less accessible



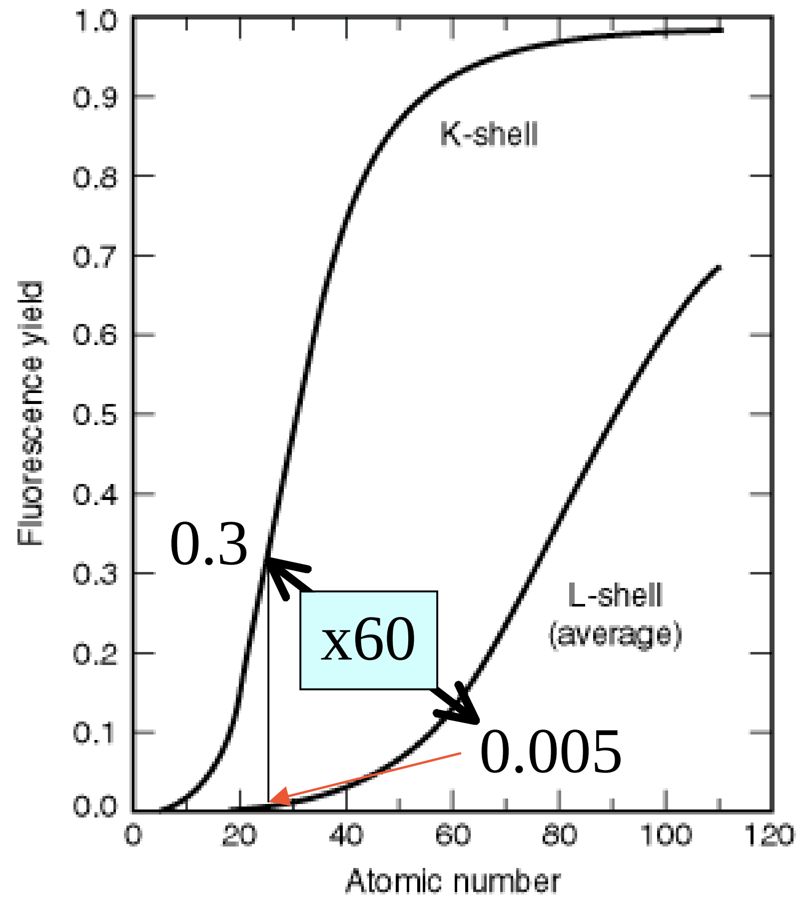
But: Considerable improvements in x-ray sources and analyzers !

Why Hard X-Rays?

X-Ray Attenuation in MnO



Fluorescence Yield



→ Sample integrity, experimental setup

Wilhelm Conrad Röntgen

1901 Nobel Laureate in Physics:

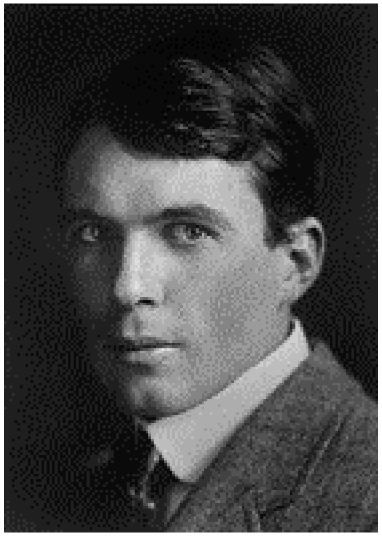
"I didn't think, I investigated."

Silvanus Thompson: “Röntgen left little for others to do beyond elaborating his work."

T. I. Hulk, 2003

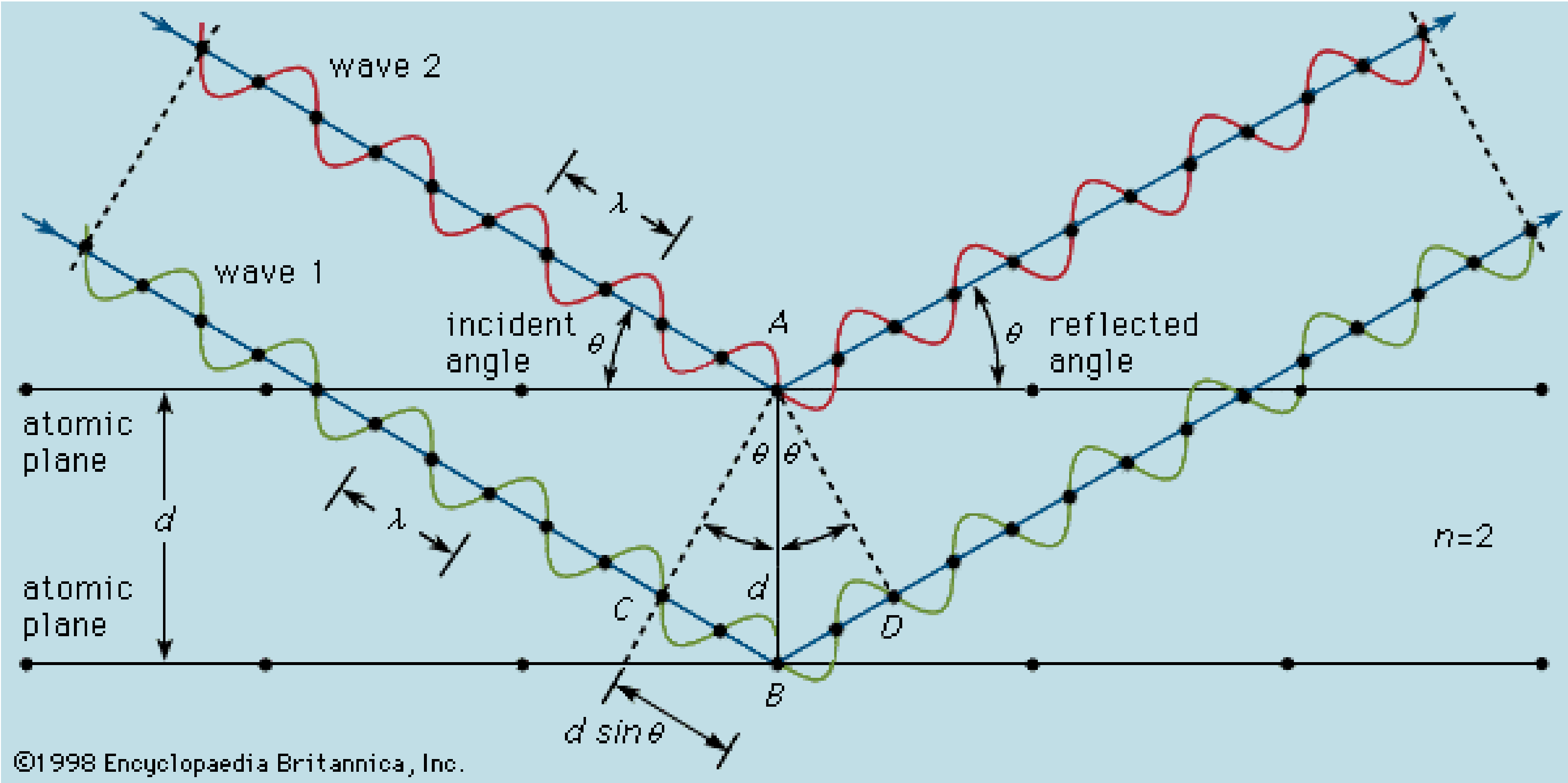
Third generation x-ray sources now enable us to …

Sir William Lawrence Bragg

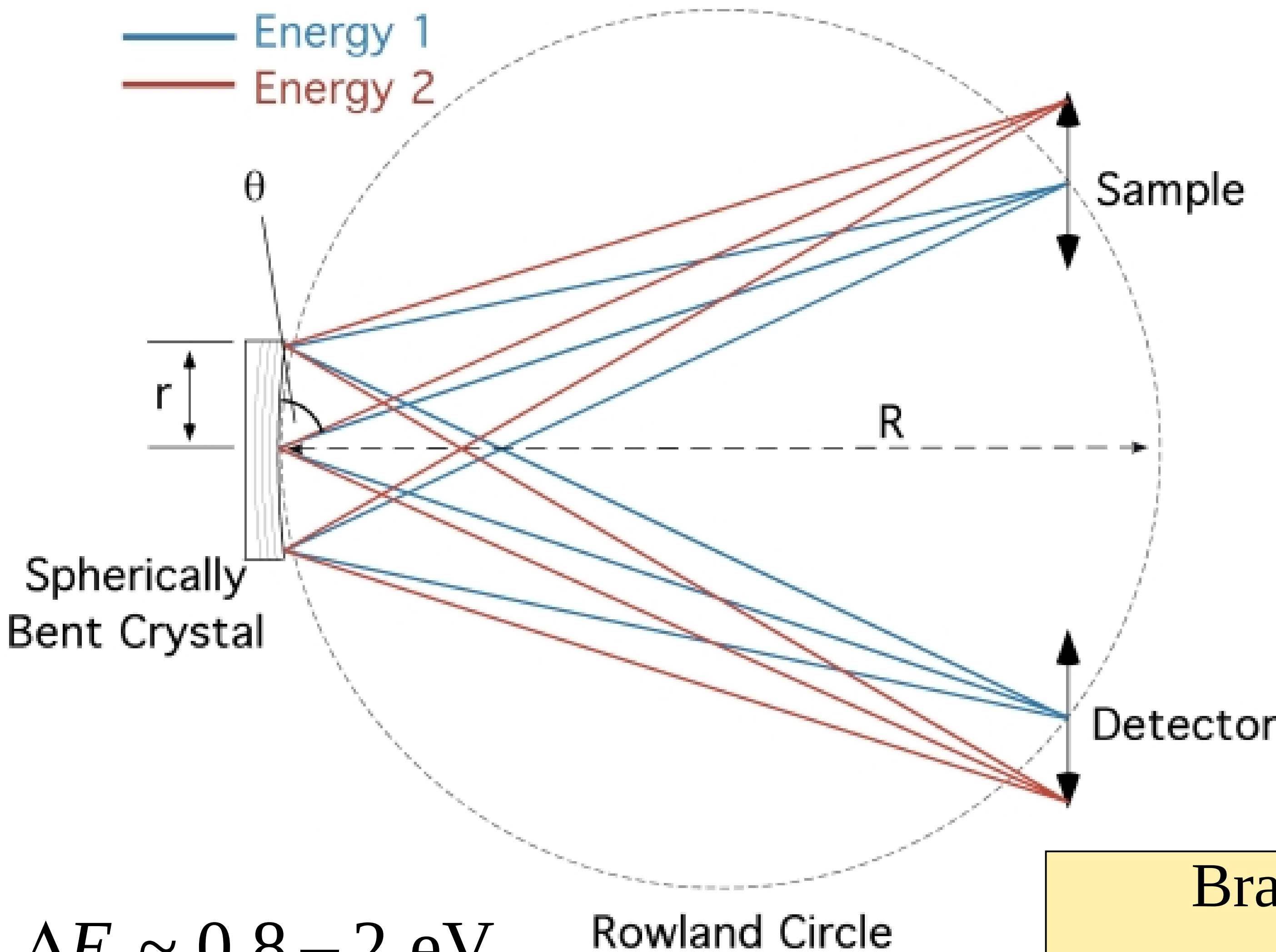


1915 Nobel Laureate in Physics

for their services in the analysis of crystal structure by means of X-rays.



