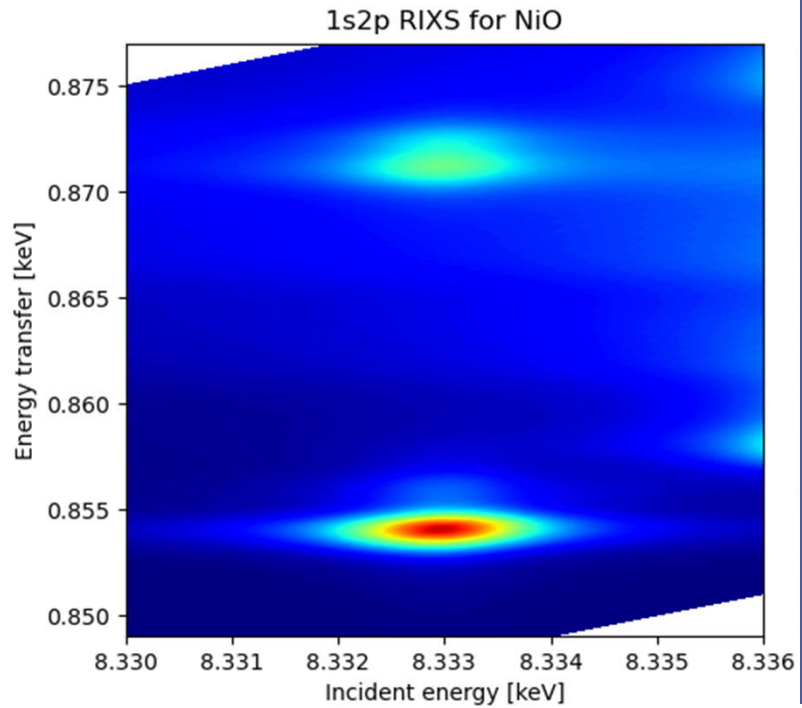




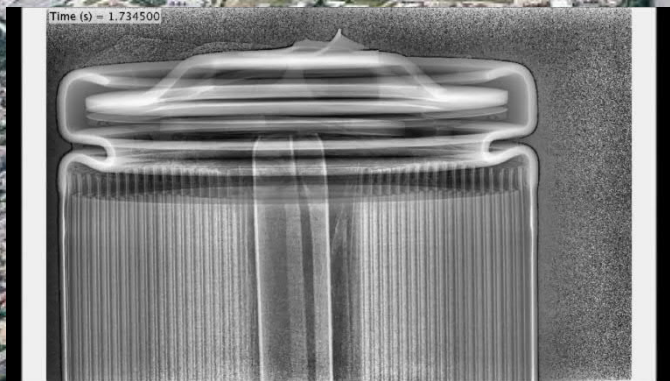
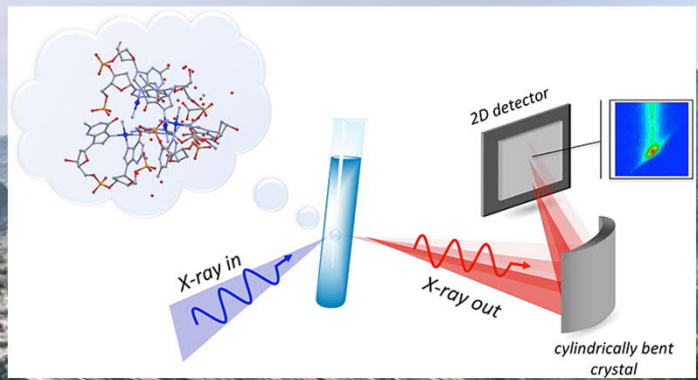
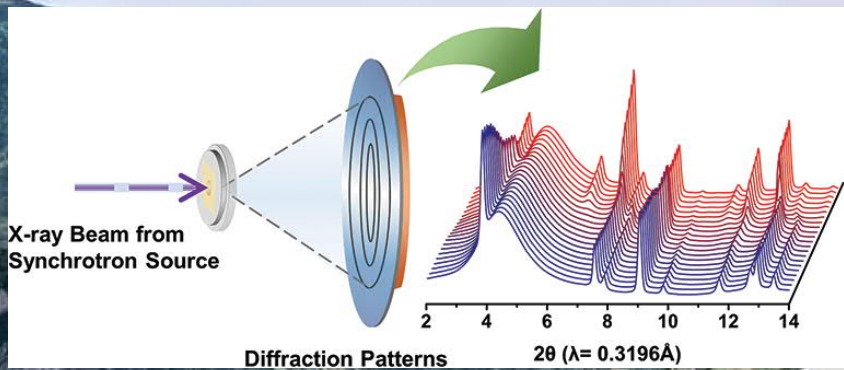
| The European Synchrotron



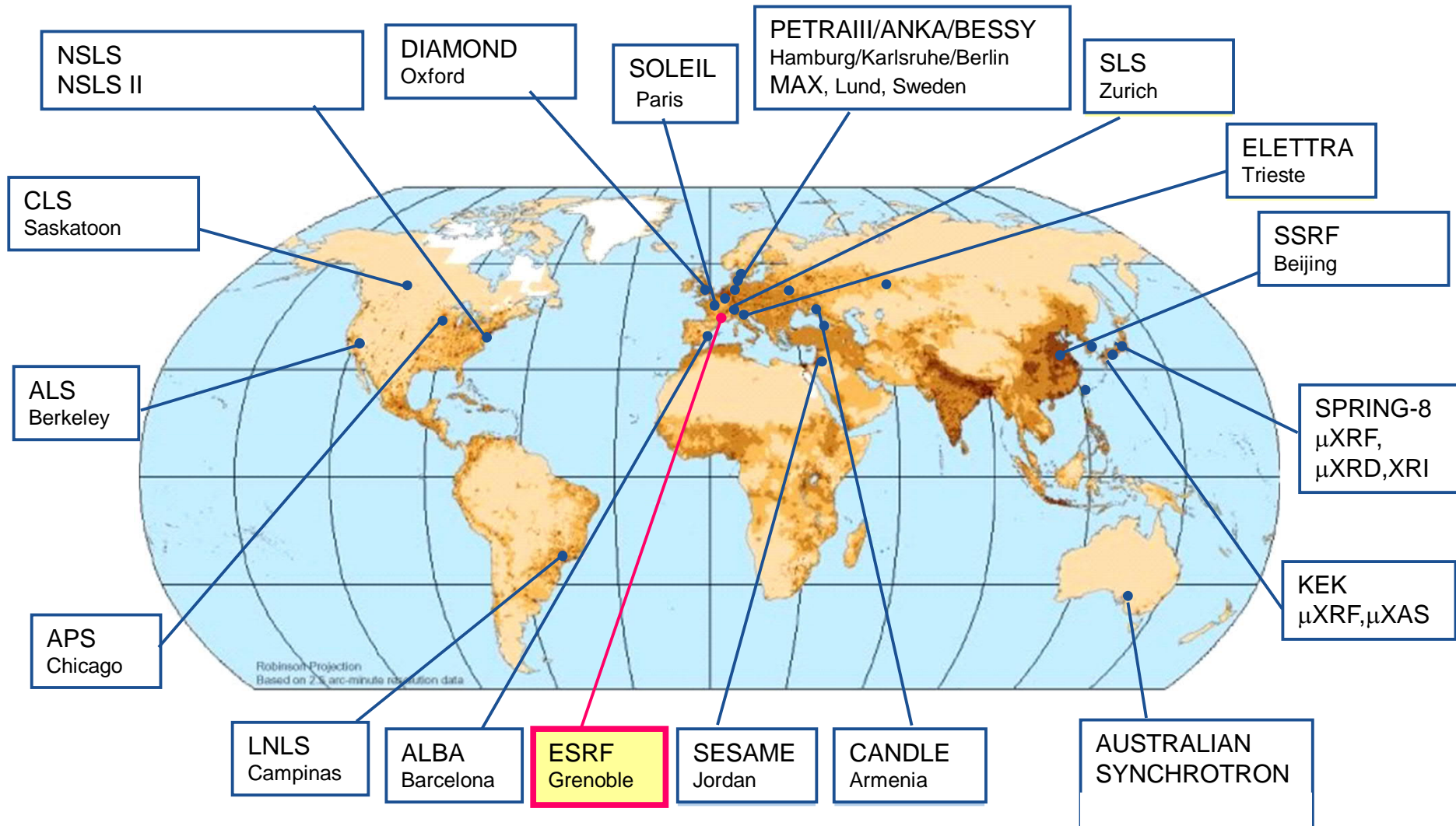
Synchrotron XAS, XES & RIXS

Sami Vasala

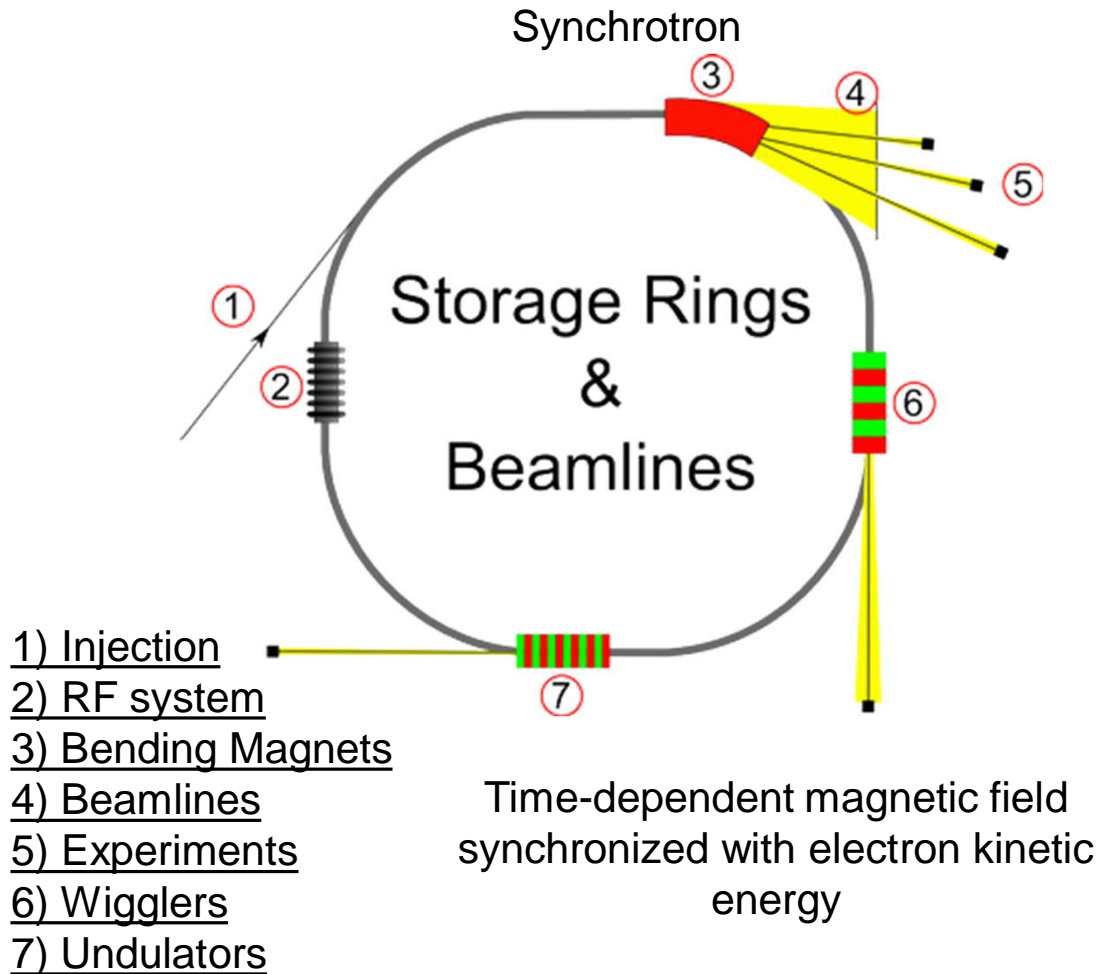




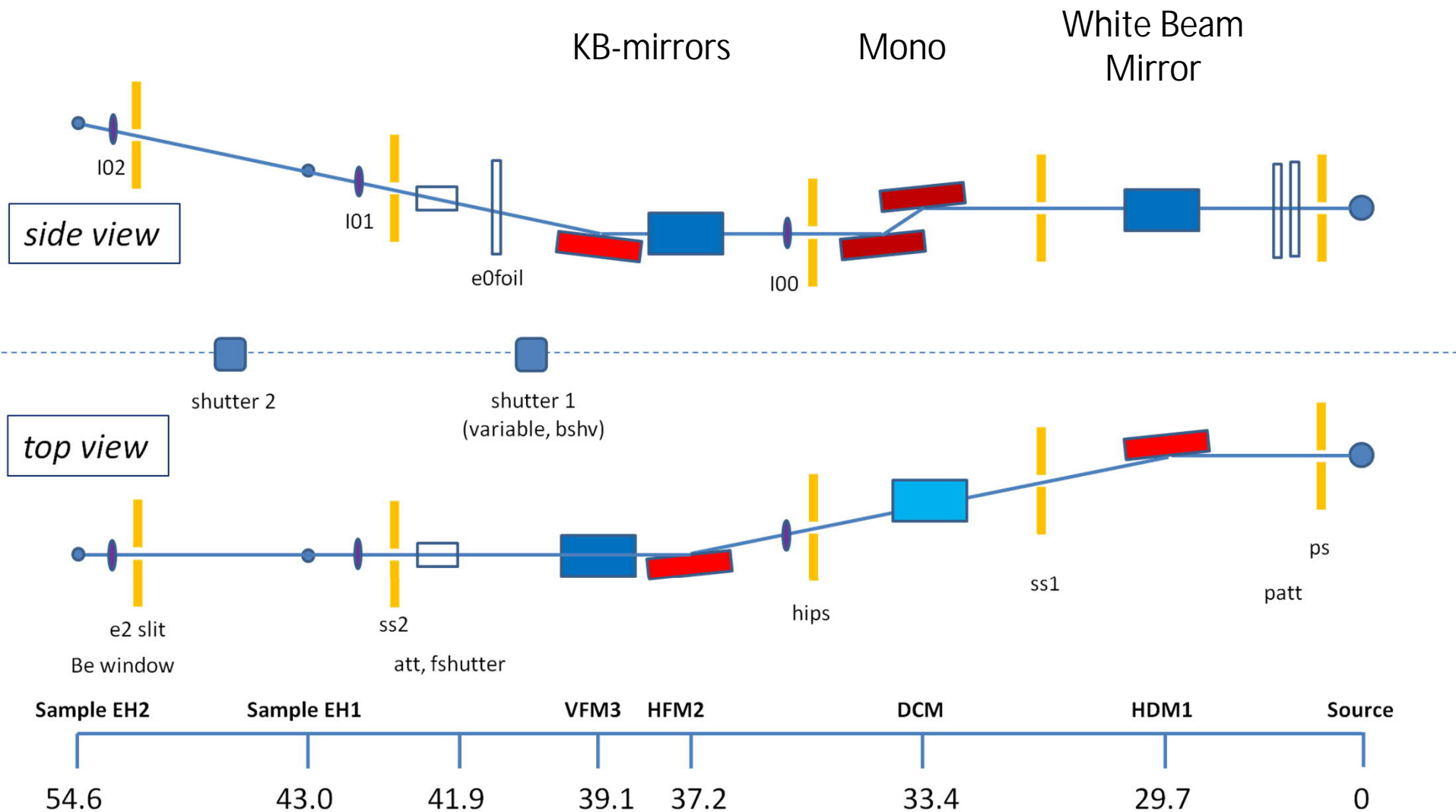
STORAGE RINGS IN THE WORLD

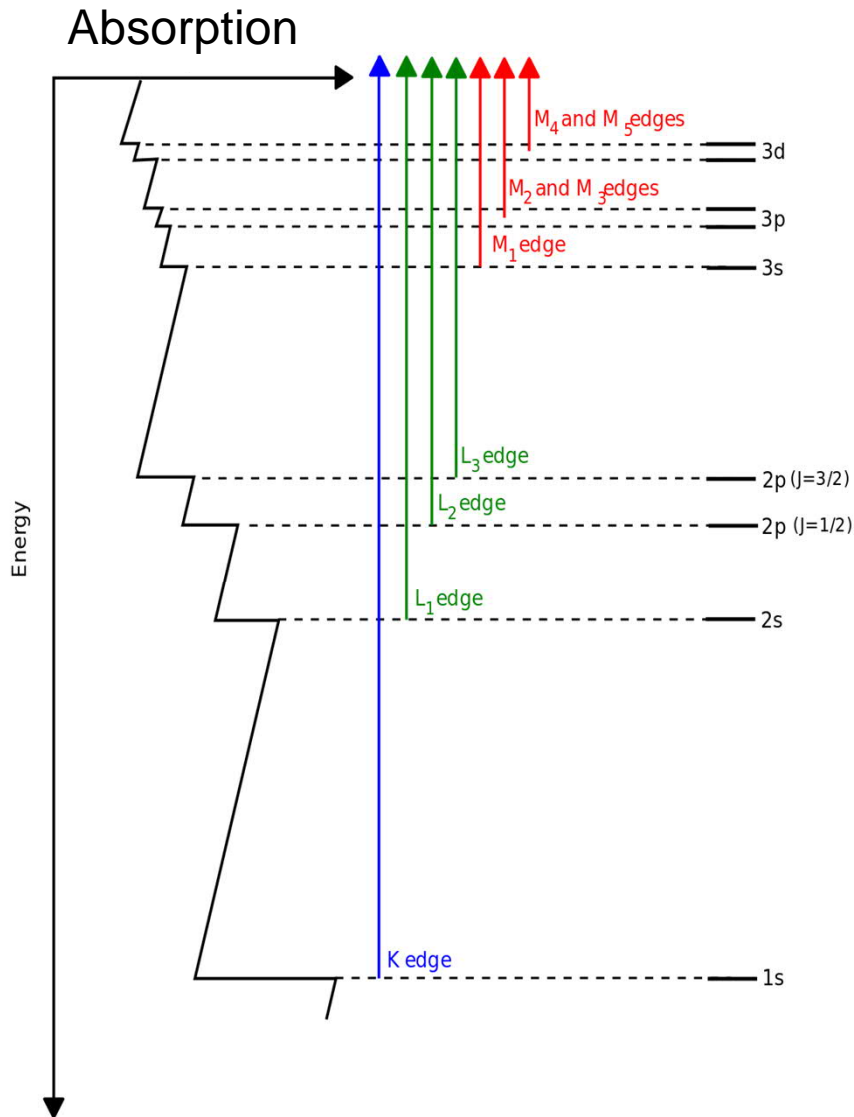


STORAGE RINGS AND SYNCHROTRON RADIATION



EXAMPLE FOR A BEAMLINE LAYOUT

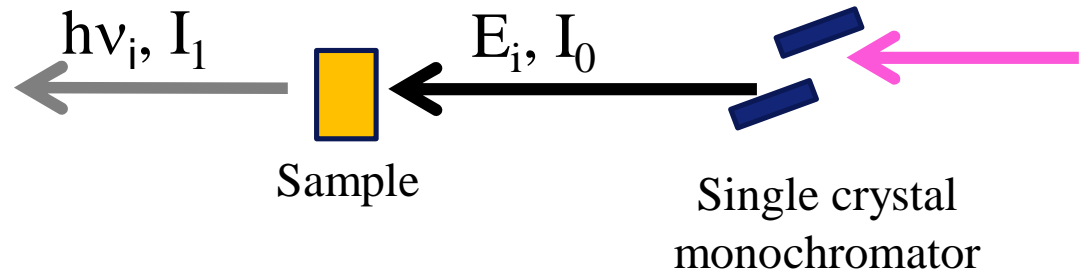
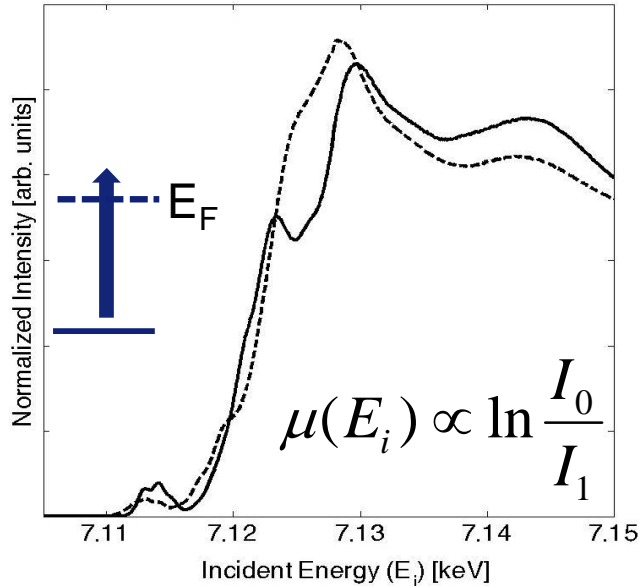