Crystal Analyzer in Johann Geometry



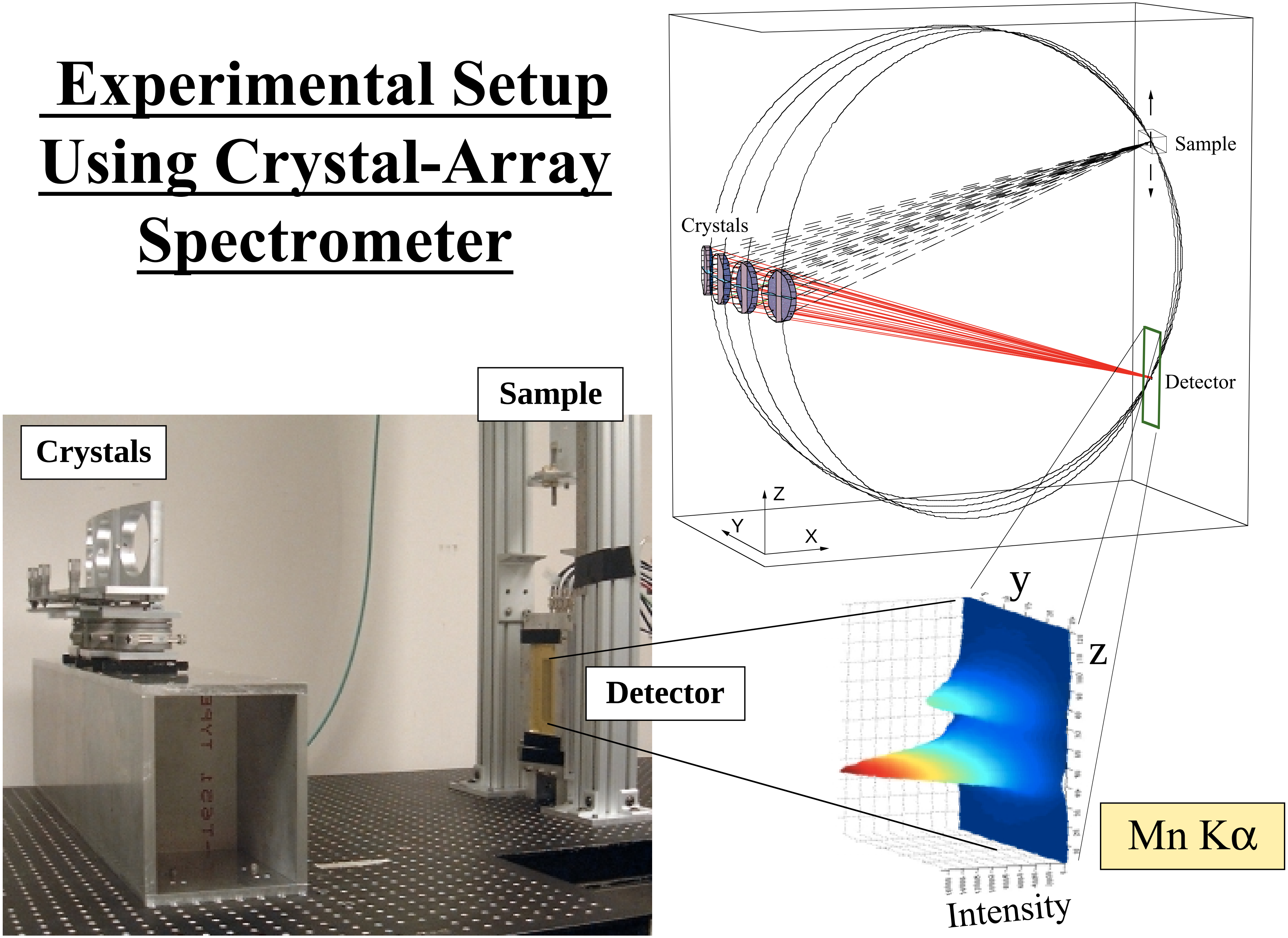
$\Delta E \sim 0.8 - 2 \text{ eV}$

(<10 meV possible)

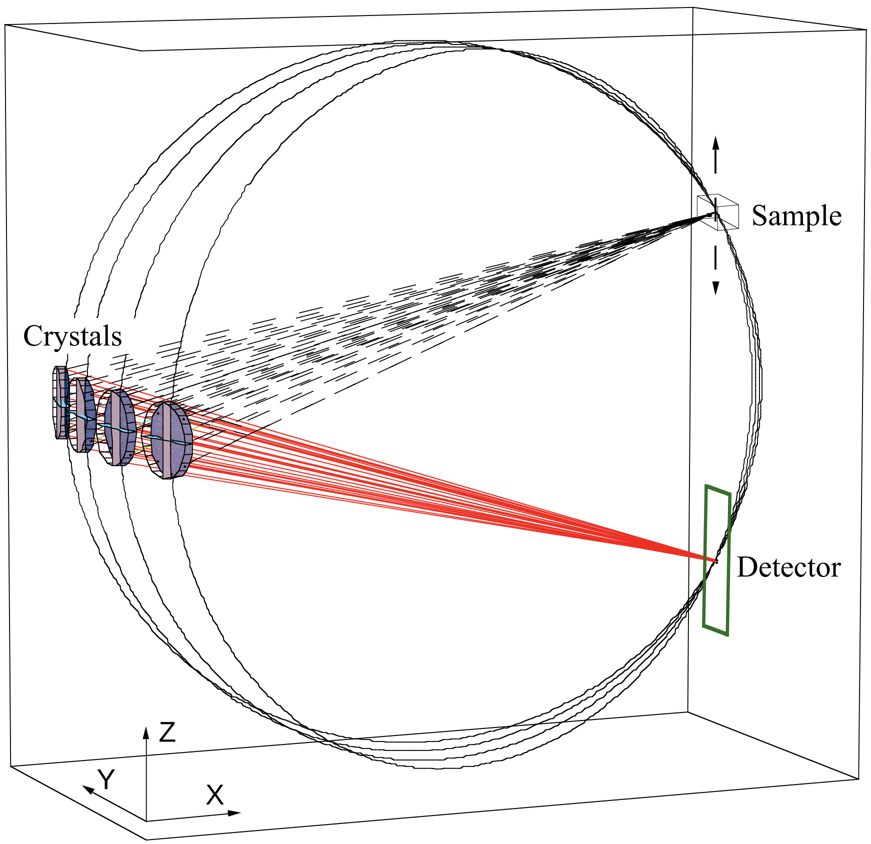
Bragg law :

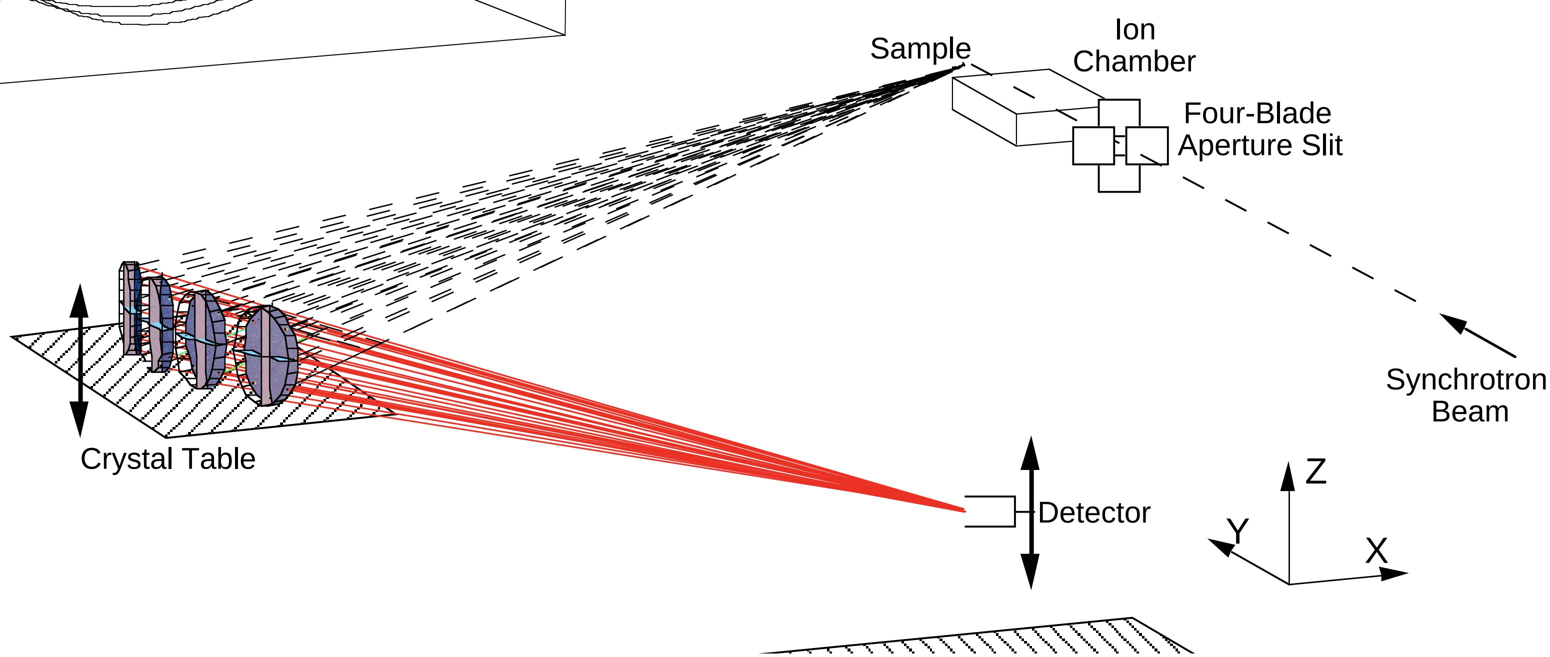
$$\lambda = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta$$

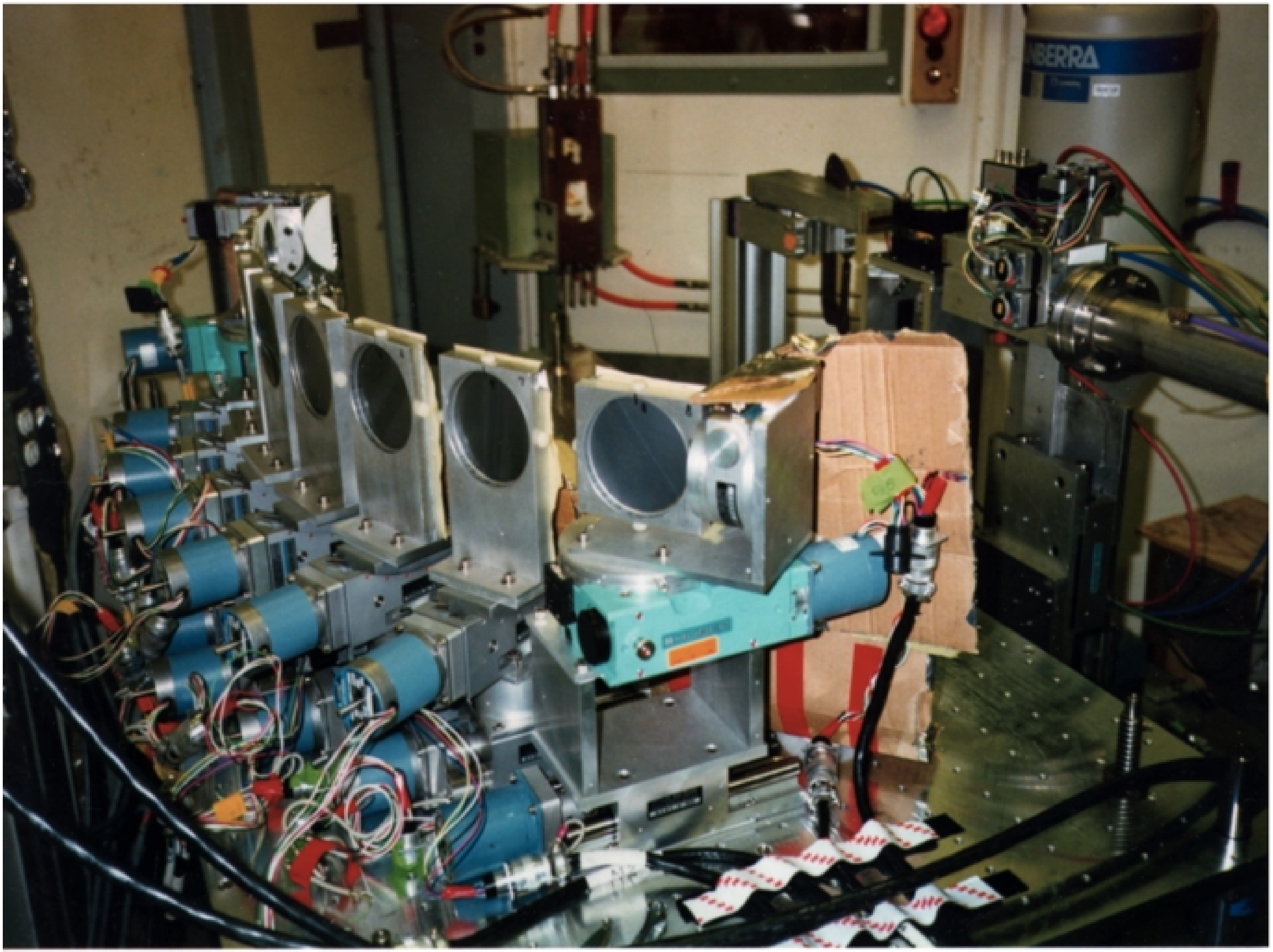
Experimental Setup Using Crystal-Array Spectrometer