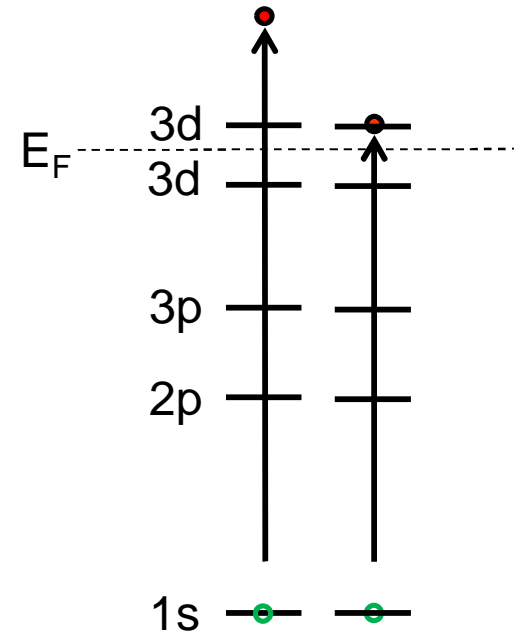
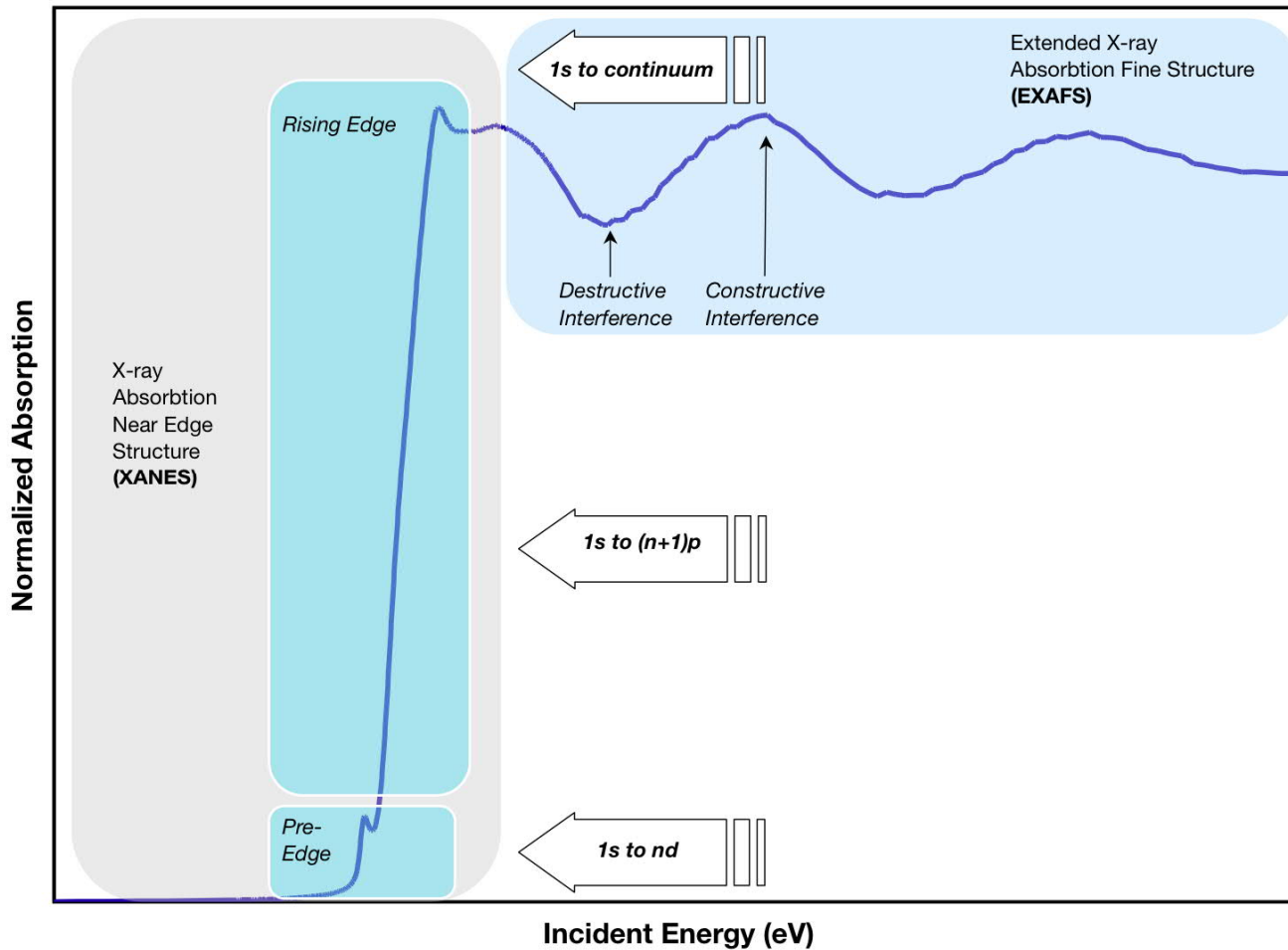


Element specific.

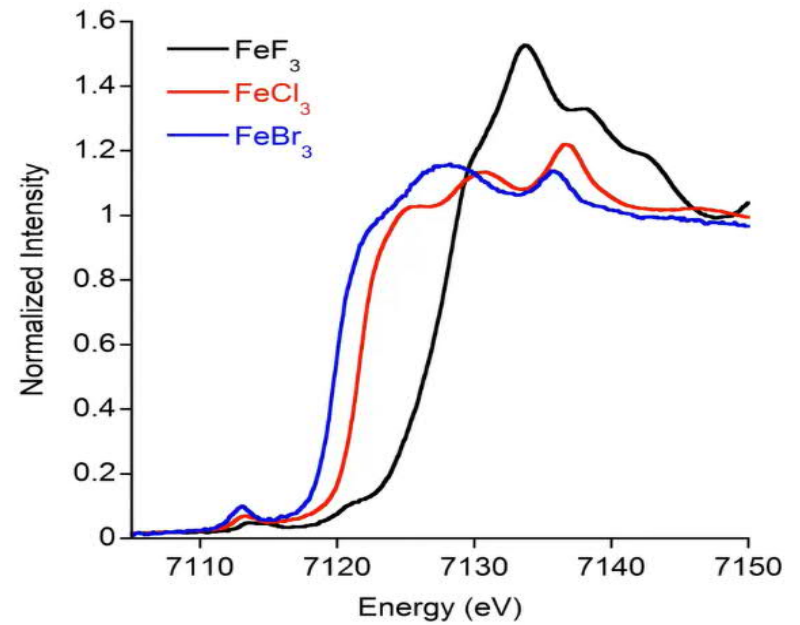
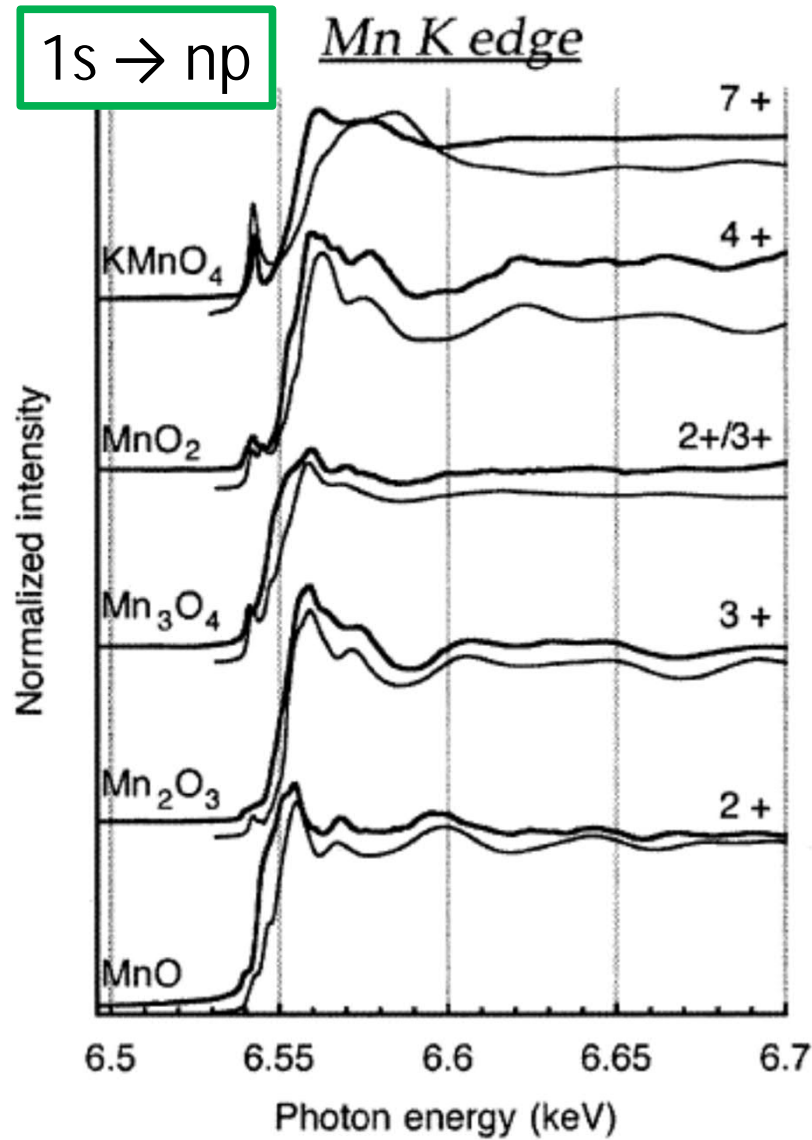
Electronic and atomic structural information on samples with or without long-range order.

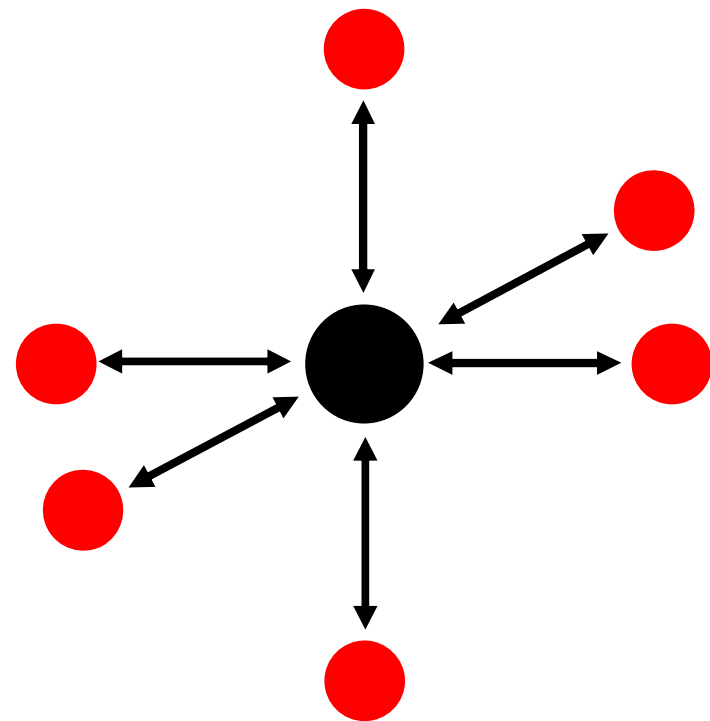
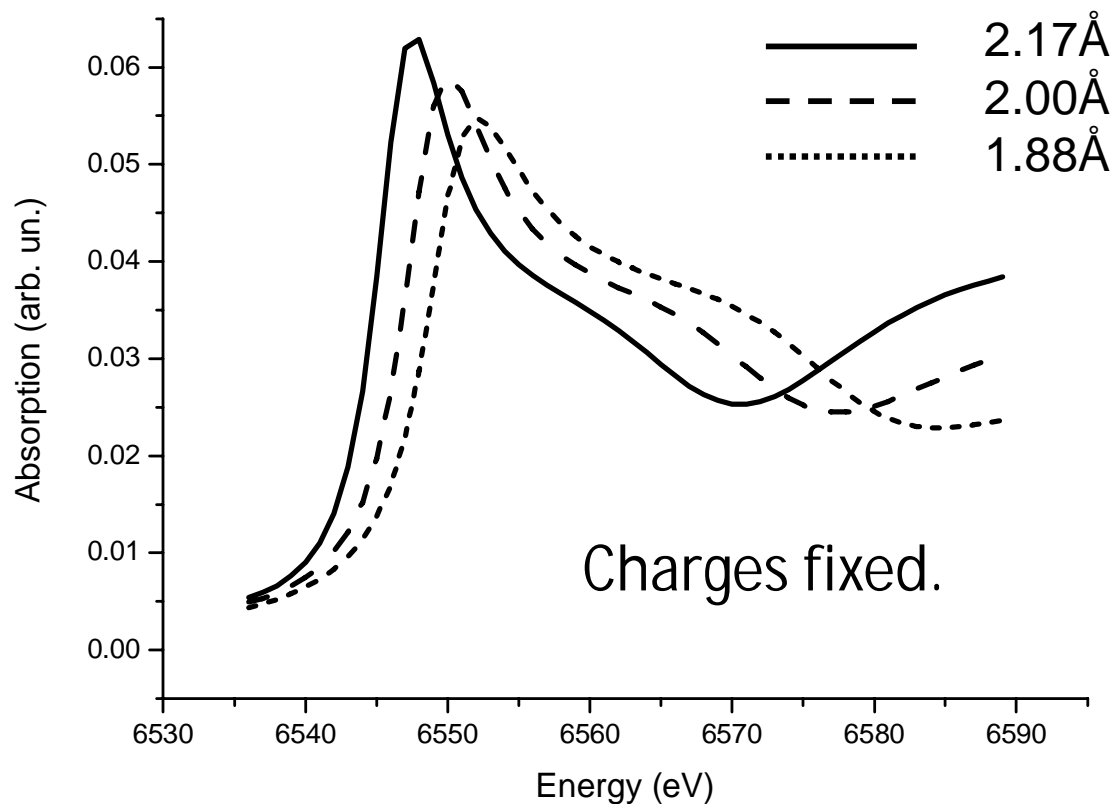
Local structure





Selection rules: dipole: $\Delta l = \pm 1$; quadrupole: $\Delta l = 0, \pm 2$



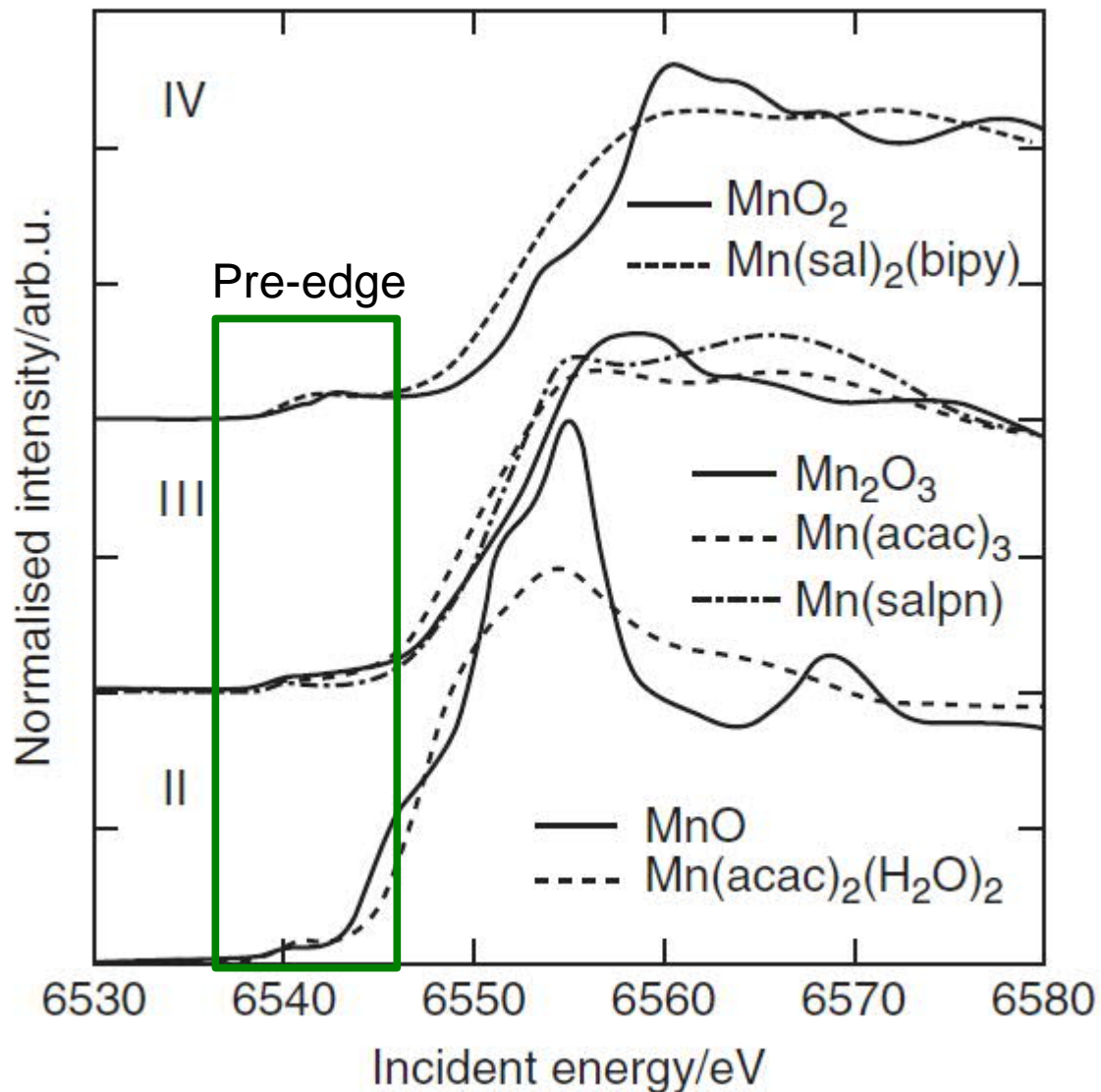


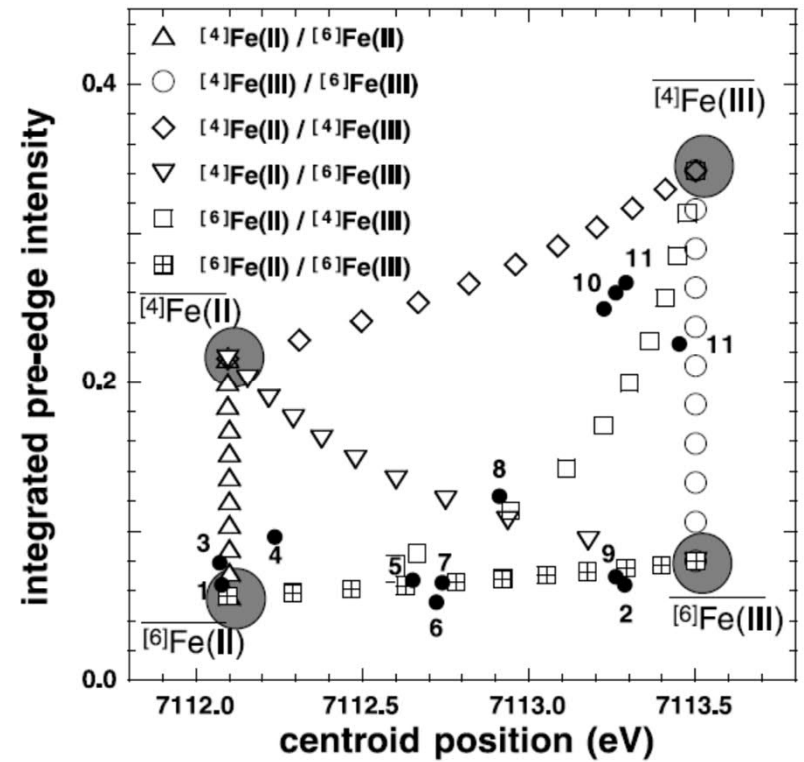
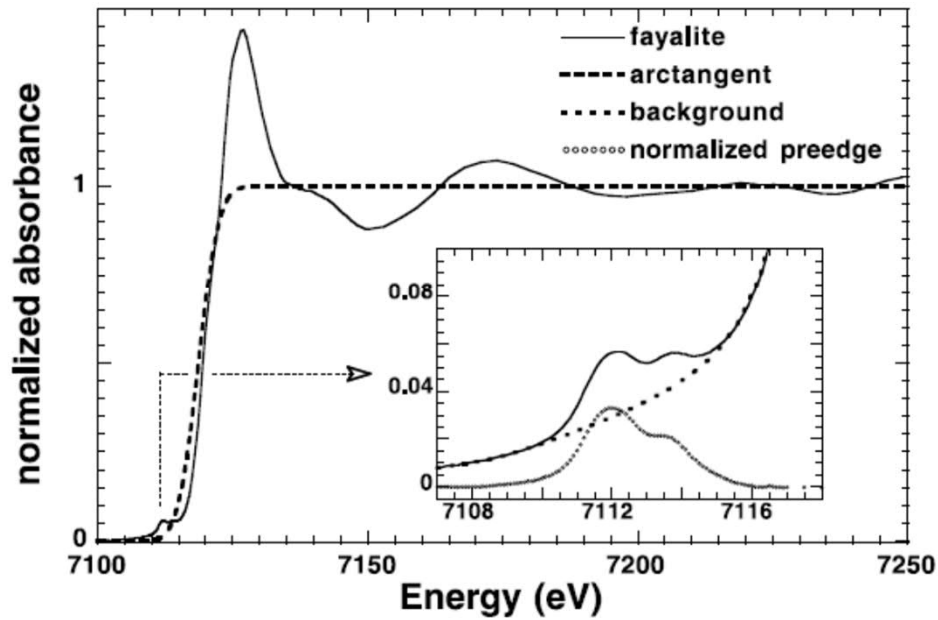
Calculated Mn K-edge XANES spectra for MnO_6 octahedrons with varying Mn-O distances.

The electronic structure of the Mn was fixed in all calculations.

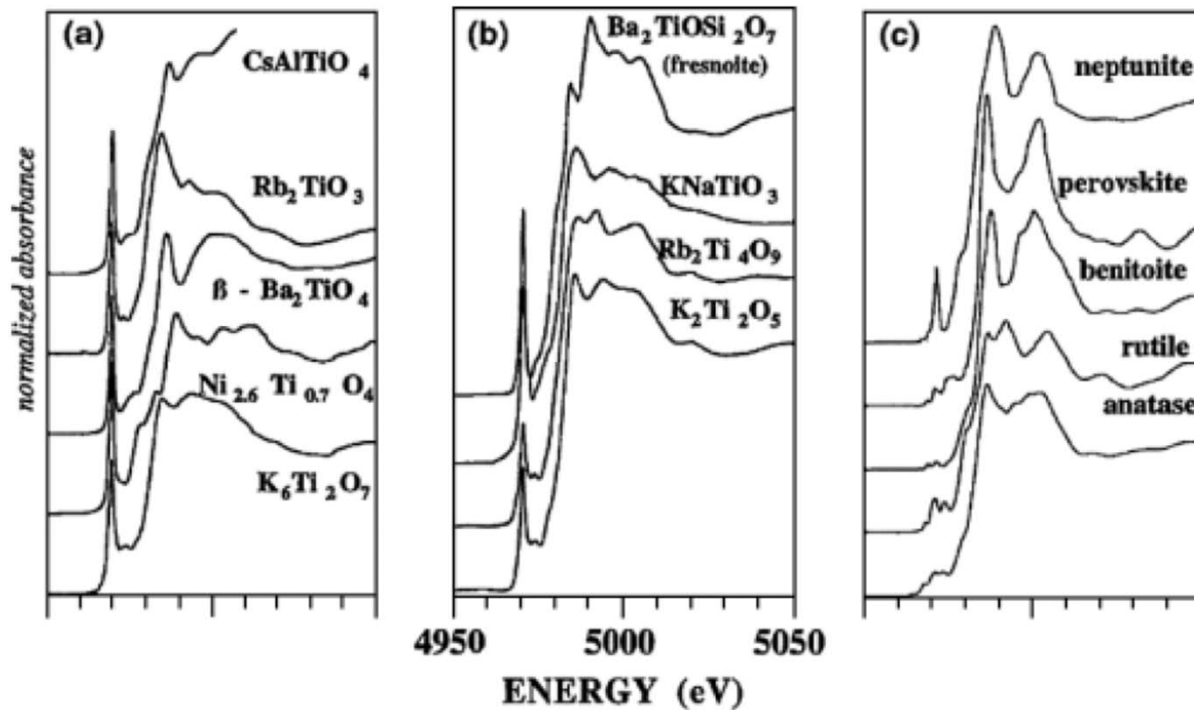
➔ XANES is sensitive to electronic *and* atomic structure.

The spectral shape depends on oxidation state and local coordination.



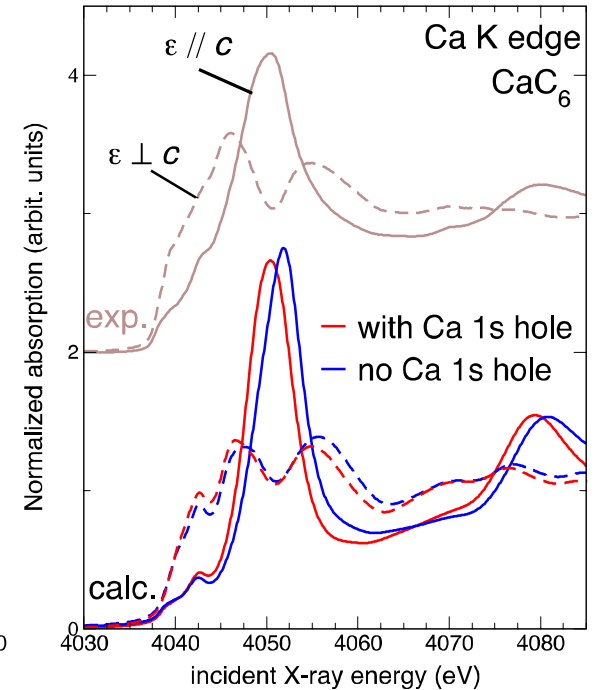
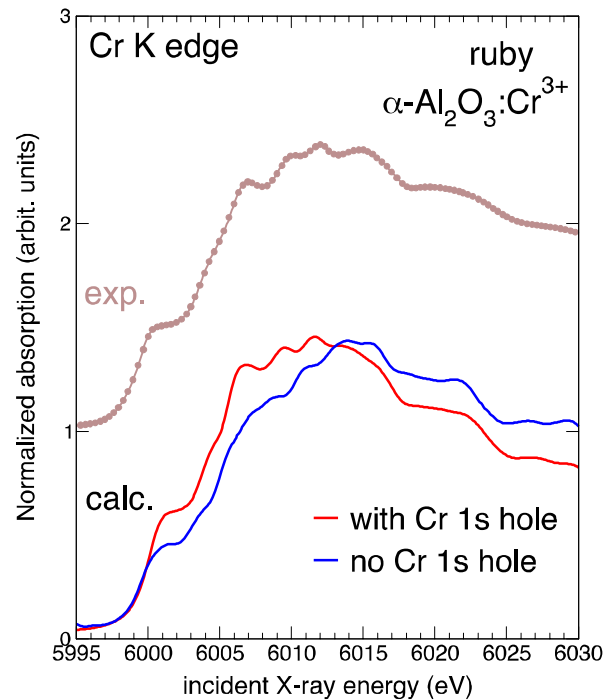
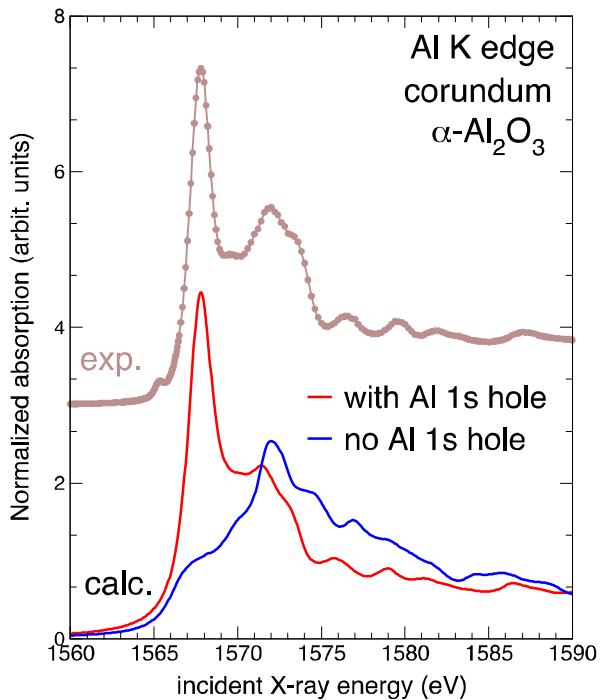


Wilke et al. American Mineralogist, 2001



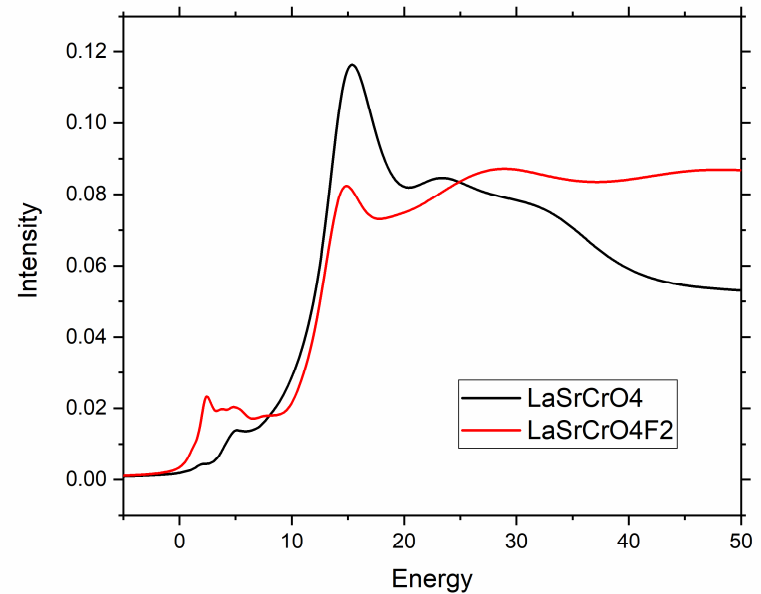
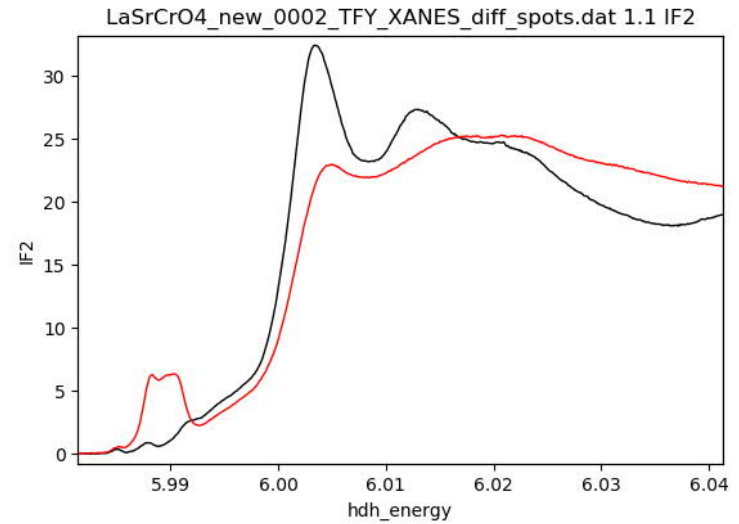
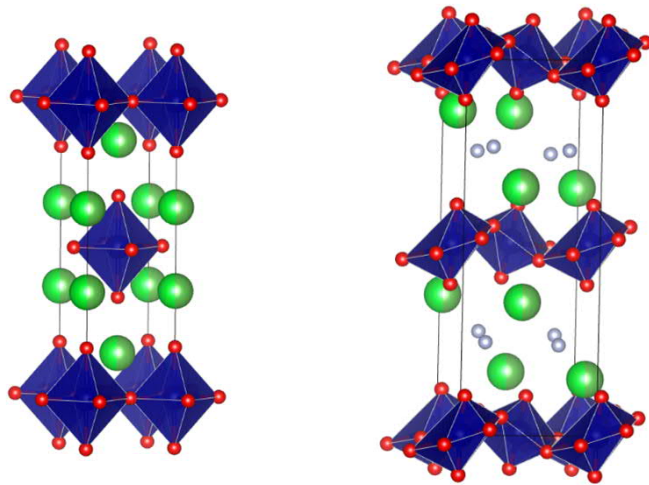
Ti K-edge XANES spectra of titanium oxides containing four- (a), five- (b), and six-coordinated titanium compounds (c).

Geochim. Cosmochim. Acta, **60**, Farges F, Brown GE, Rehr JJ, 3023–3038

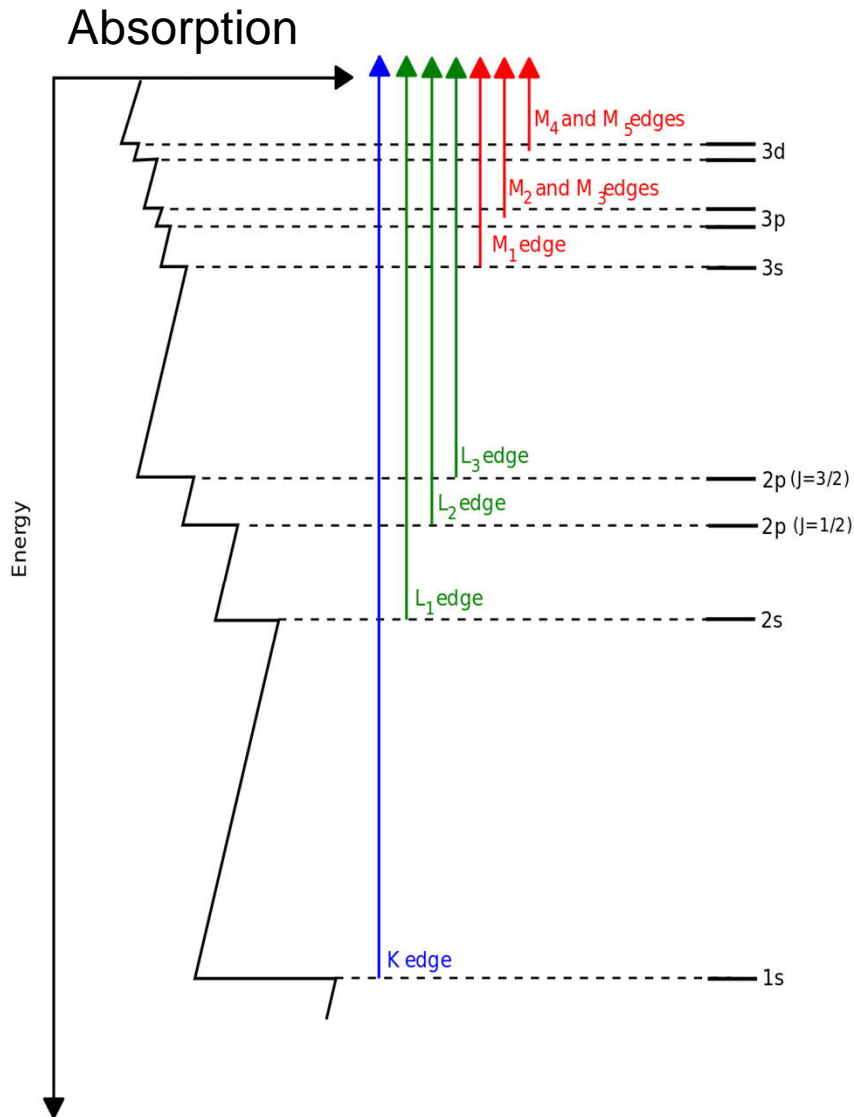


- Some XAS can be modeled using the projected density of states as calculated by DFT.
- The core hole effect may or may not have a strong influence on the spectral shape.