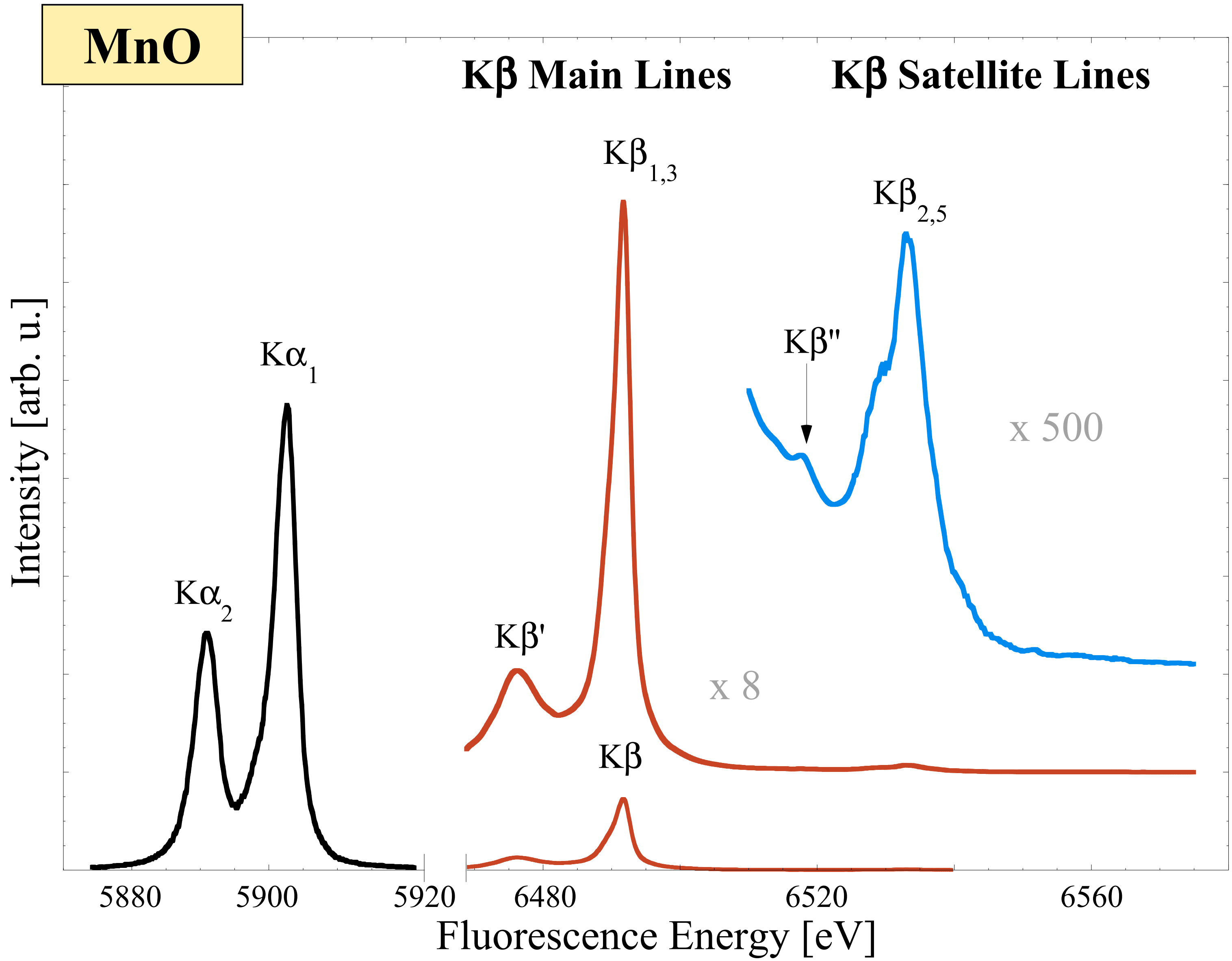
Multi-Crystal Spectrometer



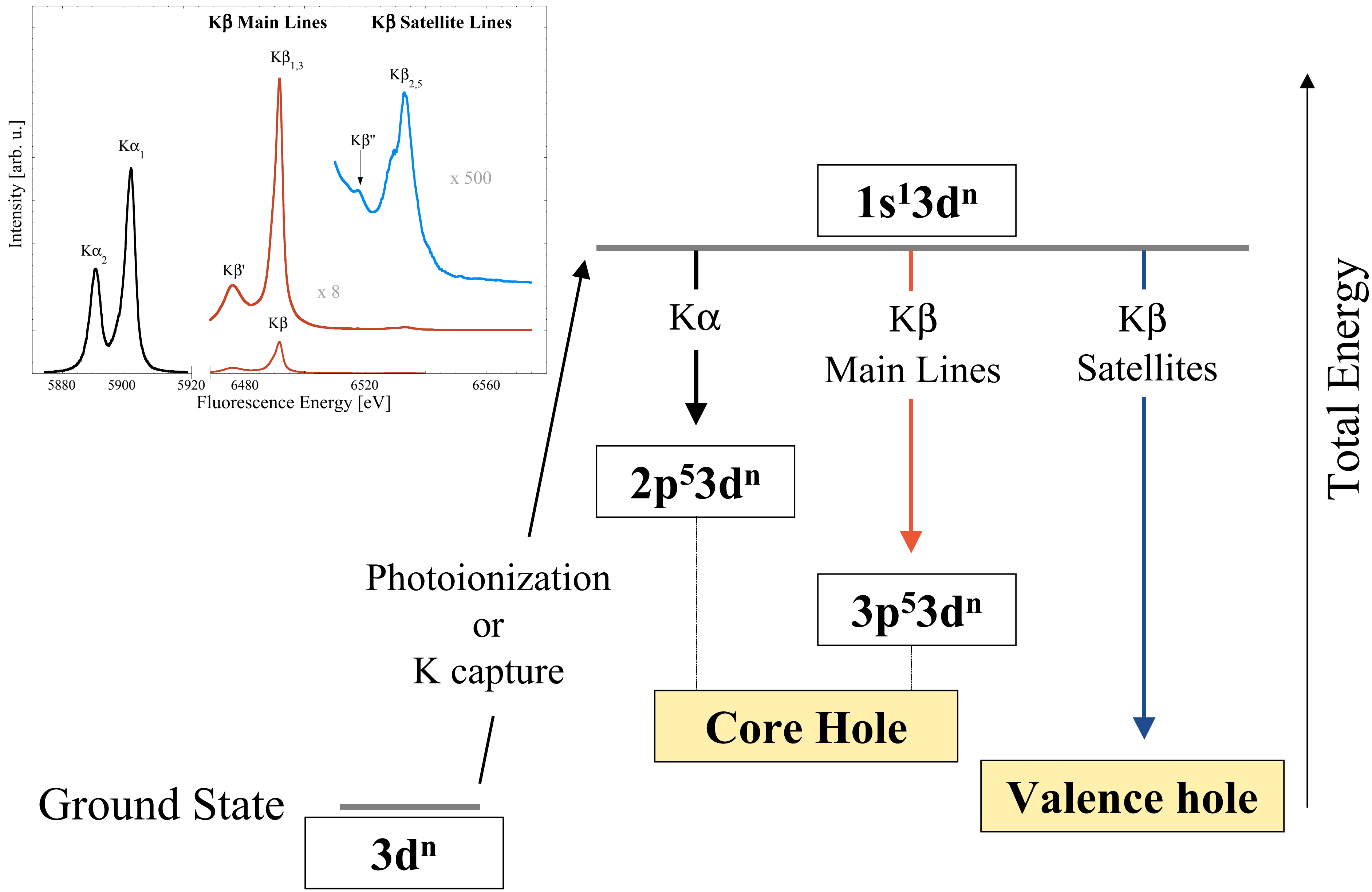




K Fluorescence Lines

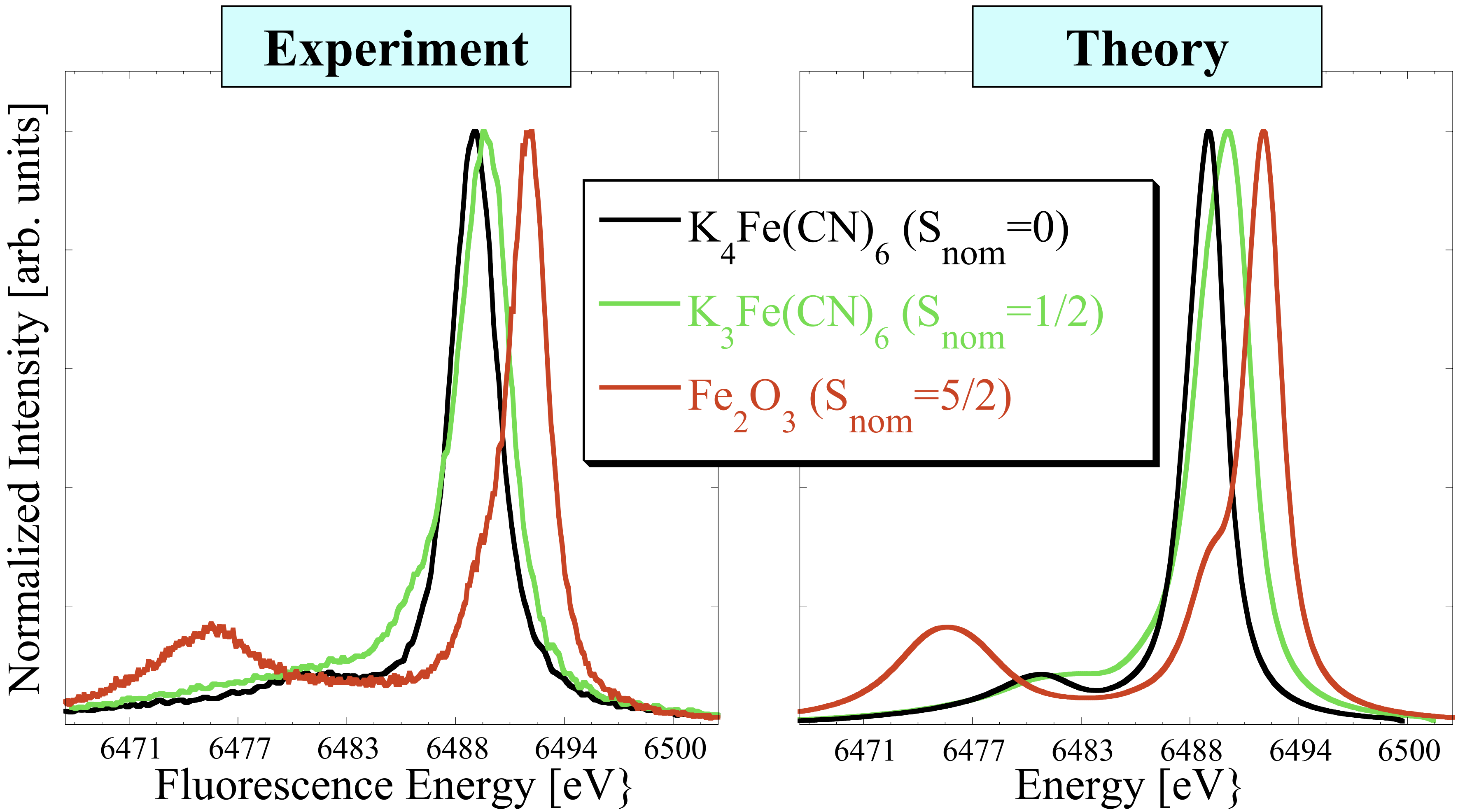


K Fluorescence Lines



Chemical Dependence of Kβ Emission

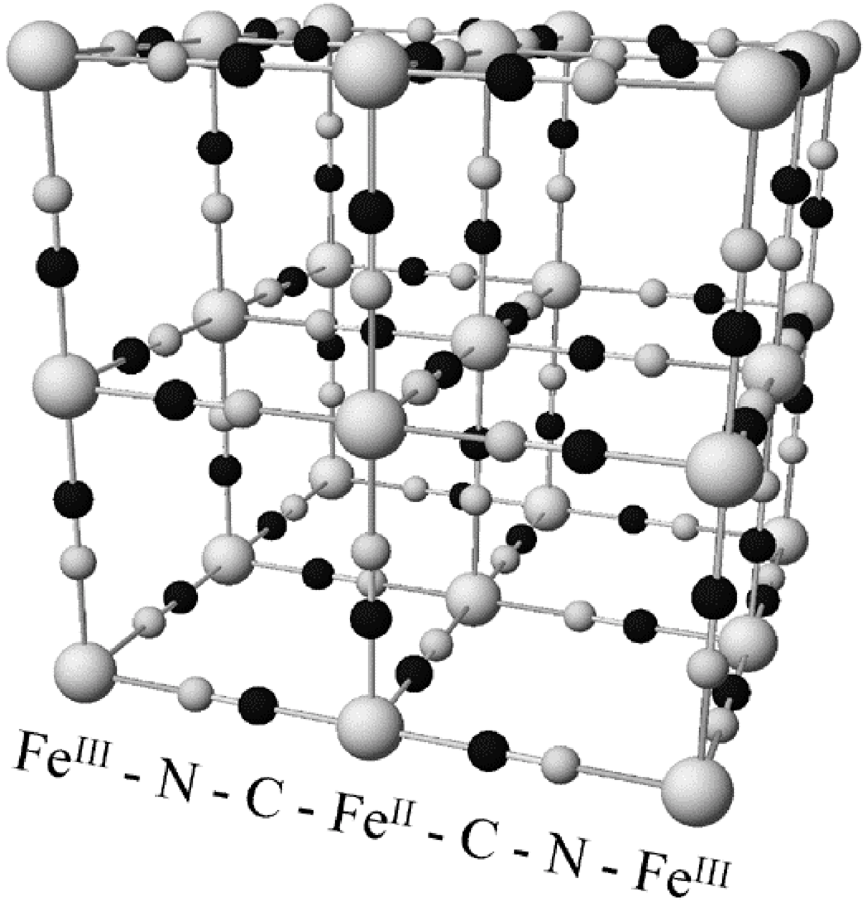
(3p,3d) exchange is dominant interaction