- $\text{LaSrCrO}_4 \rightarrow \text{LaSrCrO}_4\text{F}_2$

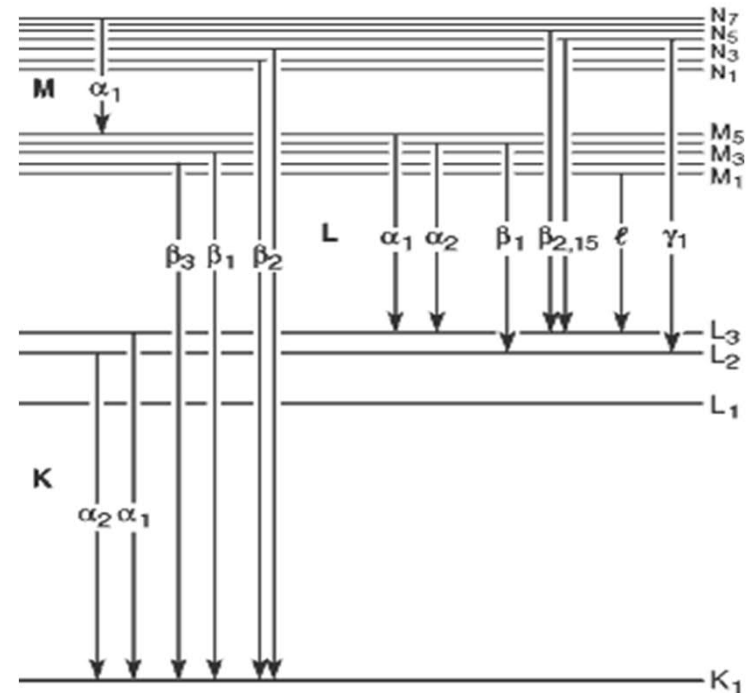


X-RAY ABSORPTION AND EMISSION

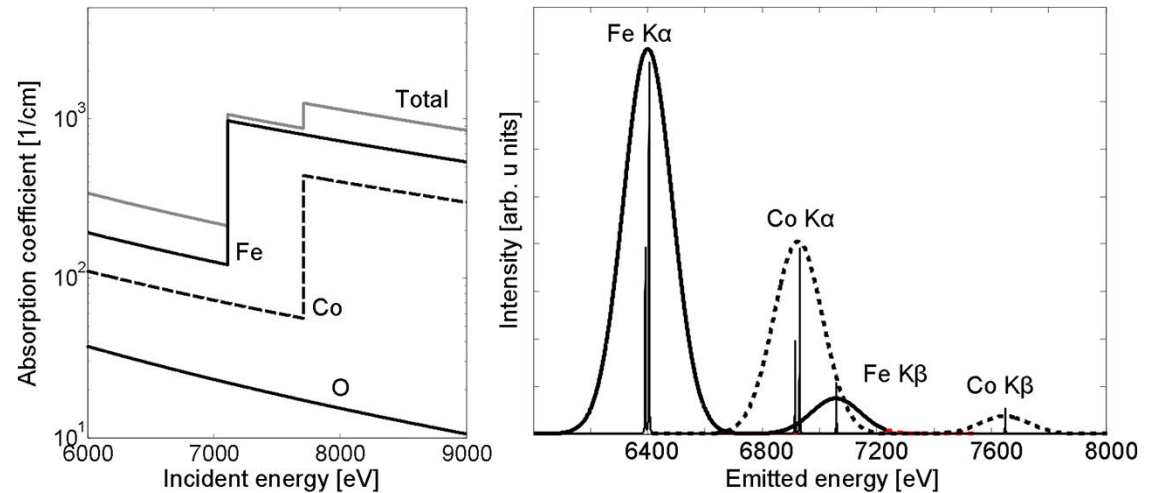


Level	Configuration	Level	Configuration	Level	Configuration
K	$1s^{-1}$	N ₁	$4s^{-1}$	O ₁	$5s^{-1}$
L ₁	$2s^{-1}$	N ₂	$4p_{1/2}^{-1}$	O ₂	$5p_{1/2}^{-1}$
L ₂	$2p_{1/2}^{-1}$	N ₃	$4p_{3/2}^{-1}$	O ₃	$5p_{3/2}^{-1}$
L ₃	$2p_{3/2}^{-1}$	N ₄	$4d_{3/2}^{-1}$	O ₄	$5d_{3/2}^{-1}$
M ₁	$3s^{-1}$	N ₅	$4d_{5/2}^{-1}$	O ₅	$5d_{5/2}^{-1}$
M ₂	$3p_{1/2}^{-1}$	N ₆	$4f_{5/2}^{-1}$	O ₆	$5f_{5/2}^{-1}$
M ₃	$3p_{3/2}^{-1}$	N ₇	$4f_{7/2}^{-1}$	O ₇	$5f_{7/2}^{-1}$
				M ₄	$3d_{3/2}^{-1}$
				M ₅	$3d_{5/2}^{-1}$

Emission



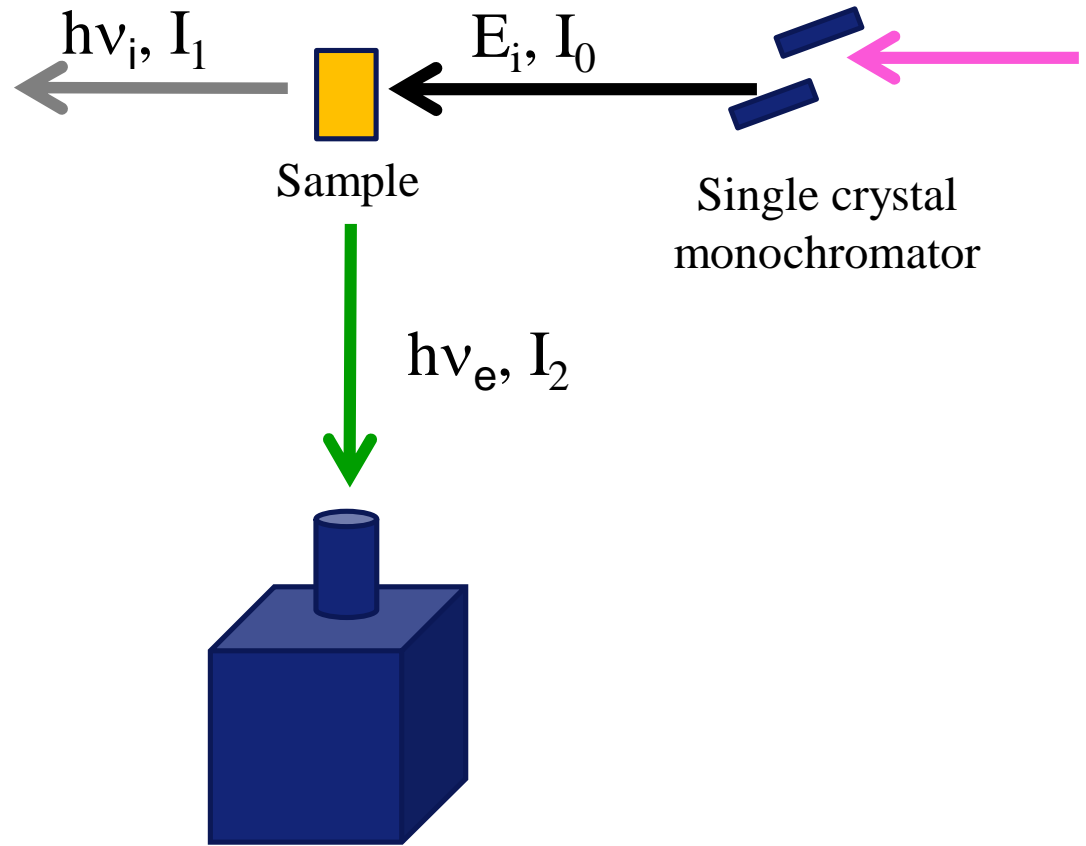
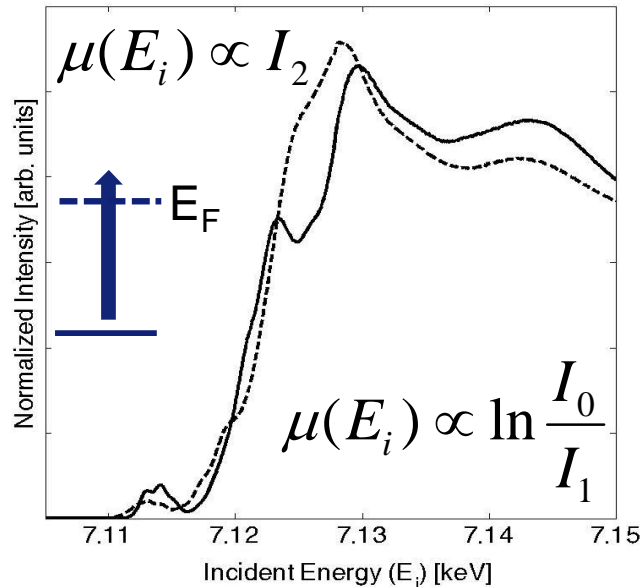
Element specific.



Electronic and atomic structural information
on samples with or without long-range order.

FLUORESCENCE YIELD XAS

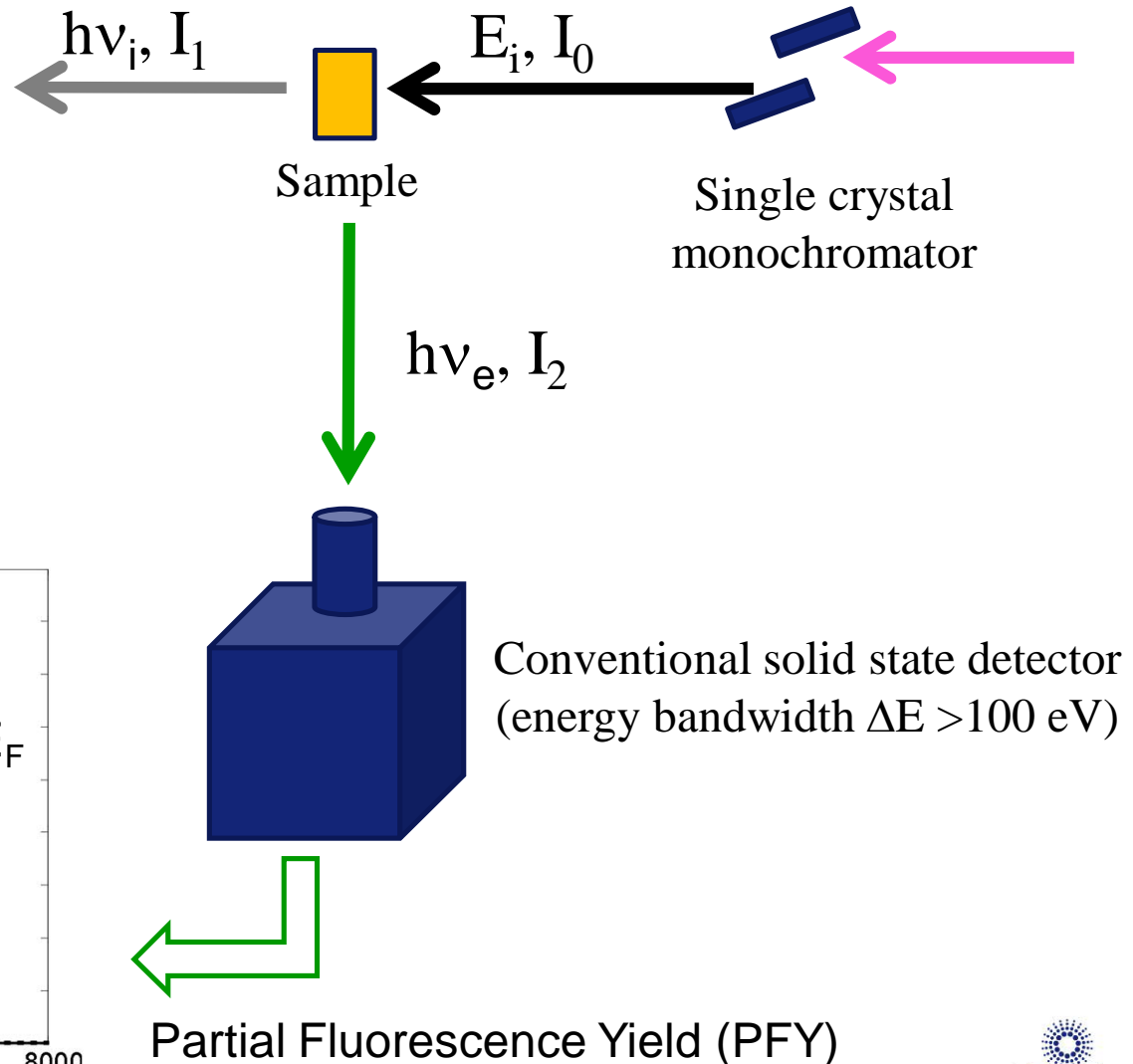
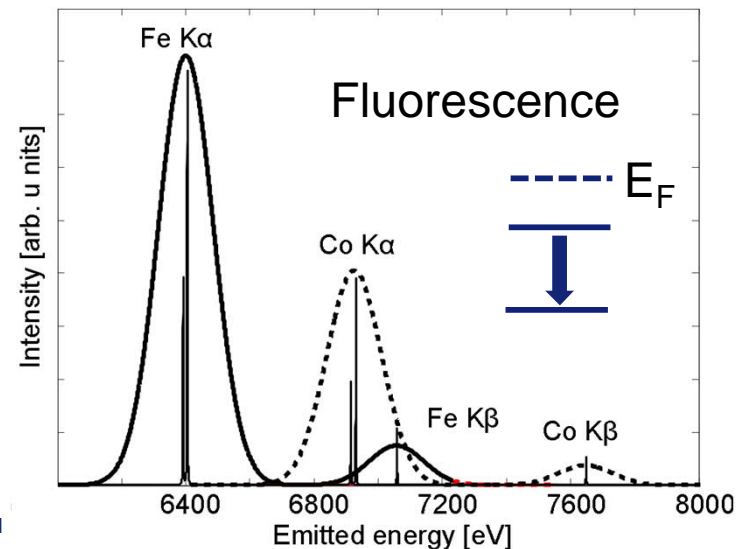
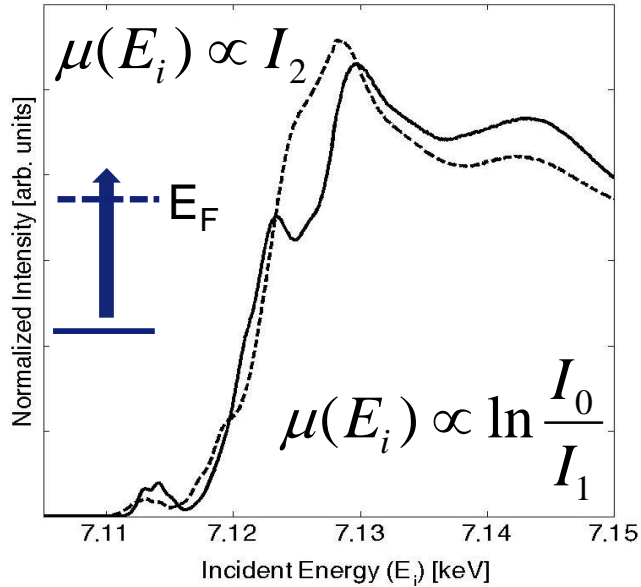
A spectrum is broadened by its natural width Γ (core hole lifetime) and the experimental setup ΔE .



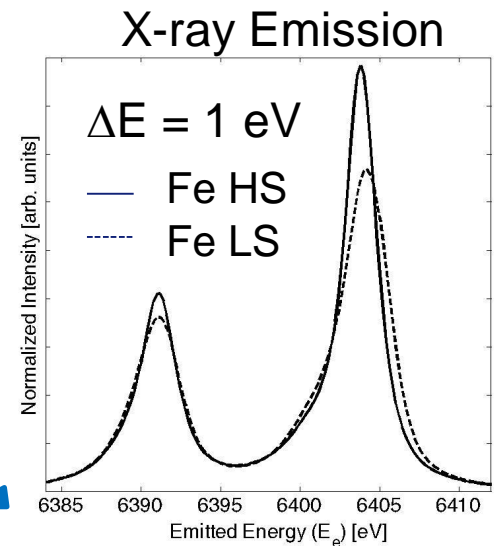
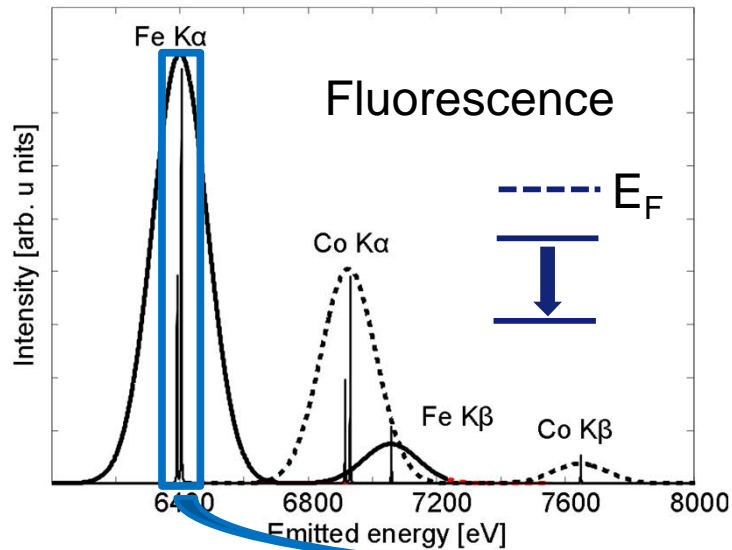
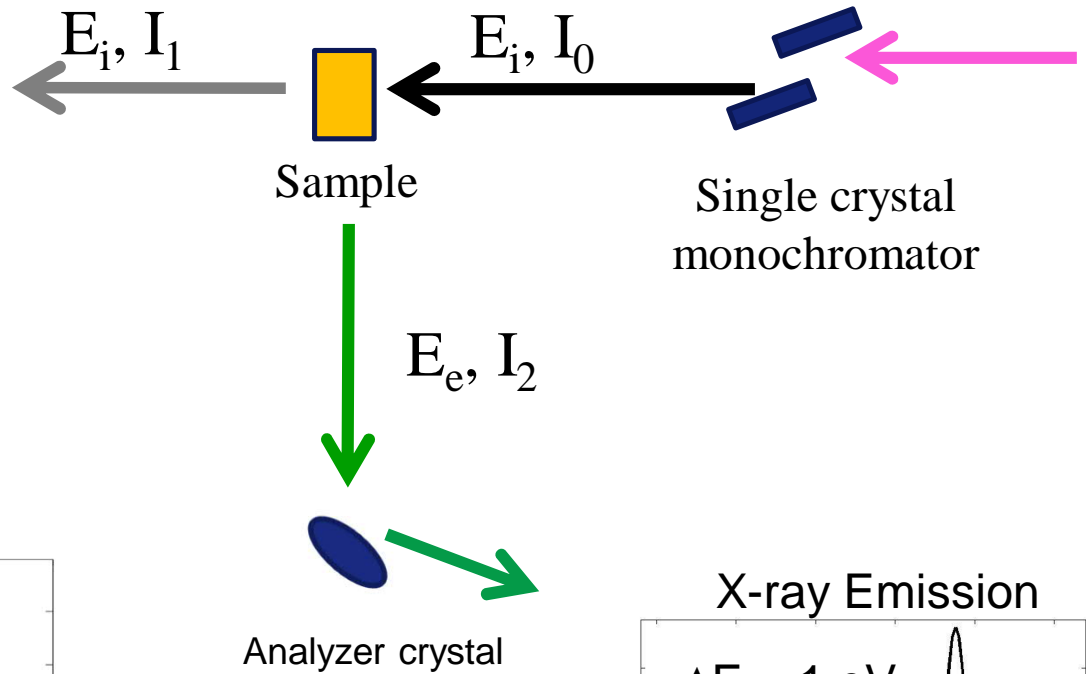
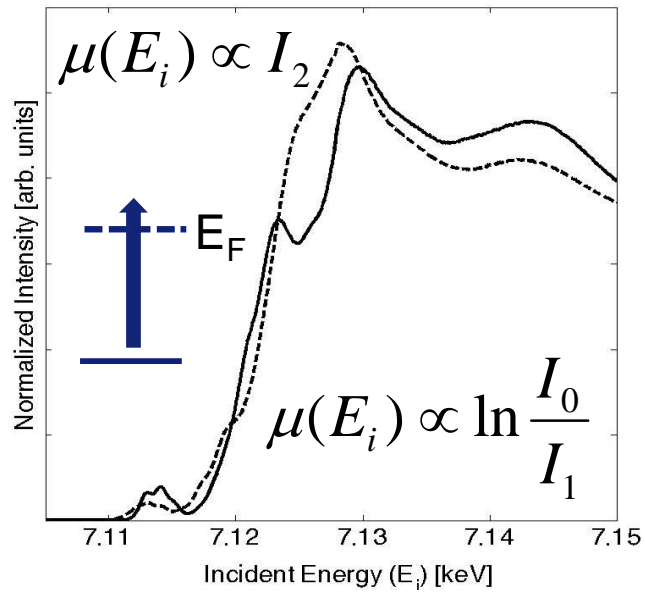
Total Fluorescence Yield (TFY)

EMISSION SPECTROSCOPY

A spectrum is broadened by its natural width Γ (core hole lifetime) and the experimental setup ΔE .



EMISSION SPECTROSCOPY

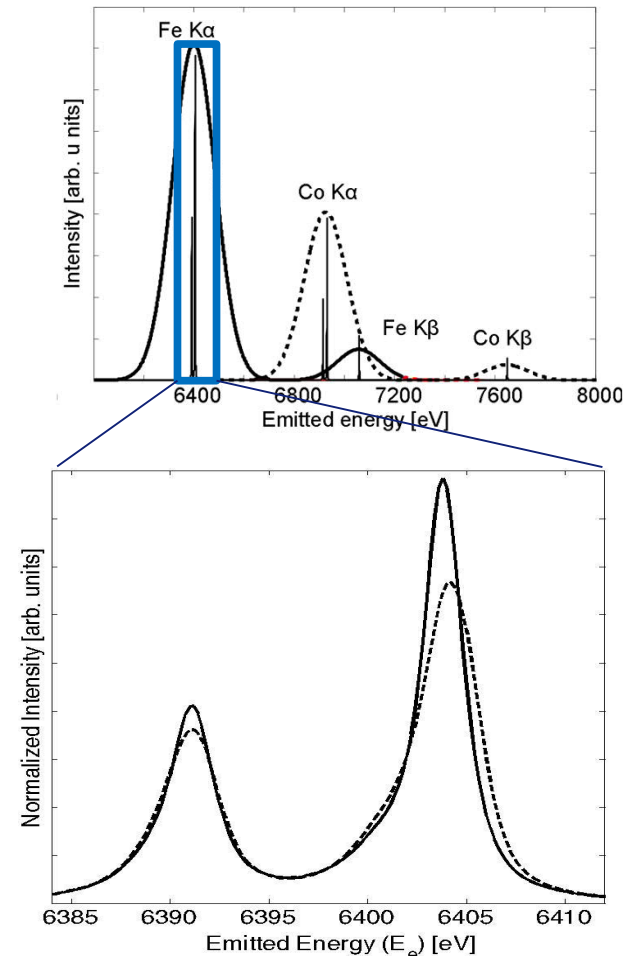


Low energy resolution spectroscopy ($\Delta E \gg \Gamma$)

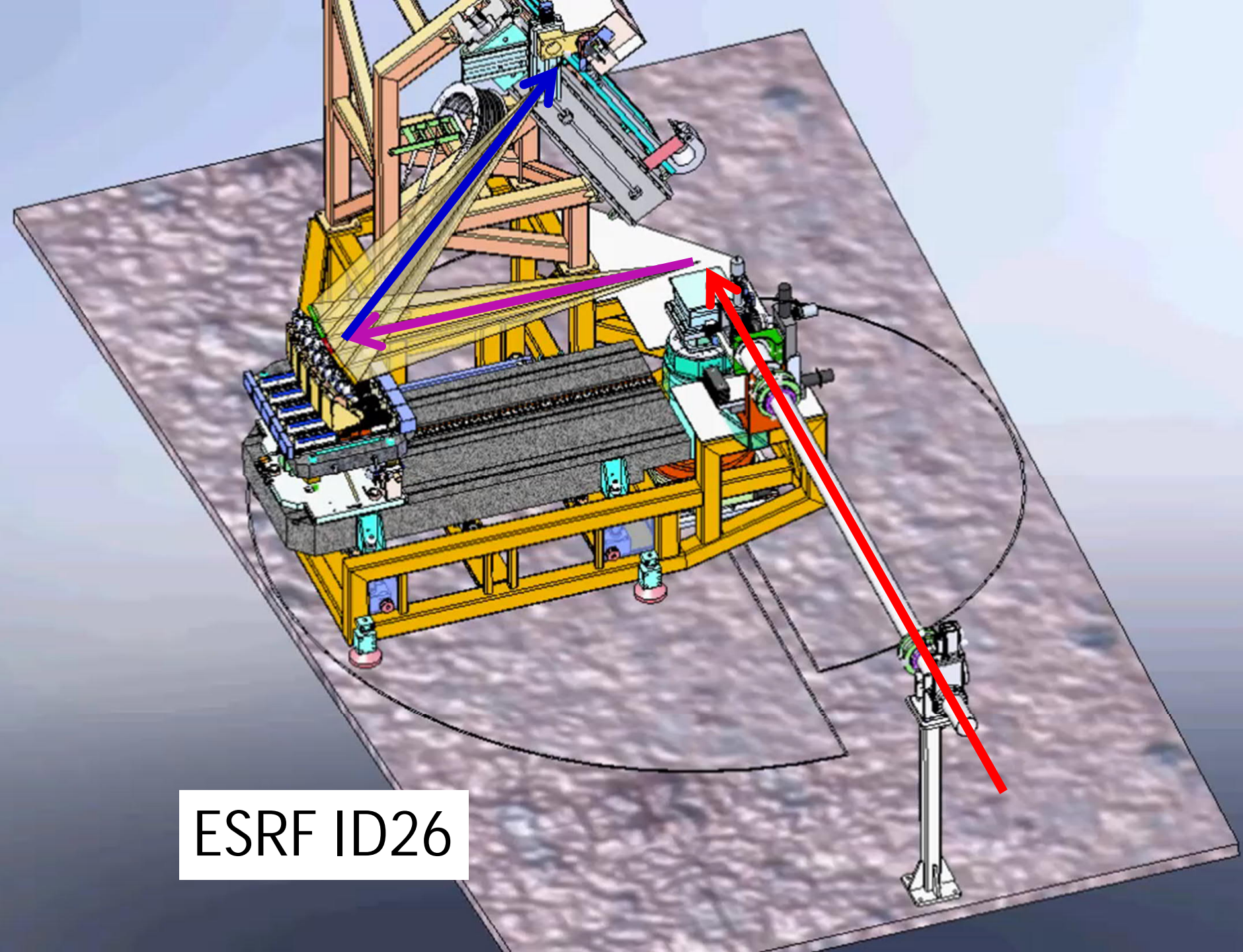
- Elemental composition because the energies of absorption and emission lines depend on the atomic number (element-selectivity).

High energy resolution spectroscopy ($\Delta E \sim \Gamma$ or very small)

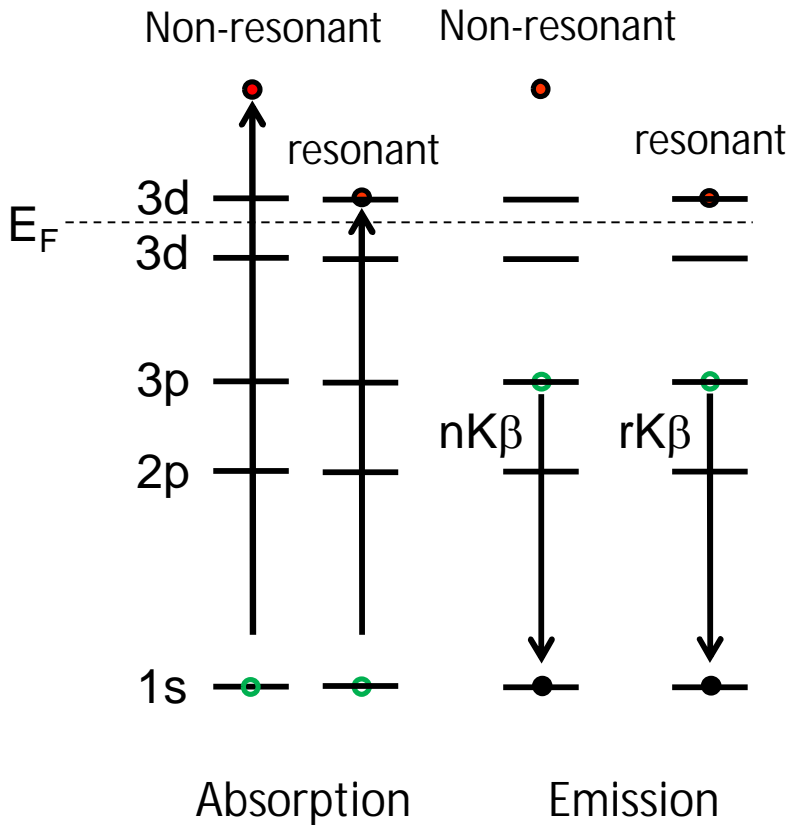
- Local atomic configuration
- Electronic structure
 - band structure
 - oxidation state
 - spin state
 - Chemical bond and coordination
 - Magnetic properties
- Kinetics
- Vibrational properties/phonons in solids
- ...



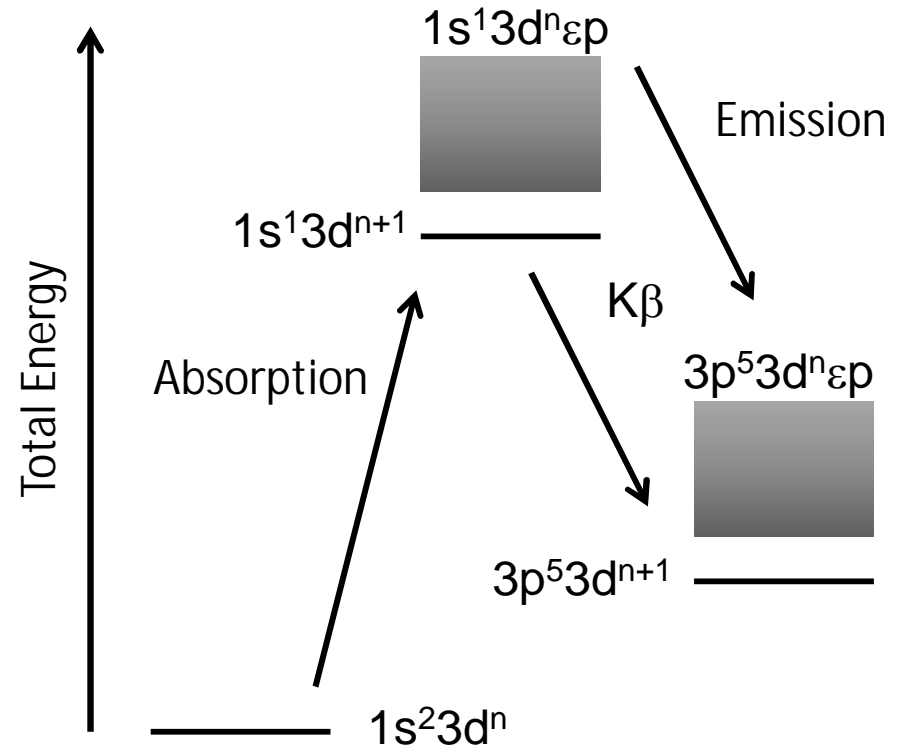
ESRF ID26



Two ways of describing the same process.

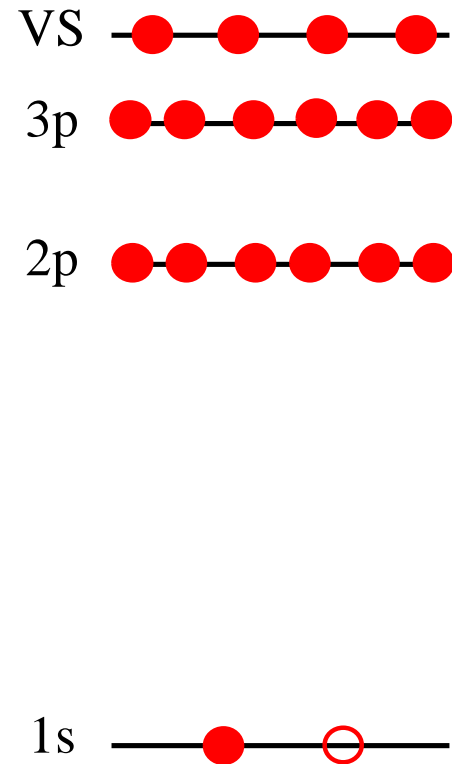
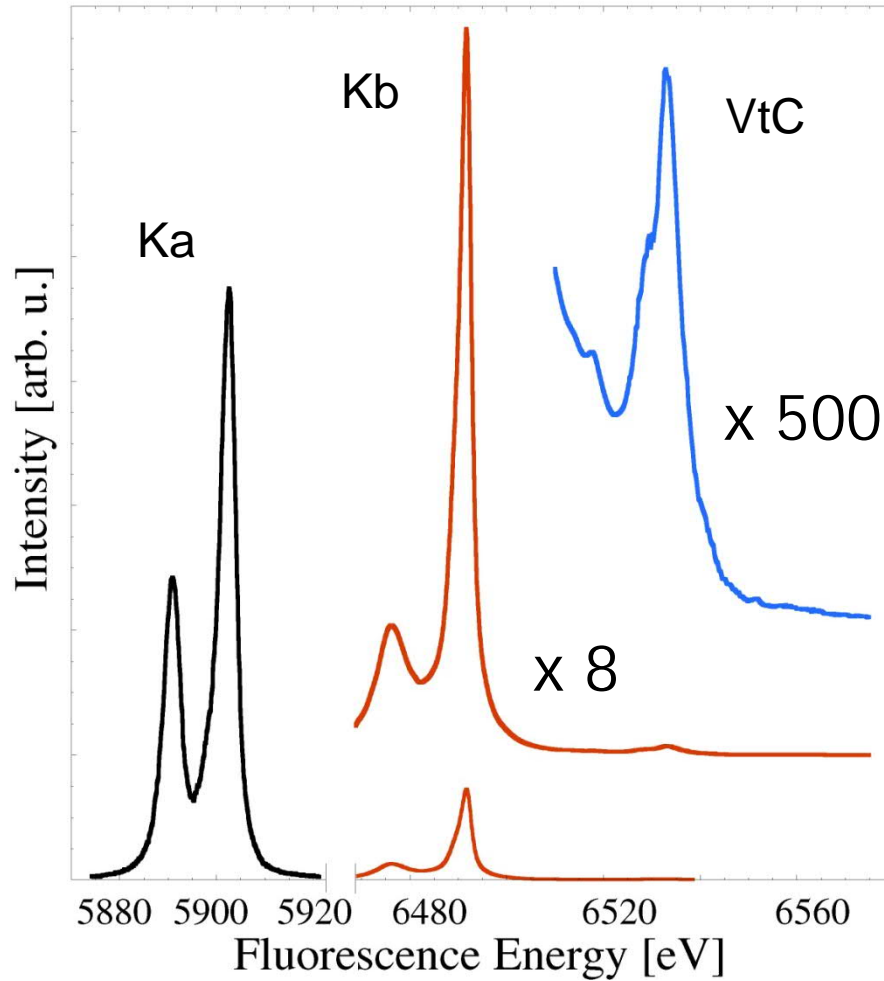


One-electron diagram



Many body diagram: Observes energy conservation

EMISSION LINES



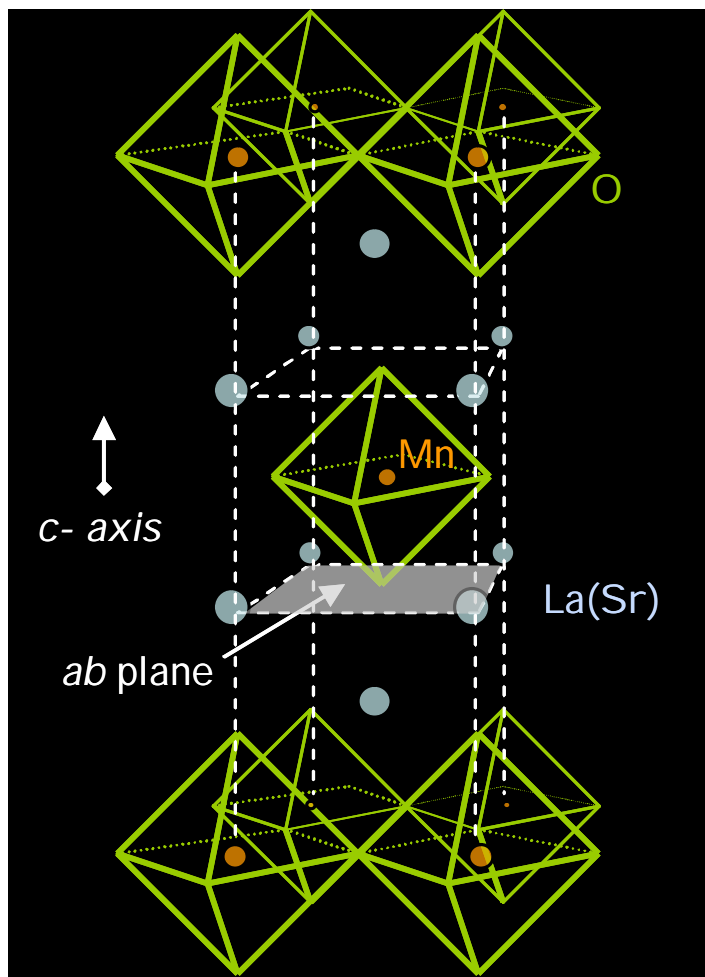
XES is less sensitive to atomic structural changes than XANES