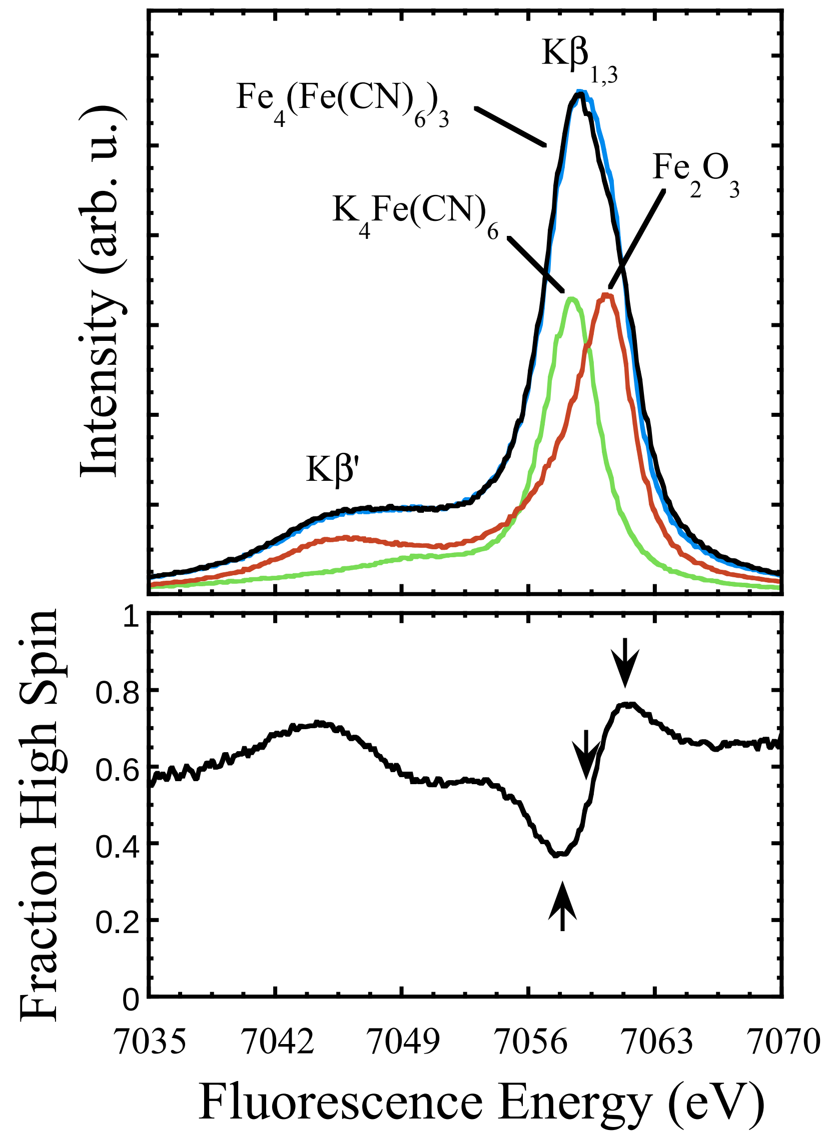
Equal center-of-gravity energies used in calculations!

Applications in Mixed-Valence Compounds

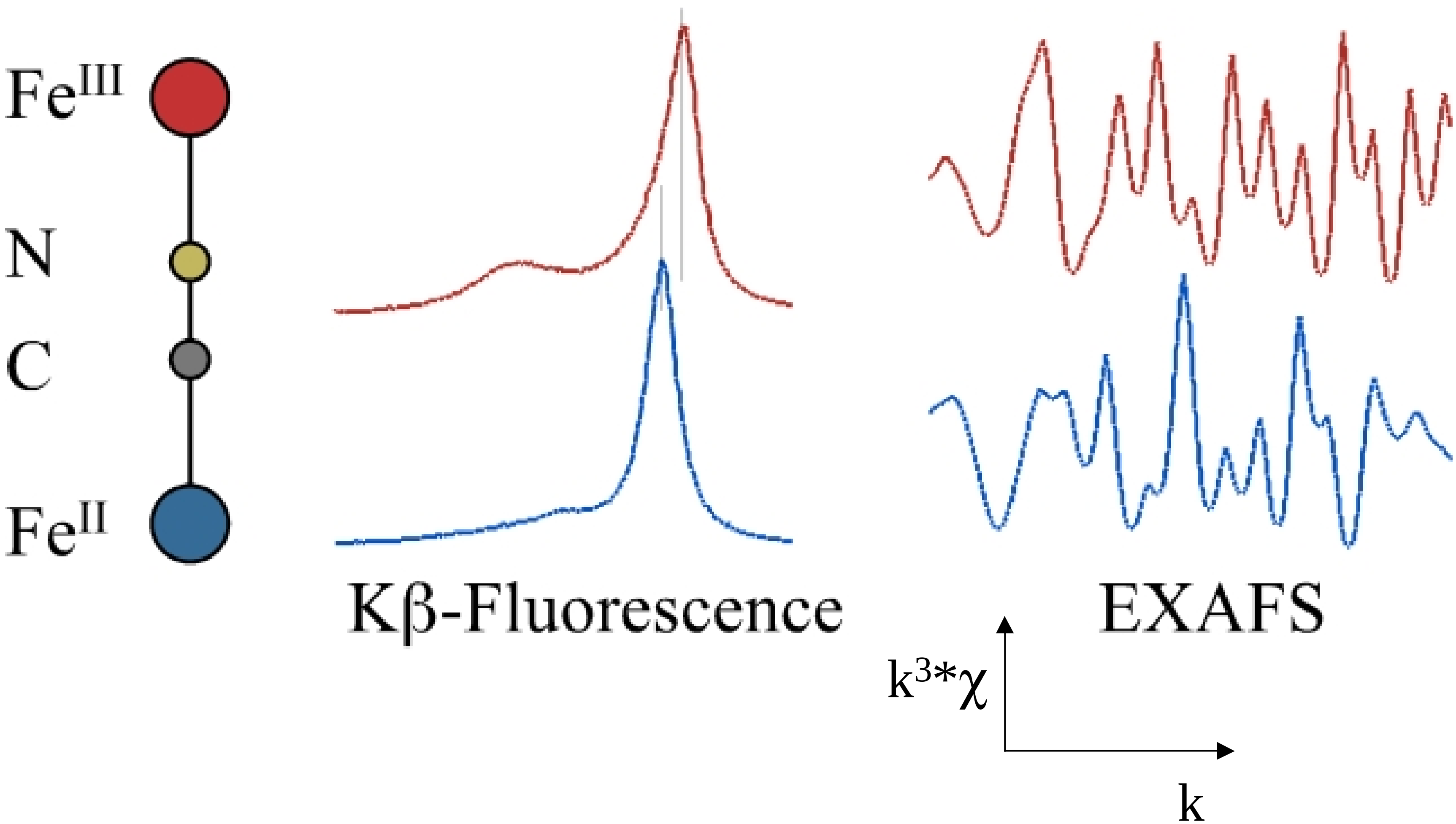
Structure of Prussian Blue



Kβ Emission



Valence-Selective EXAFS



Alternatives to Photoionization

K Capture:

The underlying nuclear reaction is:

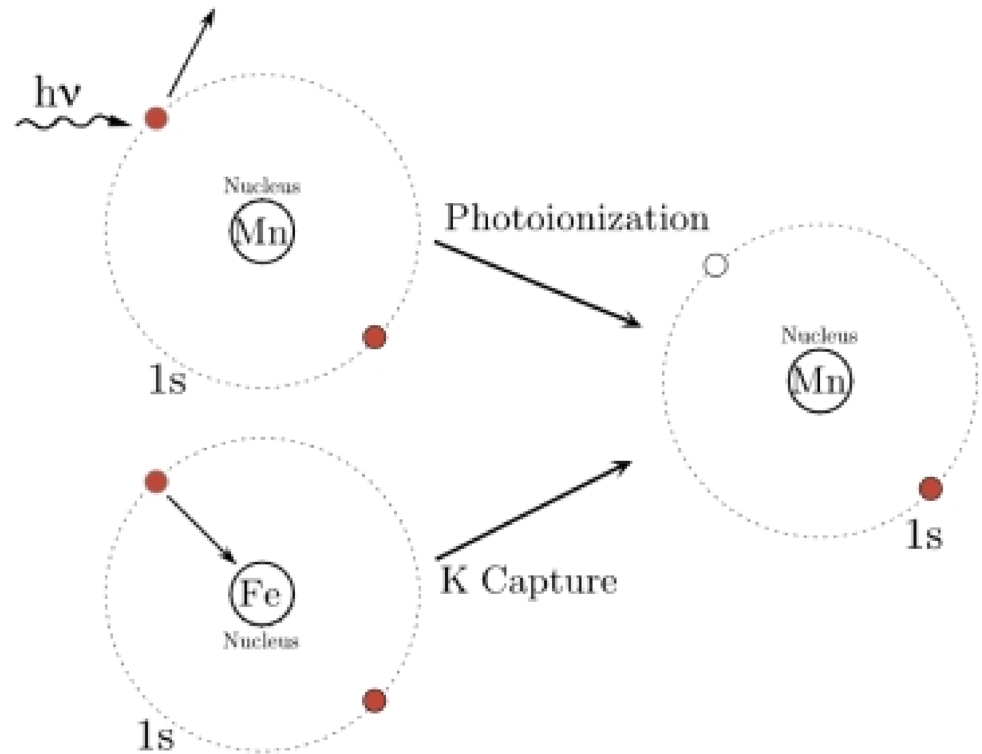
$$p + e^{-} \rightarrow n + \nu_e$$

The nuclear charge of the daughter nucleus is decreased by 1:

$$Z^{A} + e^{-} \rightarrow (Z\text{-}1)^{A} + \nu_e$$

For ^{55}Fe this means:

$$^{55}Fe \rightarrow {}^{55}Mn + \nu_e$$

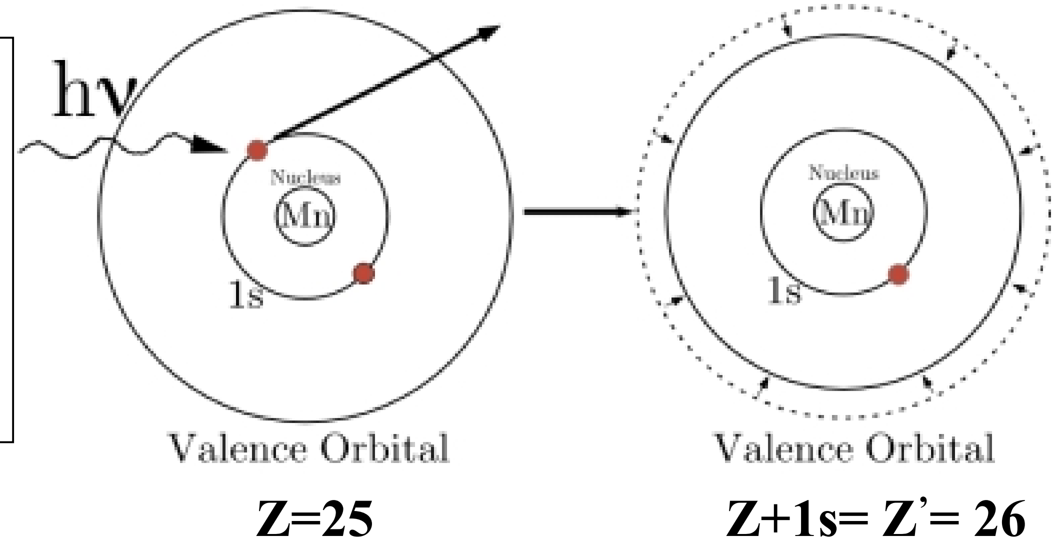


Valence Orbital Adjustment after Core Hole Creation

Photoionization

Additional effective nuclear charge due to 1s hole.

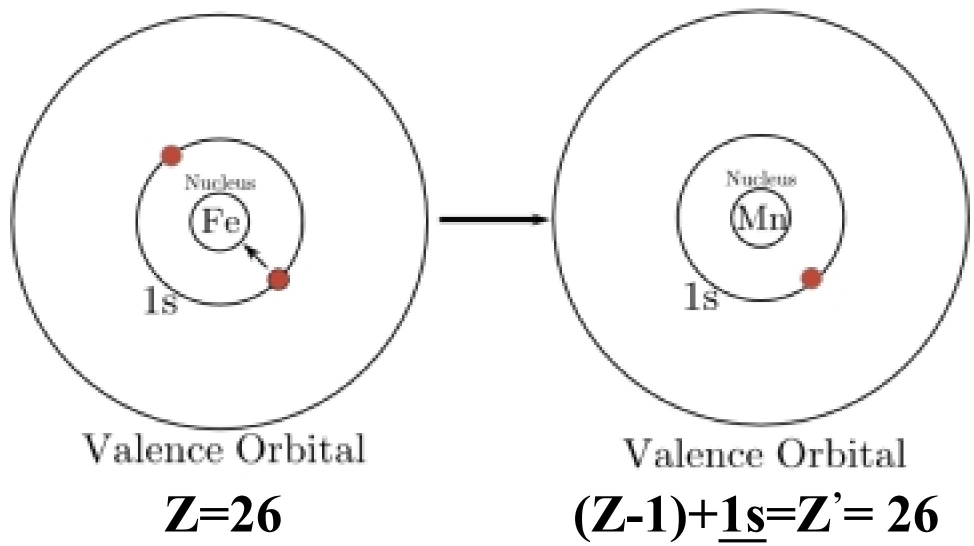
→ Orbitals change



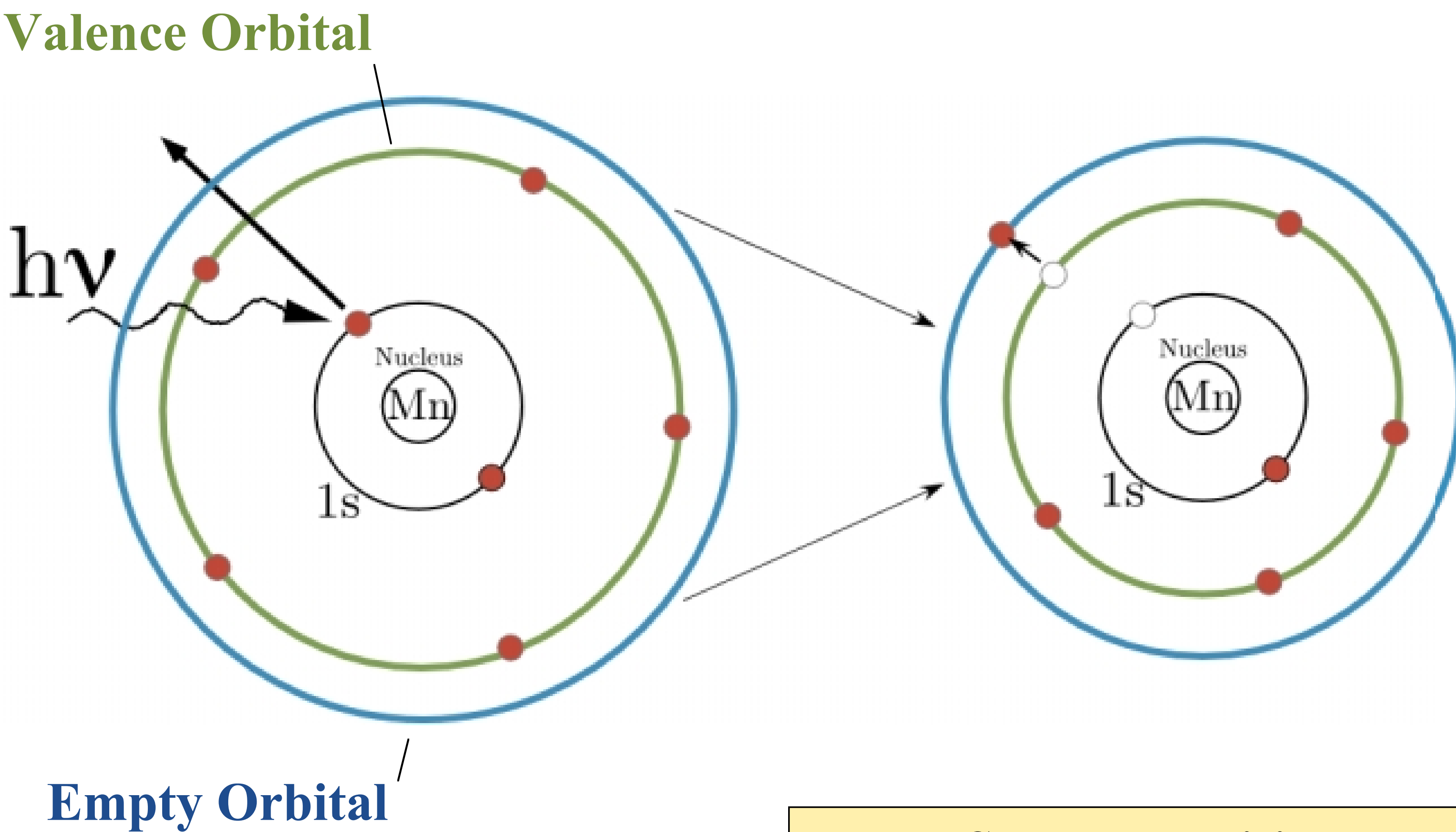
K Capture

1s hole and decrease in nuclear charge cancel each other out.

→ Orbitals unchanged



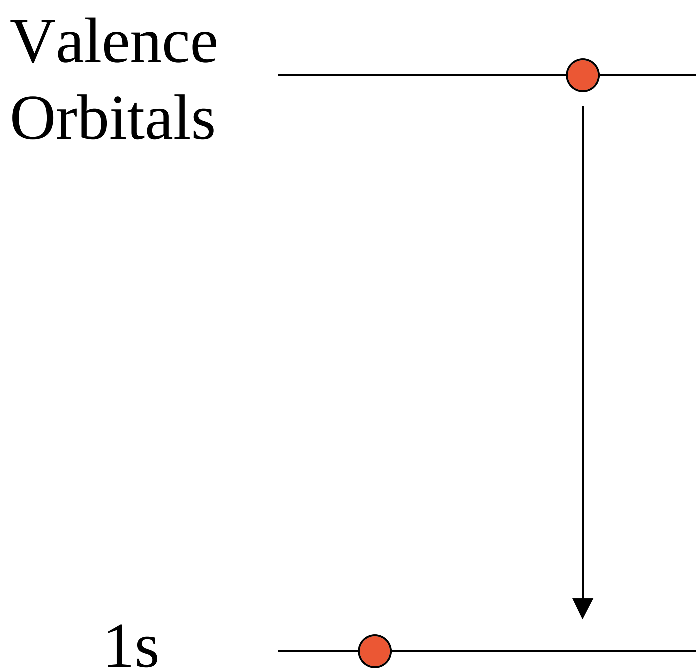
Non-Adiabatic Relaxation

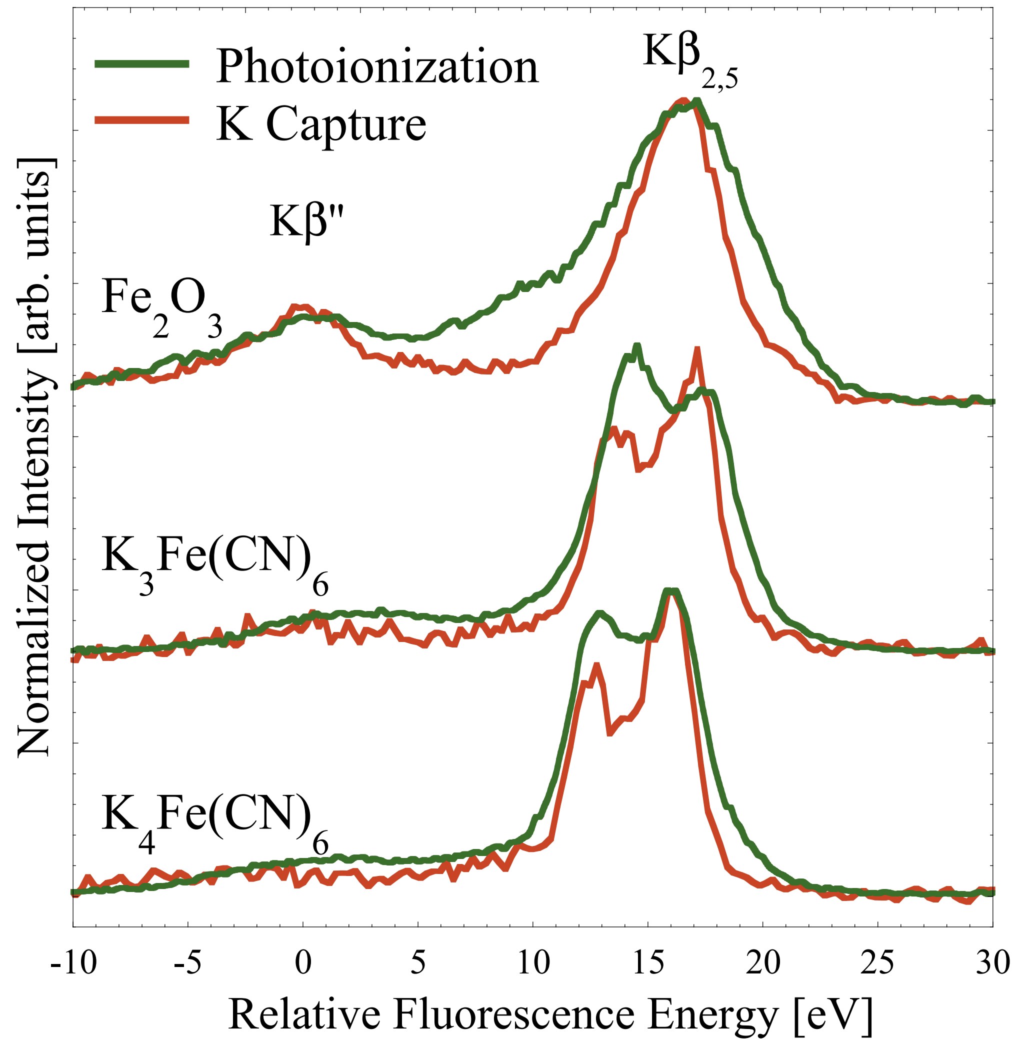


Shake transition

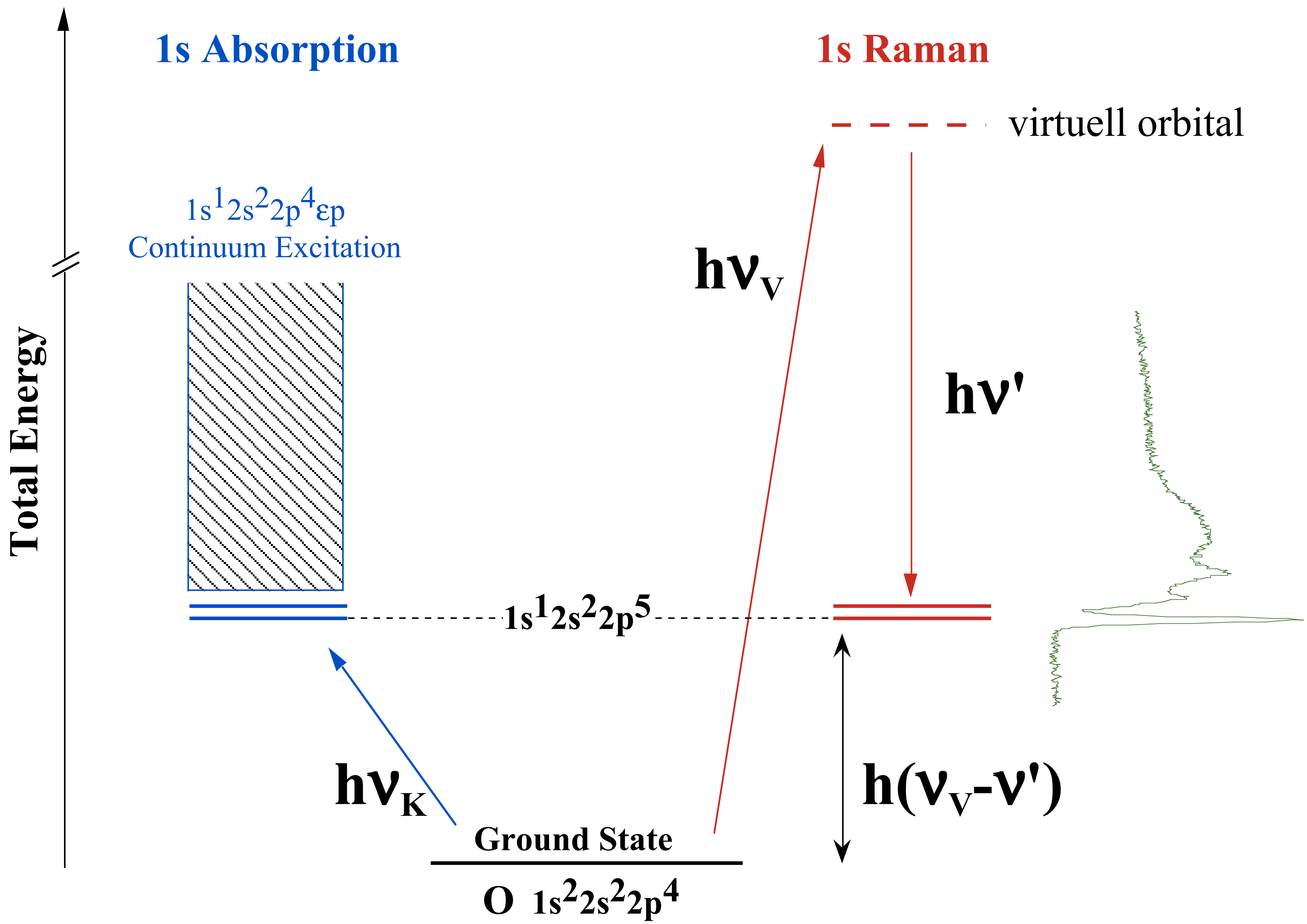
Multiple excitation

Kβ Satellite Lines Following K Capture and Photoionization in Various Fe Compounds

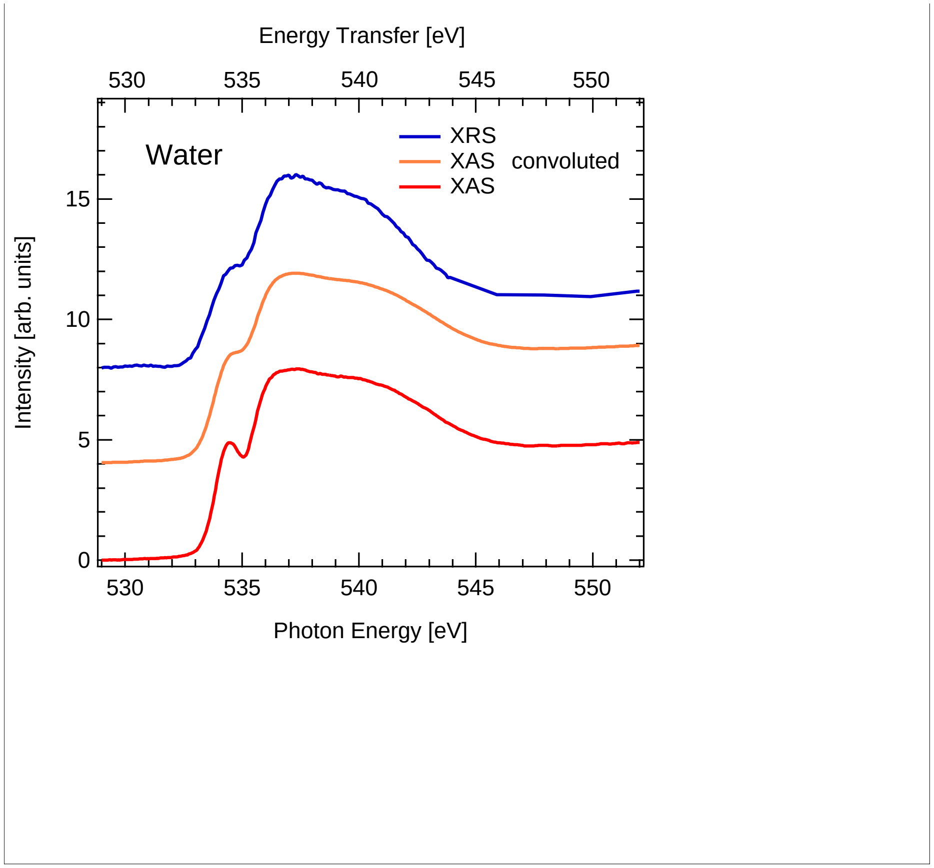


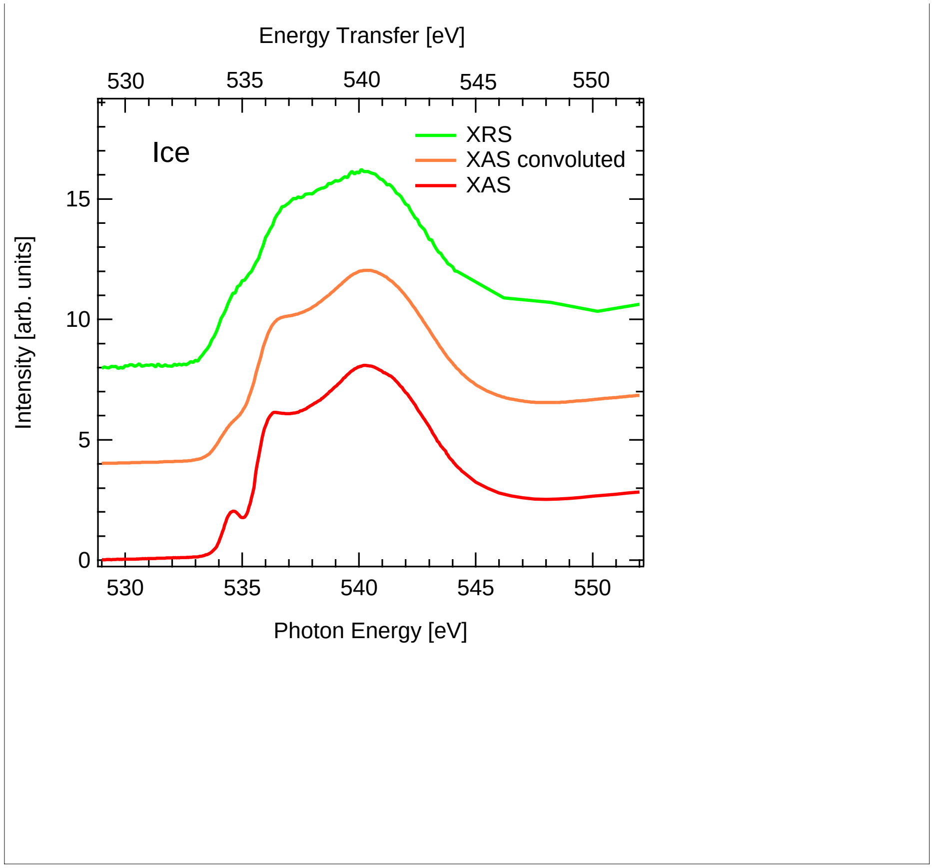


Non-Resonant Inelastic X-Ray (Raman) Scattering



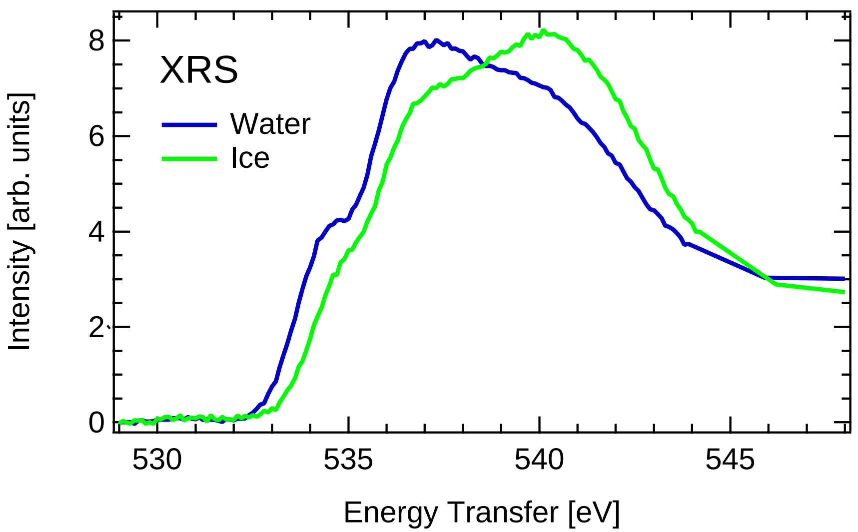
O K-Edge in Water and Ice - Comparison XAS and XRS





Task for the Spectroscopist !