XES can be used to study electronic structure

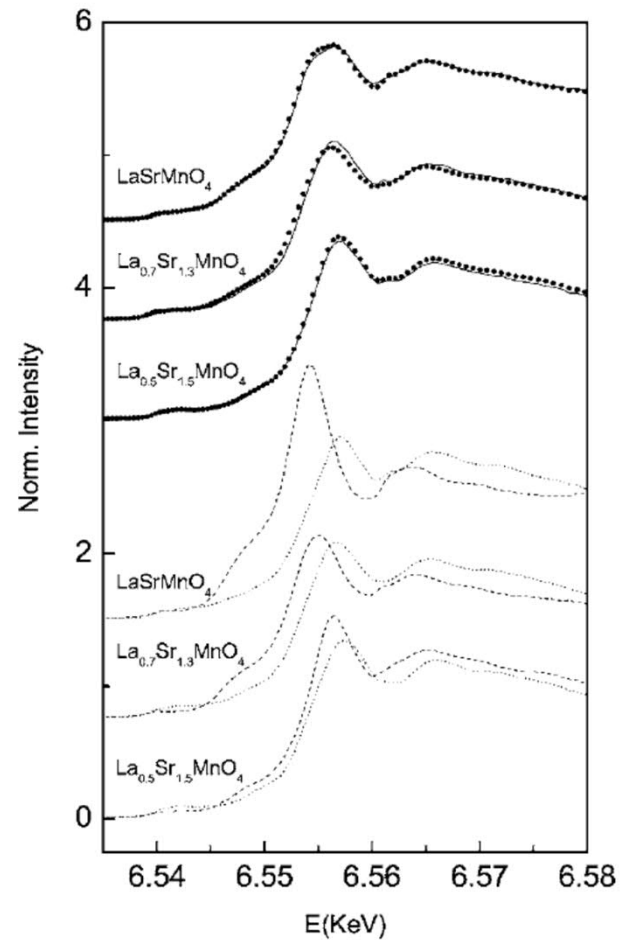
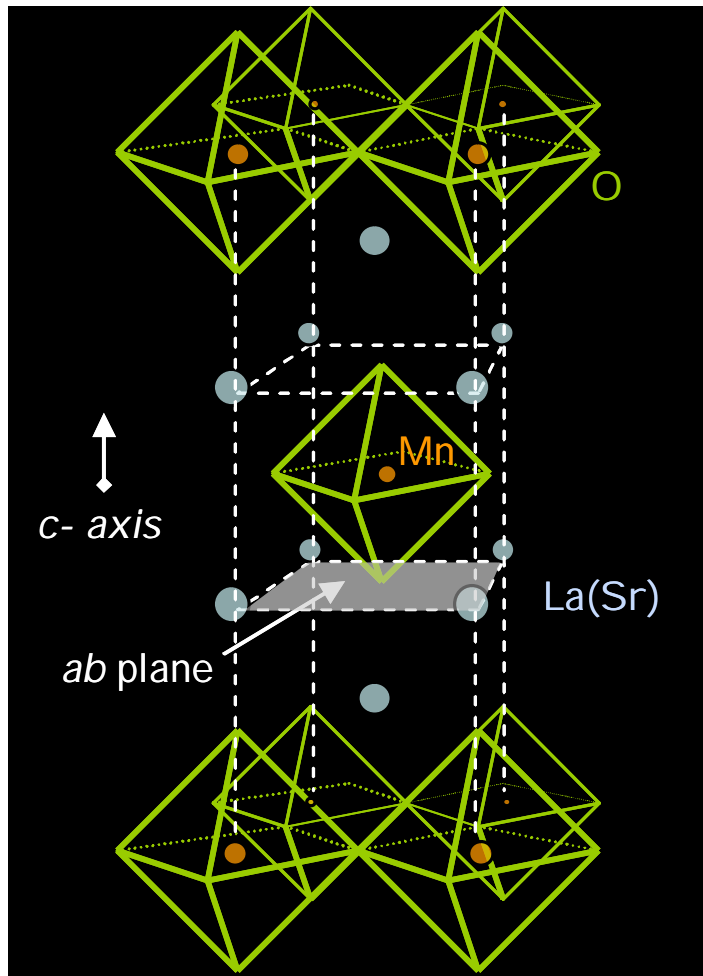
However...

In comparison with XANES, XES can be used to separate the electronic and atomic effects

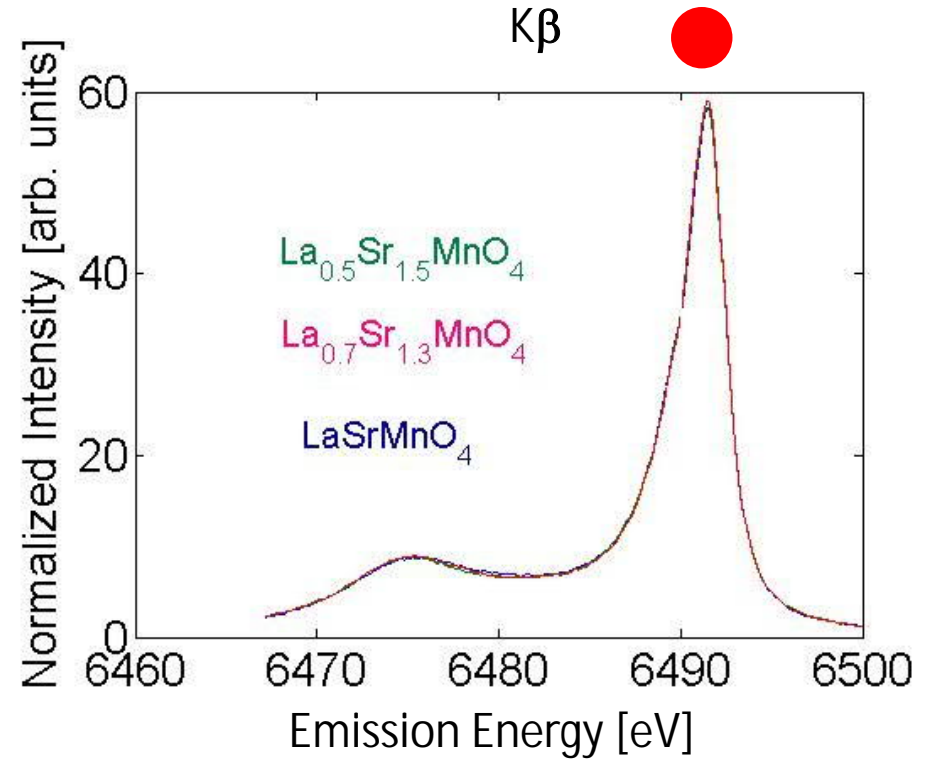
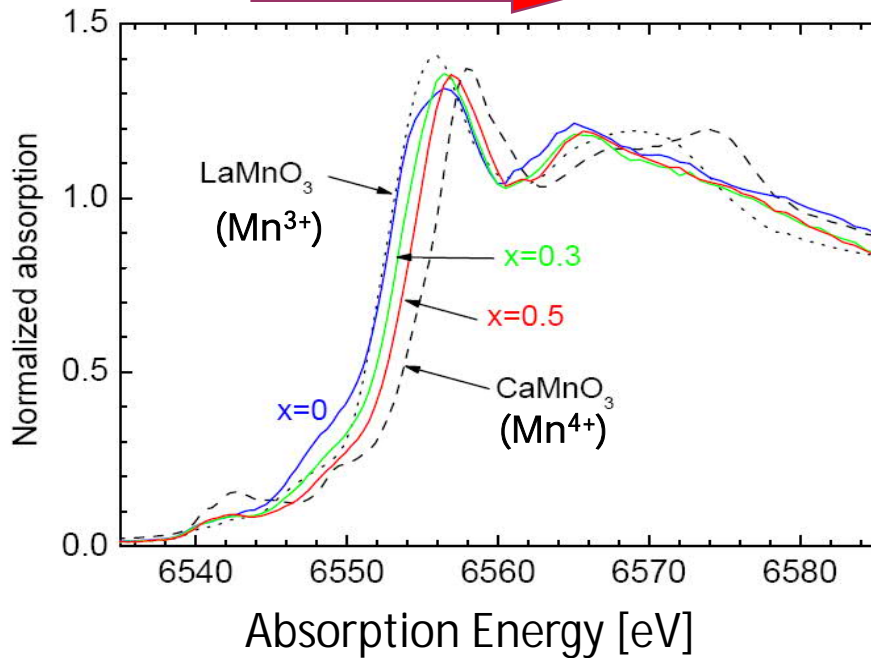
The $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ series: doping dependence


MnO₆ local **anisotropy** is large and inversely proportional to hole content

	<u>N</u>	<u>r (Mn-O) (Å)</u>	
LaSrMnO_4	4	1.90(1)	x=0
	2	2.27(3)	
$\text{La}_{0.7}\text{Sr}_{1.3}\text{MnO}_4$	4	1.92(1)	x=0.3
	2	2.05(2)	
$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$	4	1.92(1)	x=0.5
	2	1.98(1)	

The $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ series: doping dependence


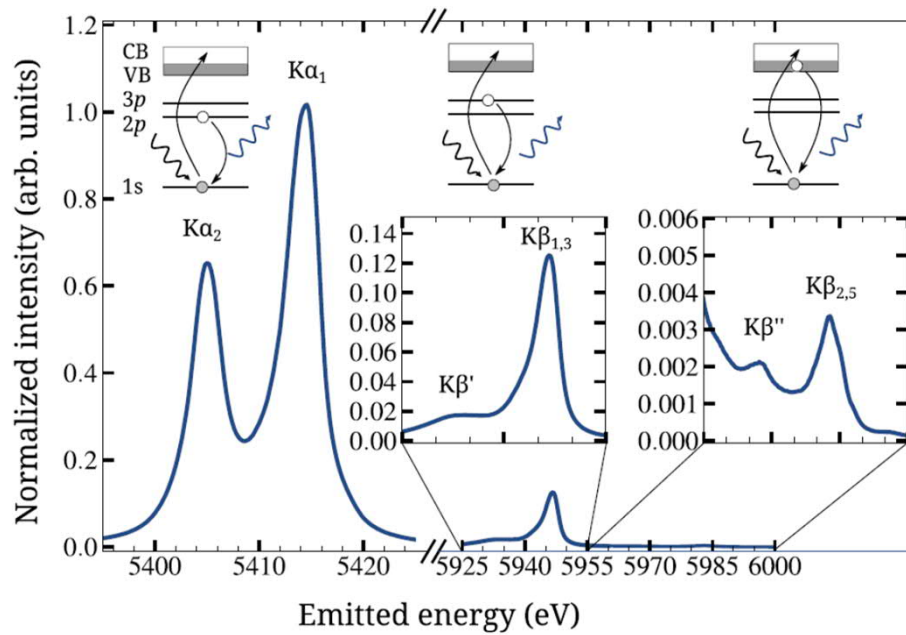
X XANES

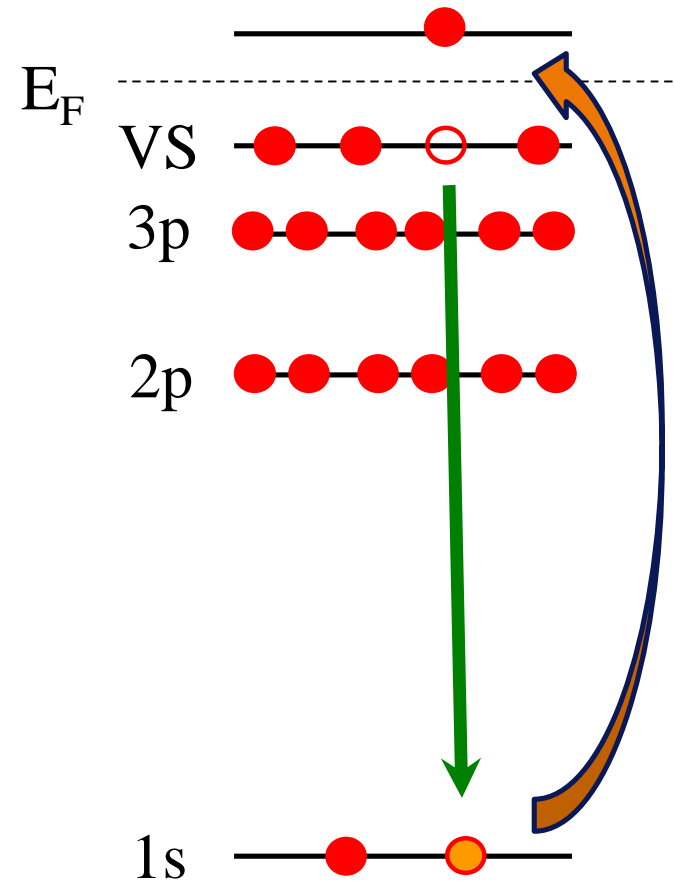
Replace La³⁺ by Sr²⁺ → Formally: Mn³⁺ → Mn^{3.5+}

XANES changes, Kβ invariant.

XANES shift due to structural changes! Angle-integrated electron density unchanged.

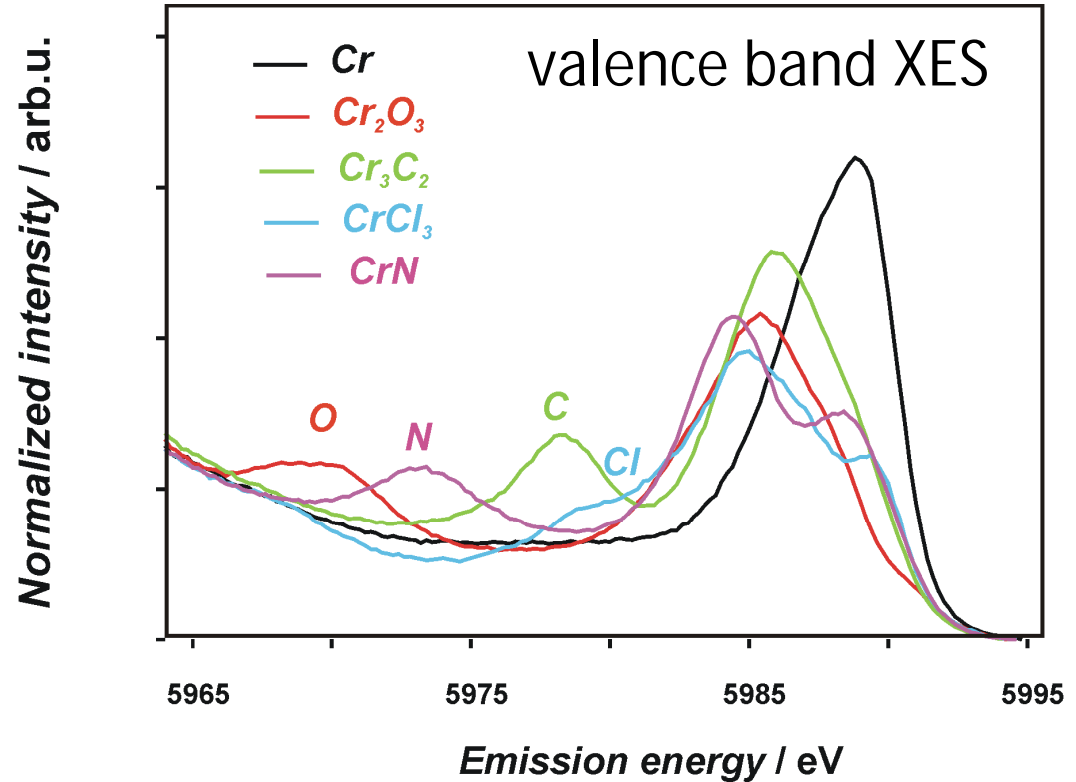
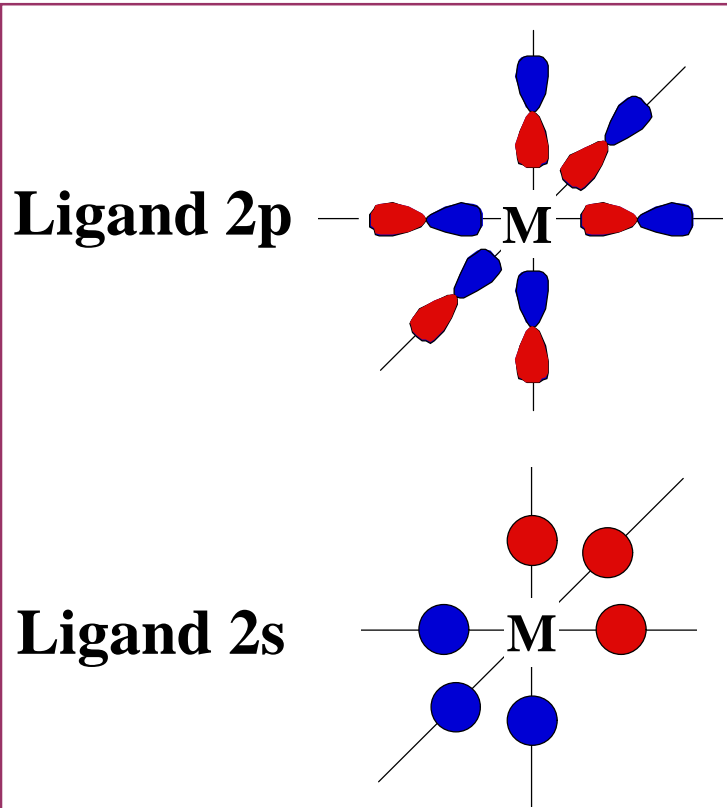


Valence to core (vtc)

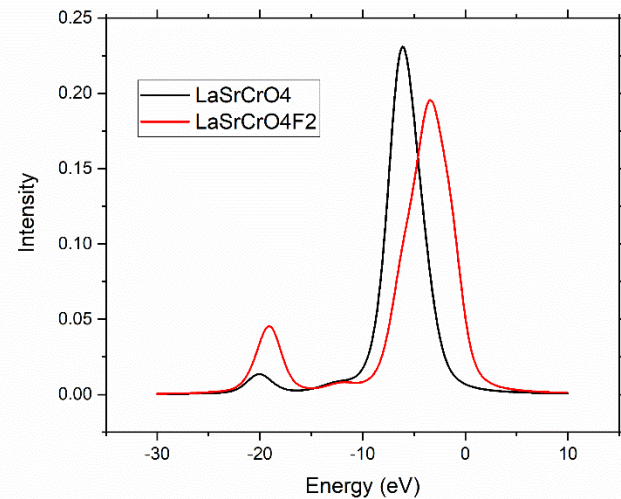
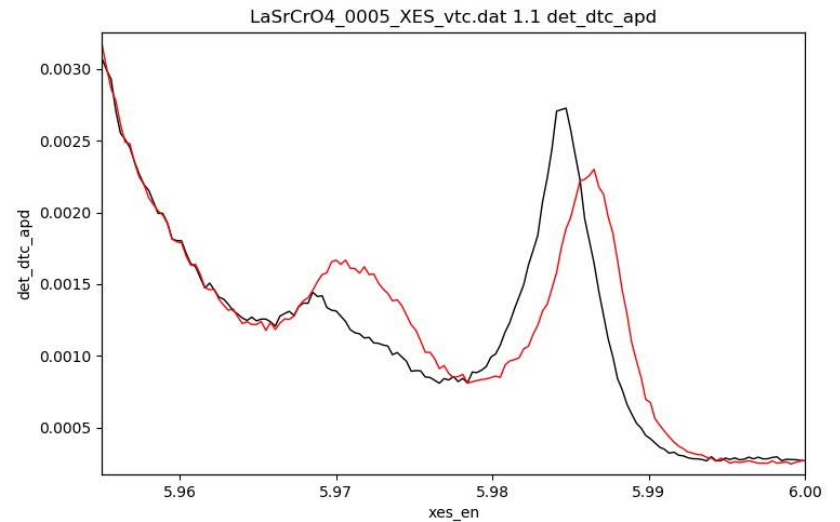
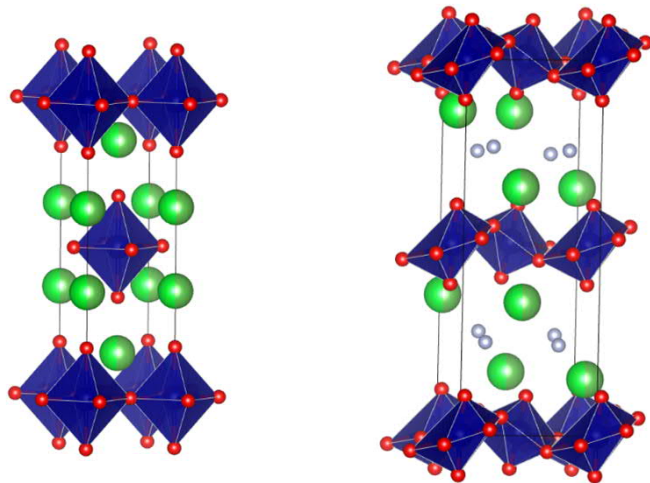


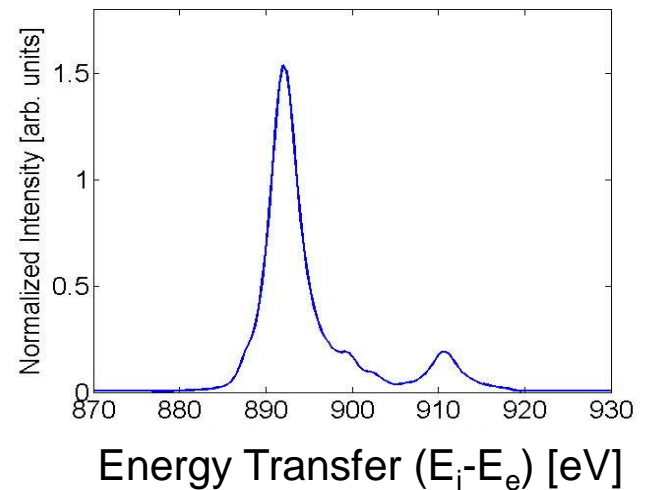
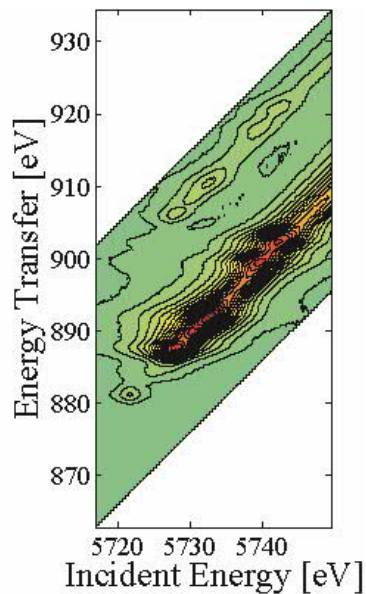
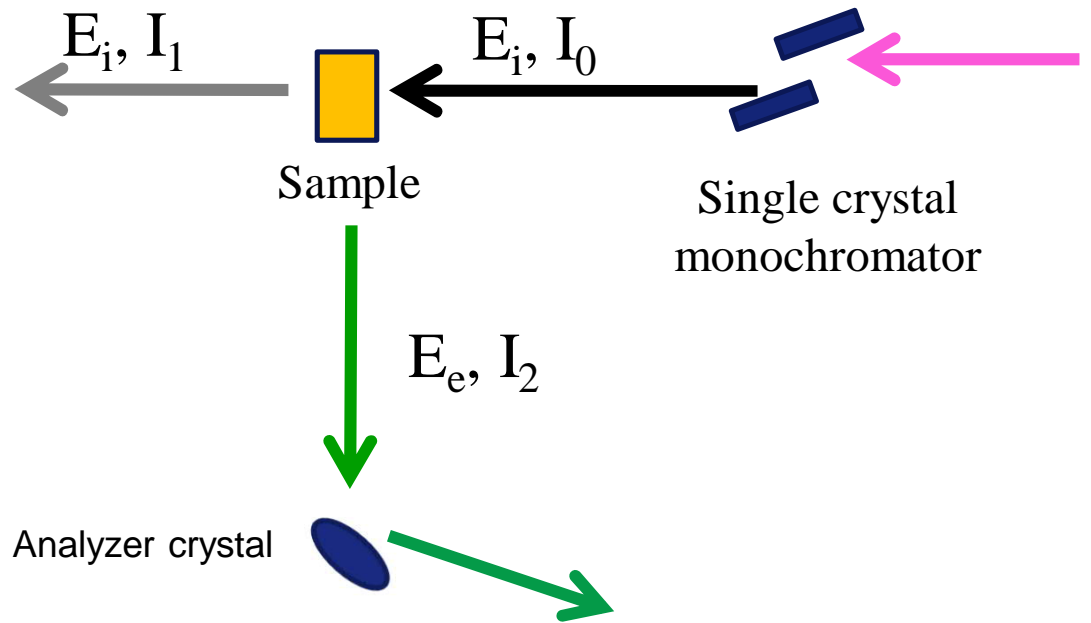
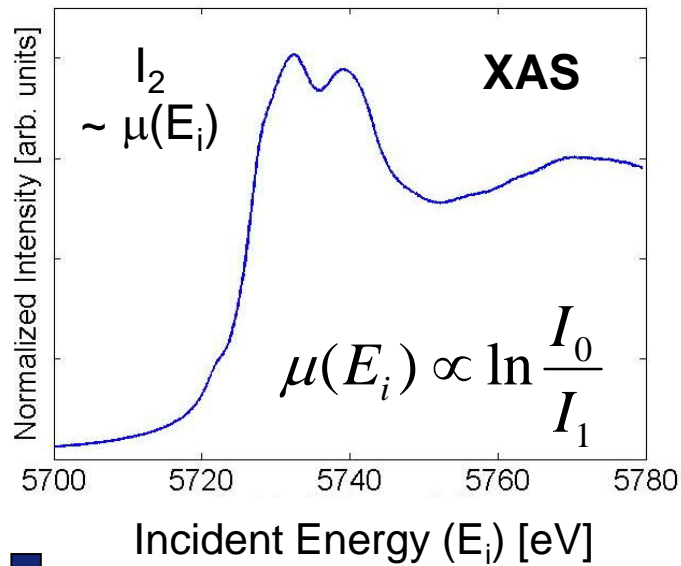
Mainly sensitive to orbitals that are centered on ligands.

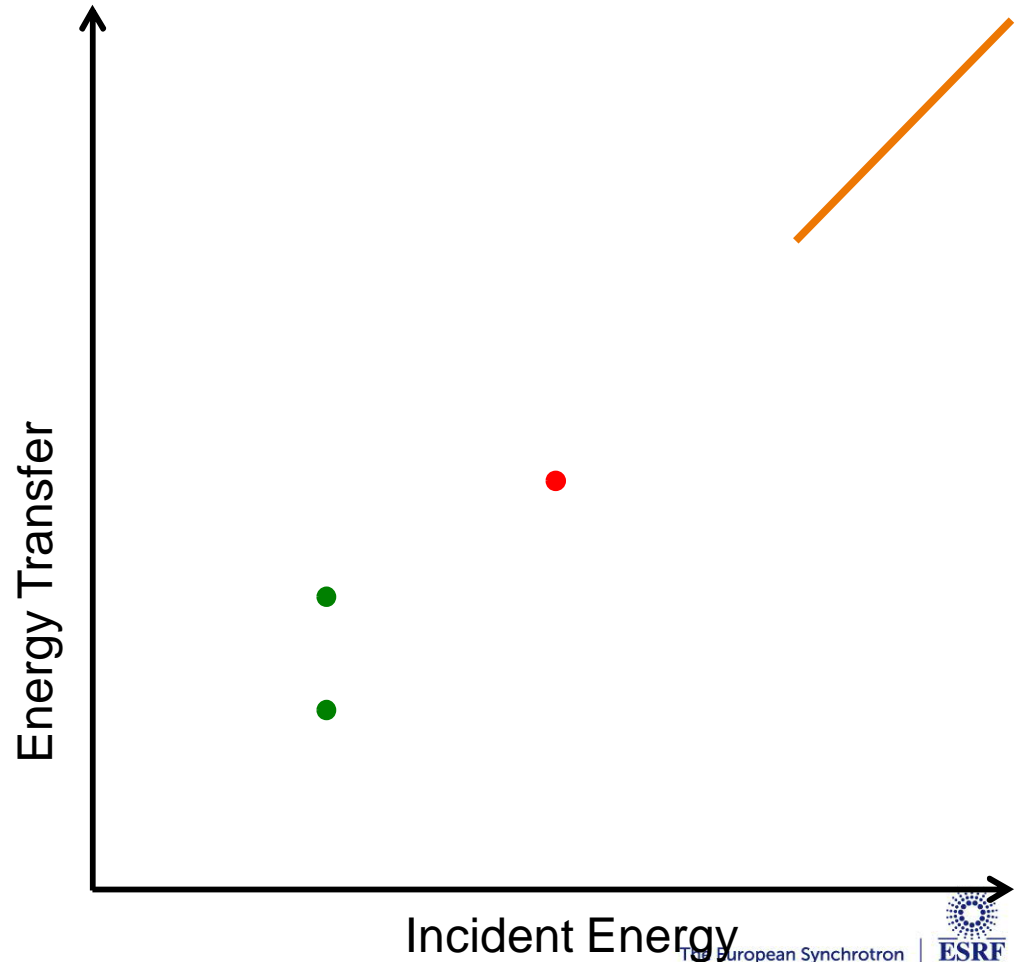
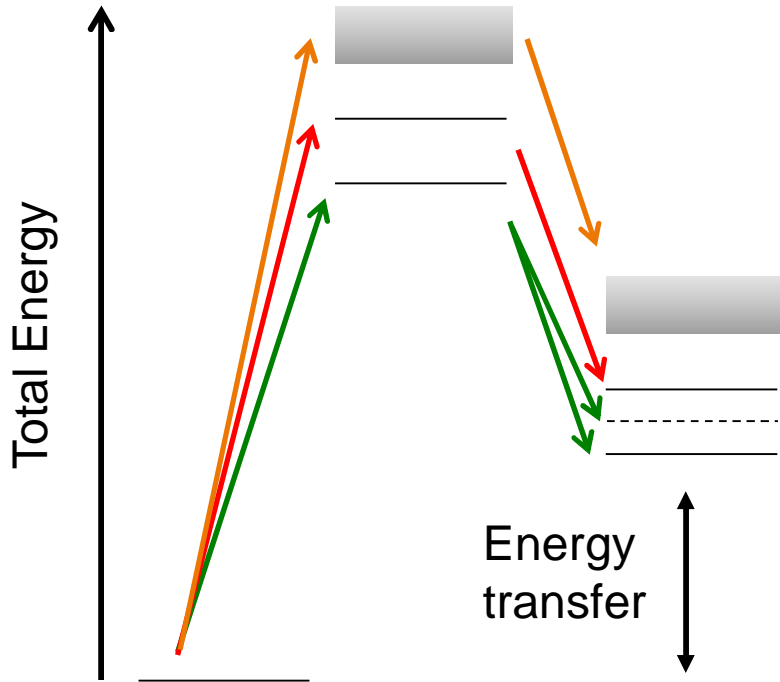
Transitions from:



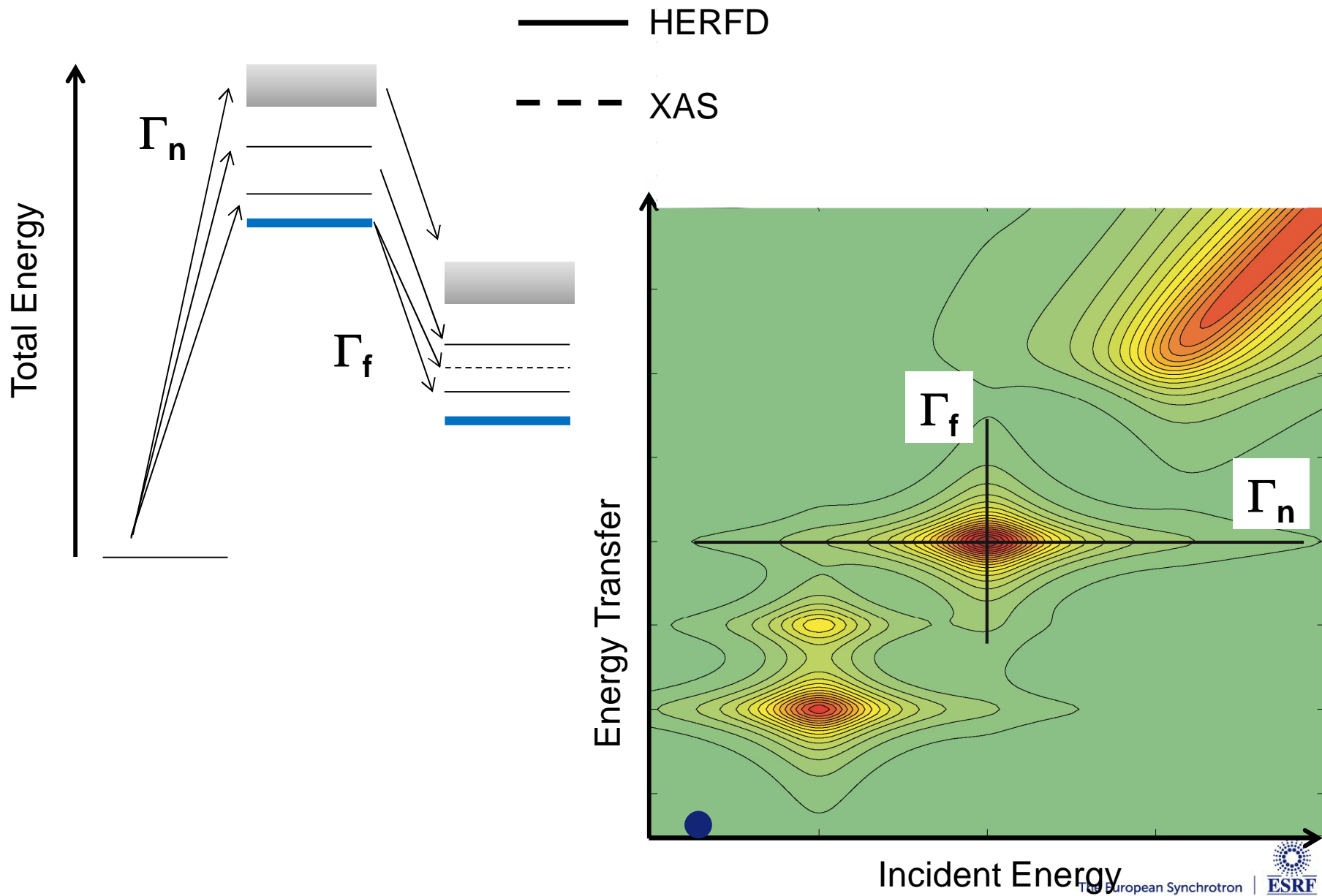
- $\text{LaSrCrO}_4 \rightarrow \text{LaSrCrO}_4\text{F}_2$