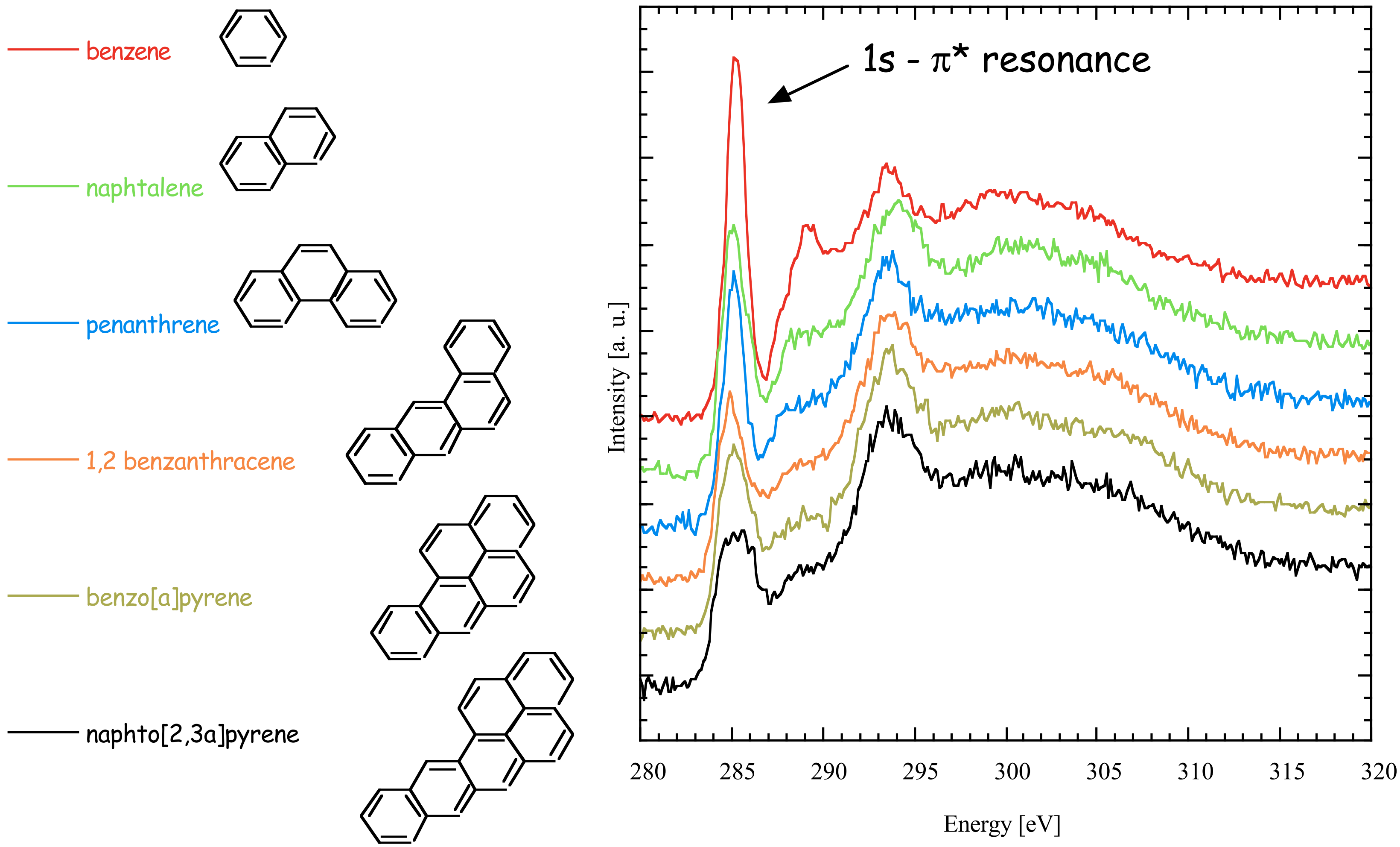
Comparison O K-Edge in Water and Ice



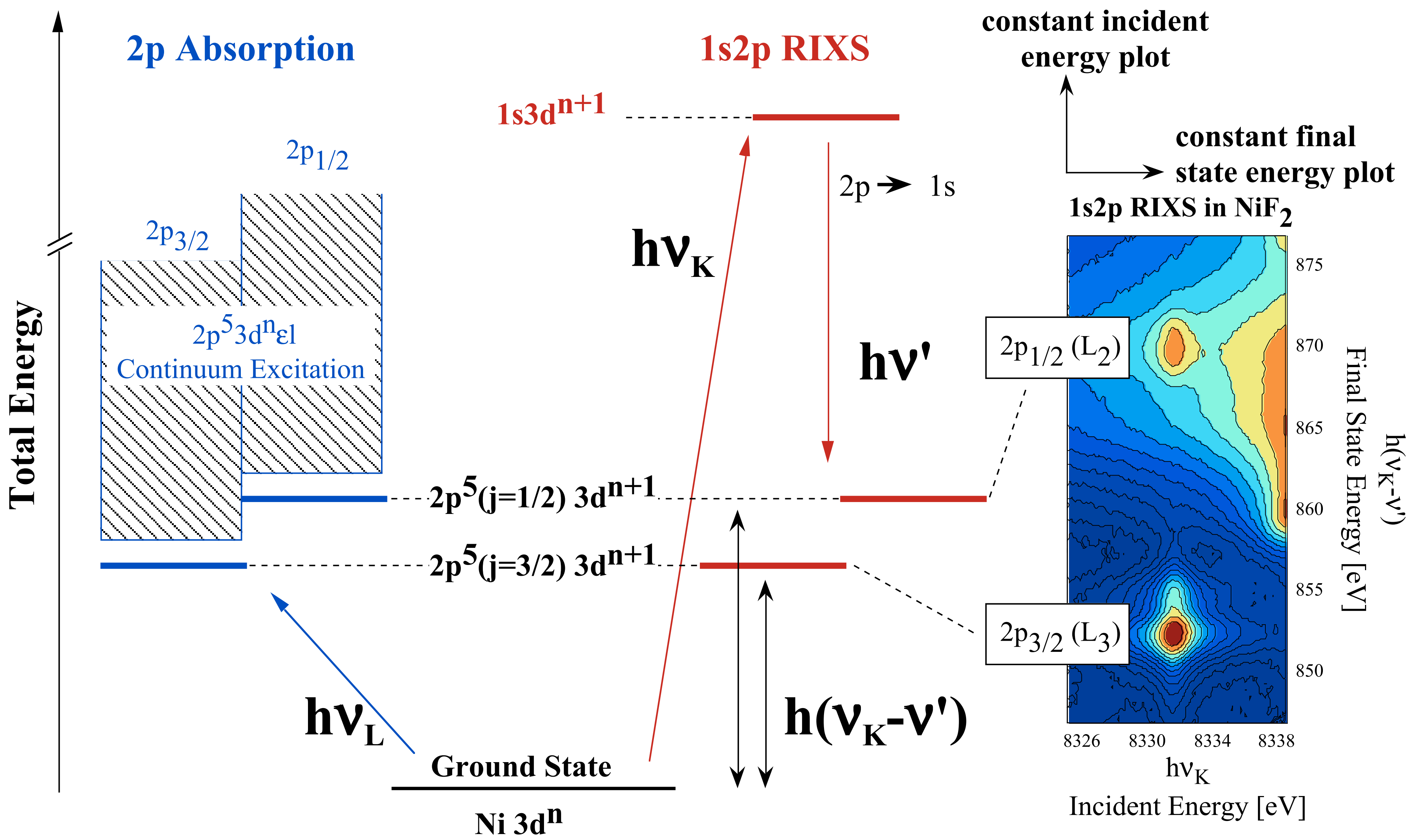
Task for the (theoretical) chemist !

C K-Edge - Aromatic Series

Series of K edge spectra from aromatic ring systems with increasing number of rings

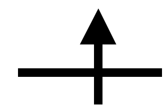


Resonant Inelastic Scattering

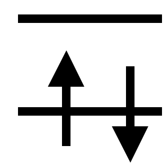


Ni Compounds Studied by RIXS

a) **Ni(I)** in $[PhTt^{tBu}]NiCO$

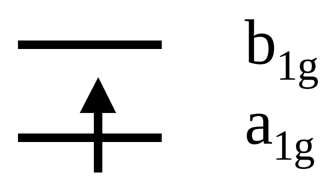


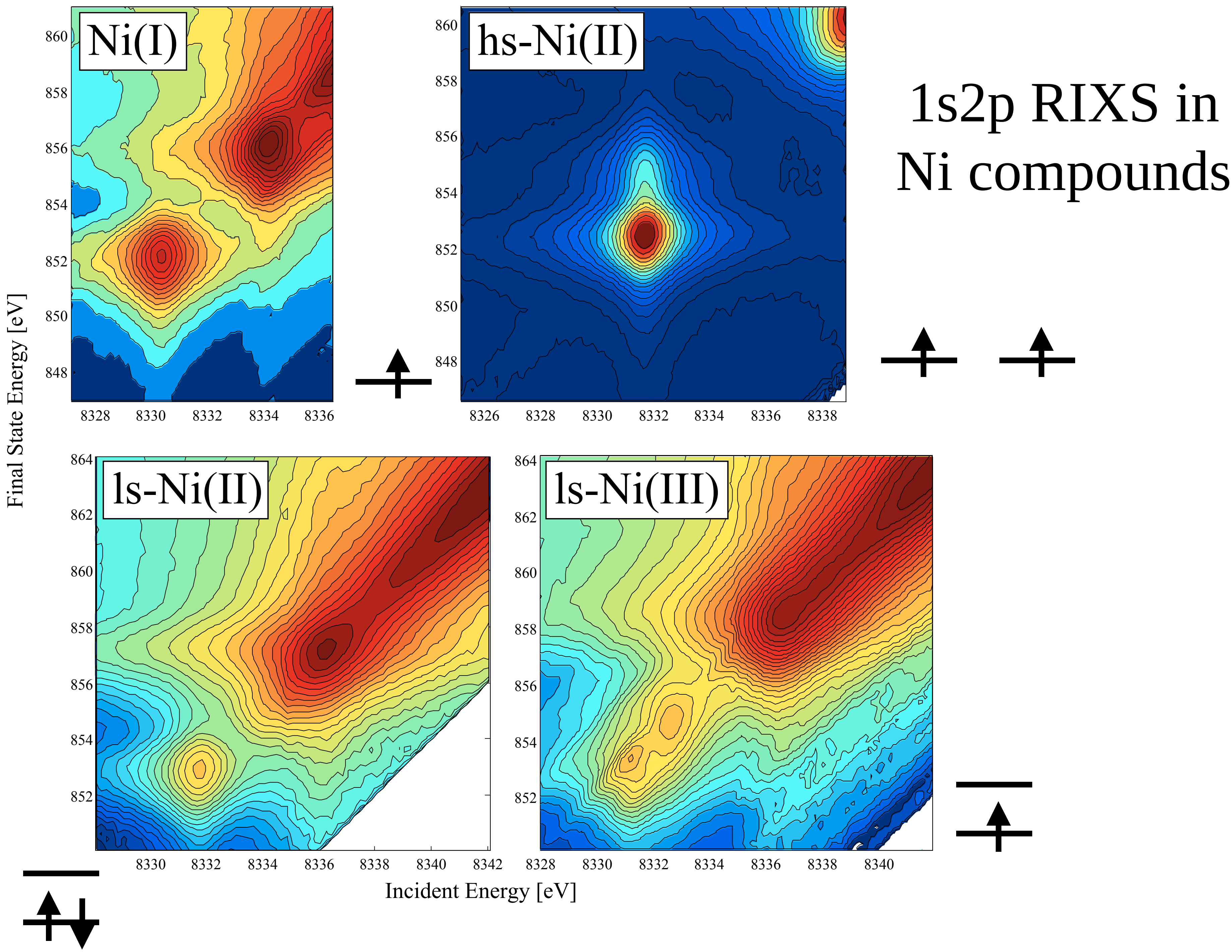
b) **Ni(II) low-spin** (ls) in $(Ph_4As)_2Ni(S_2C_2(CF_3)_2)_2$



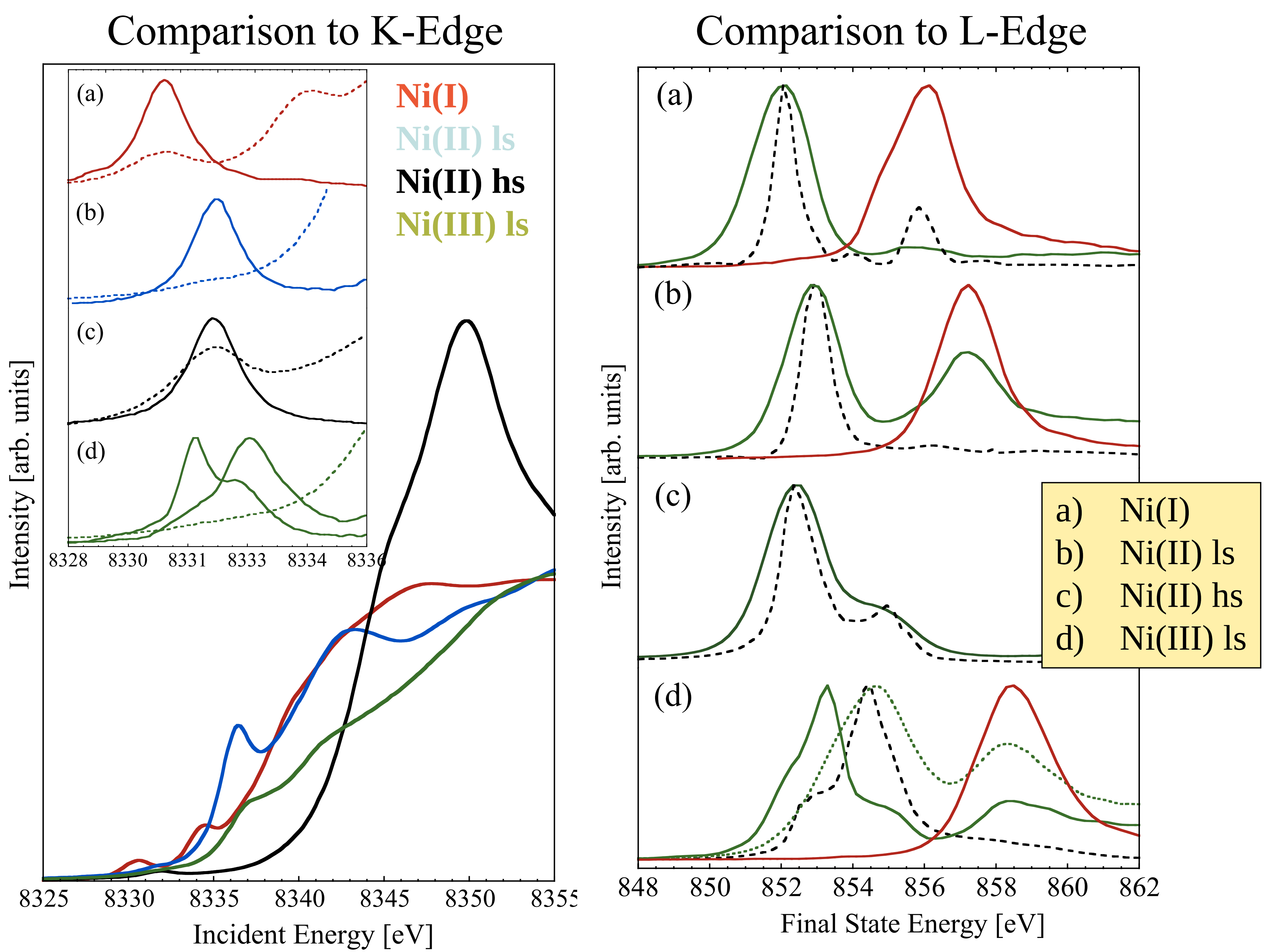
c) **Ni(II) high-spin** (hs) in NiF_2

d) **Ni(III) low-spin** in $[Ni(\eta^4\text{-}DEMAMPA\text{-}DCB)]^-$





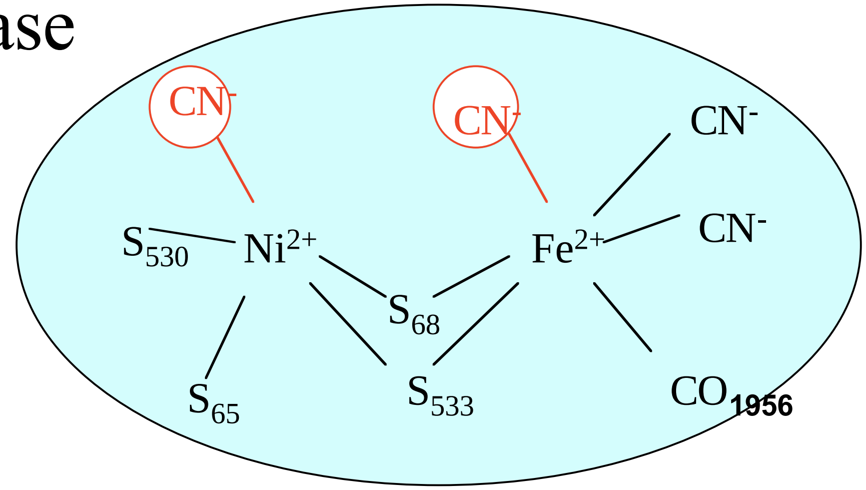
1s2p RIXS in Ni compounds
Ni(I)
hs-Ni(II)
ls-Ni(II)
ls-Ni(III)
Final State Energy [eV]
Incident Energy [eV]

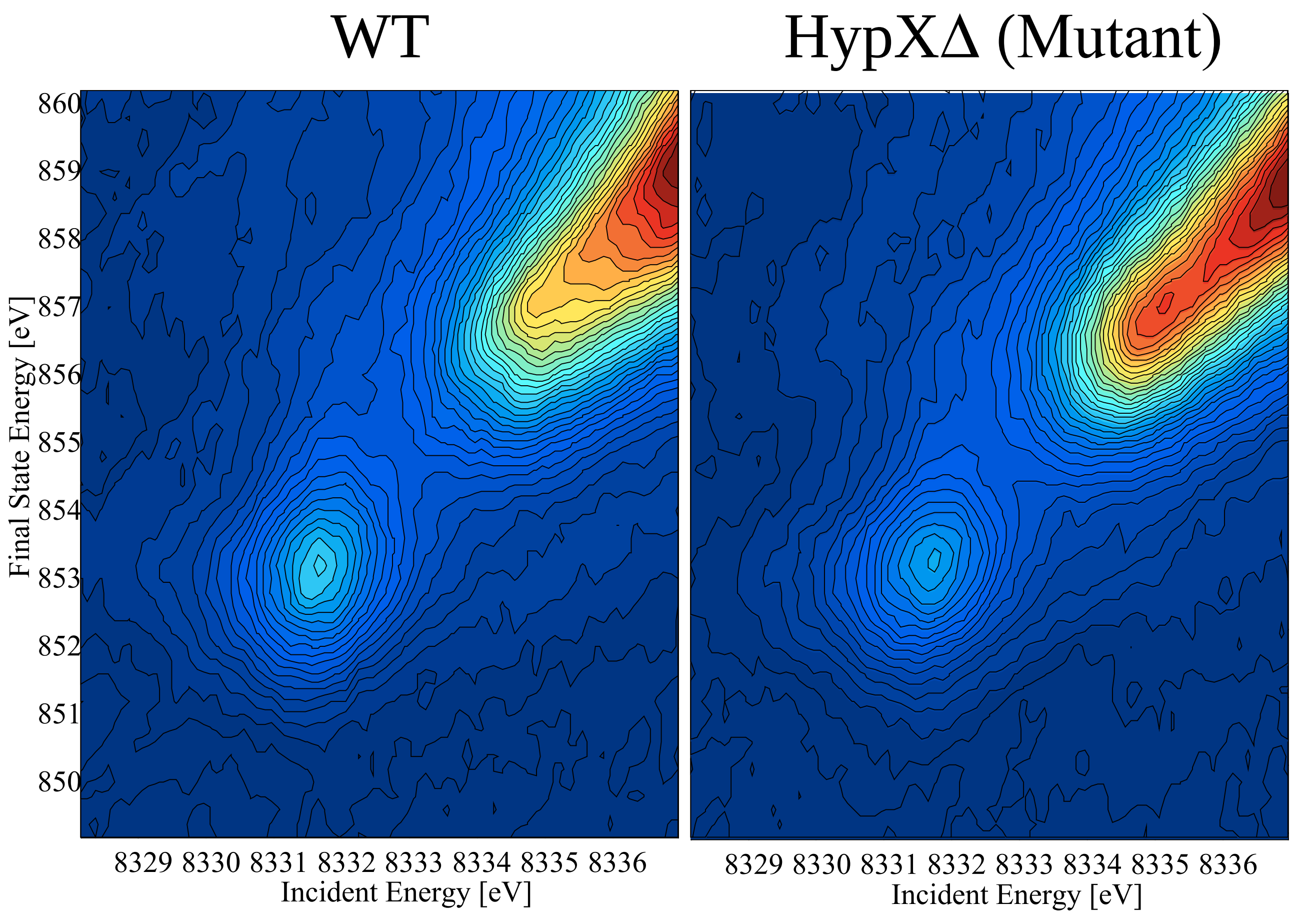


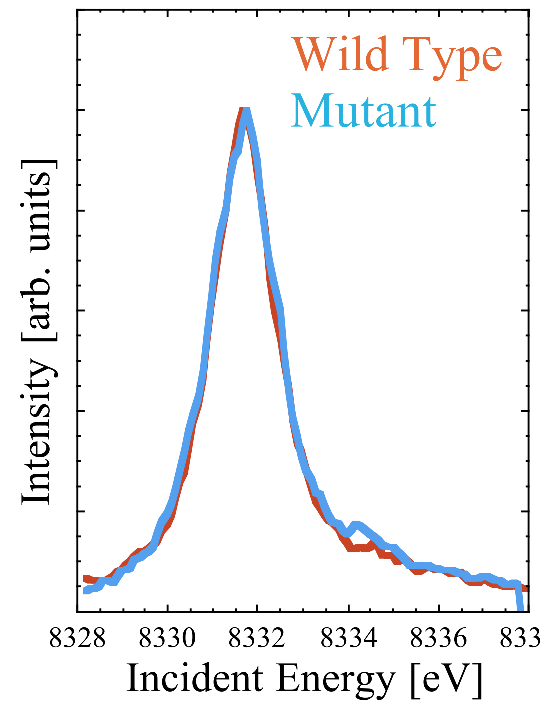
Comparison to K-Edge
Comparison to L-Edge
Ni(I)
Ni(II) ls
Ni(II) hs
Ni(III) ls
(a)
(b)
(c)
(d)
8328
8330
8331
8333
8334
8336
Intensity [arb. units]
8325
8330
8335
8340
8345
8350
8355
Incident Energy [eV]
a) Ni(I)
b) Ni(II) ls
c) Ni(II) hs
d) Ni(III) ls
848
850
852
854
856
858
860
862
Final State Energy [eV]

1s2p Ni RIXS in Proteins: SH_2ase (Ralstonia eutropha)

Wild Type:







Outlook

- In-situ studies
- Very high resolution monochromators and analyzers
- Low energy transfer RIXS (‘dd’ excitations)
- Quadrupole excitations in Raman spectra
- MCD-RIXS

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