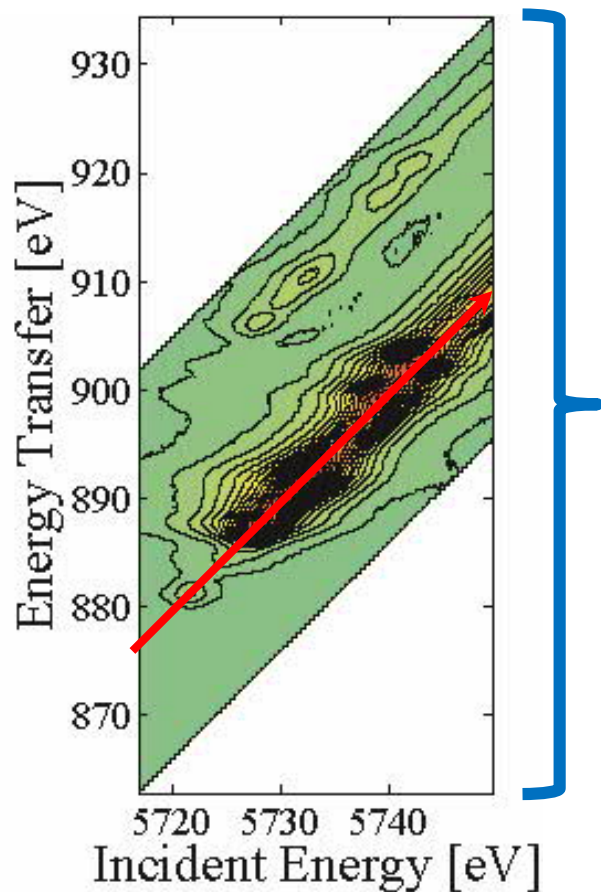




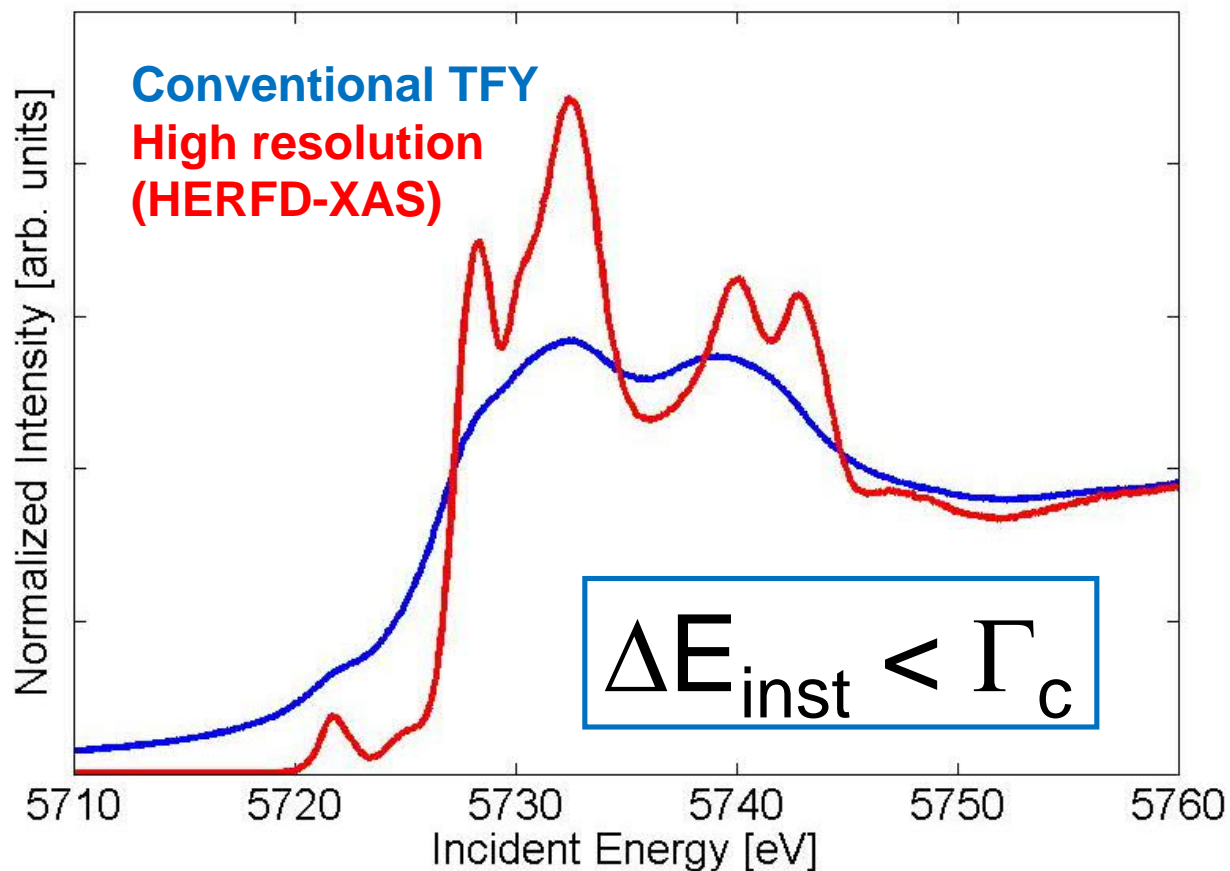


RIXS PROCESS

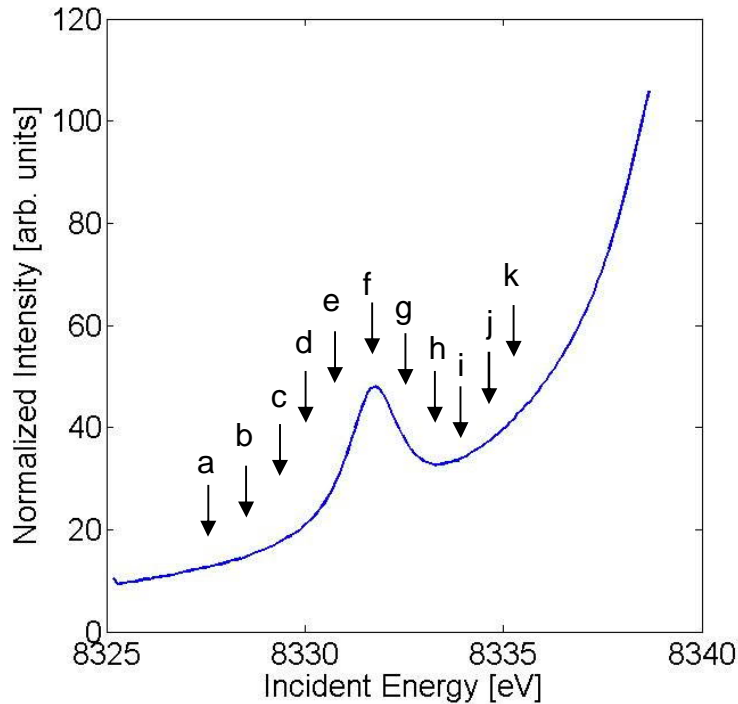




Fine structure of 5d band

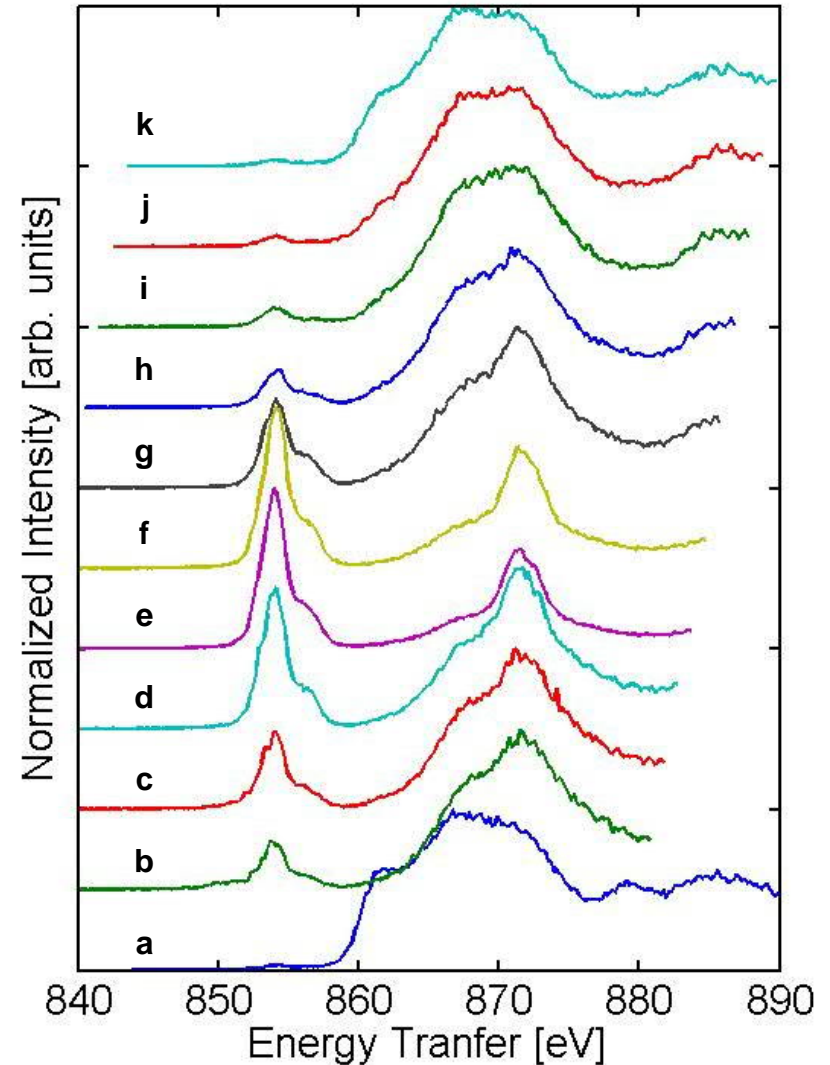


K pre-edge in NiF₂

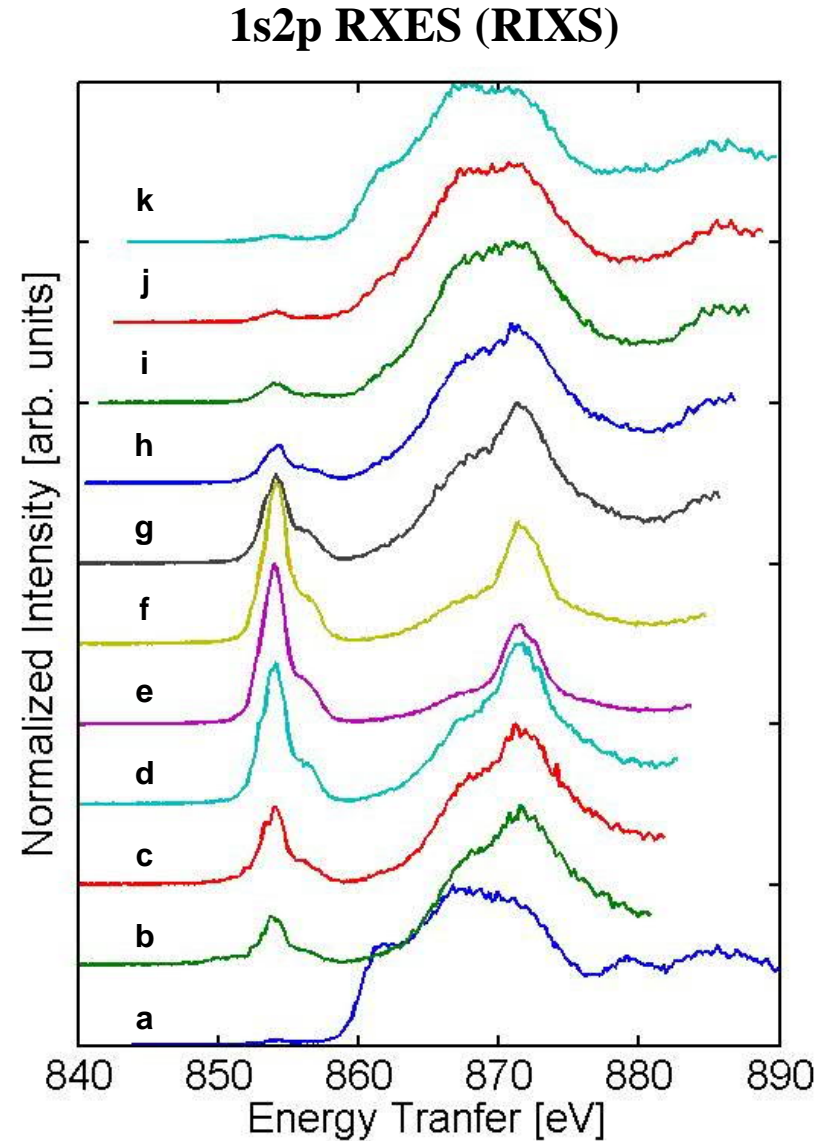
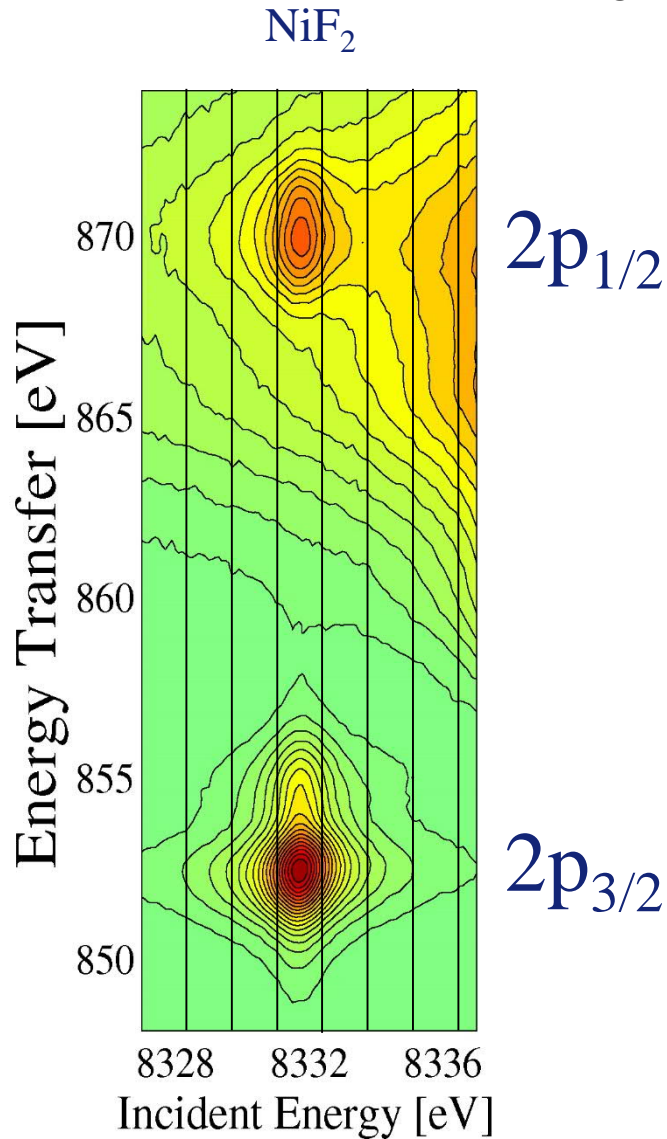


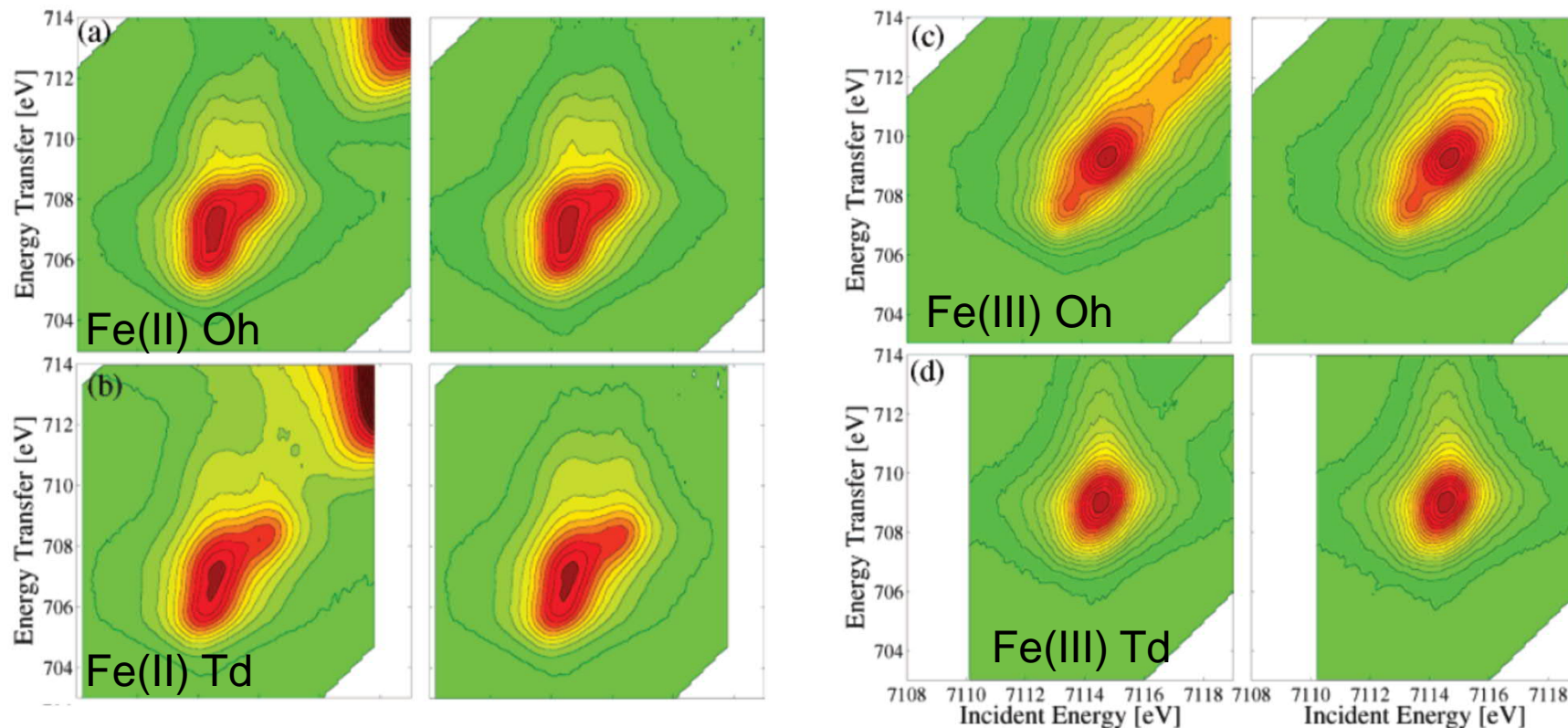
Often, RIXS is shown as line plots with the scattered intensity versus the energy transfer or final state energy. The incident energy must be indicated with each RIXS scan.

1s2p RXES (RIXS)

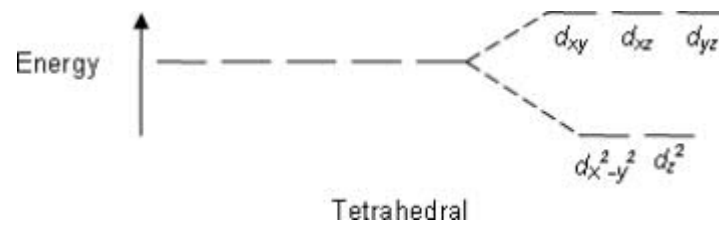
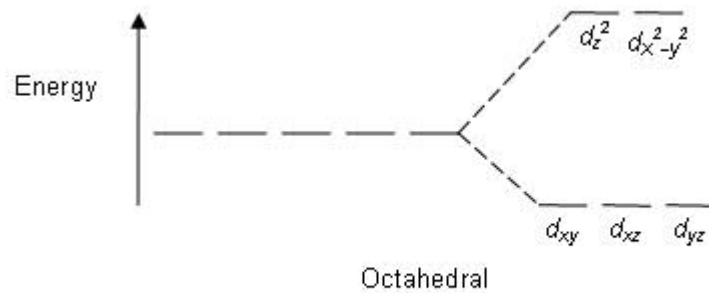


The two figures show the same thing.

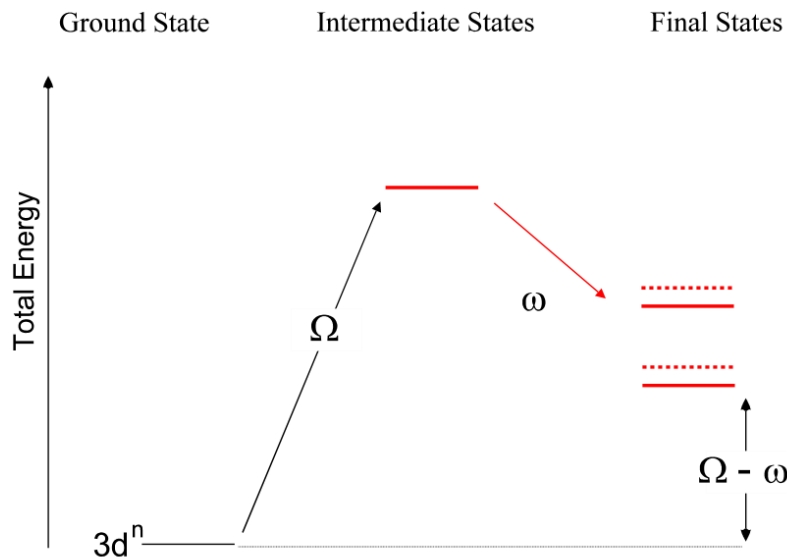
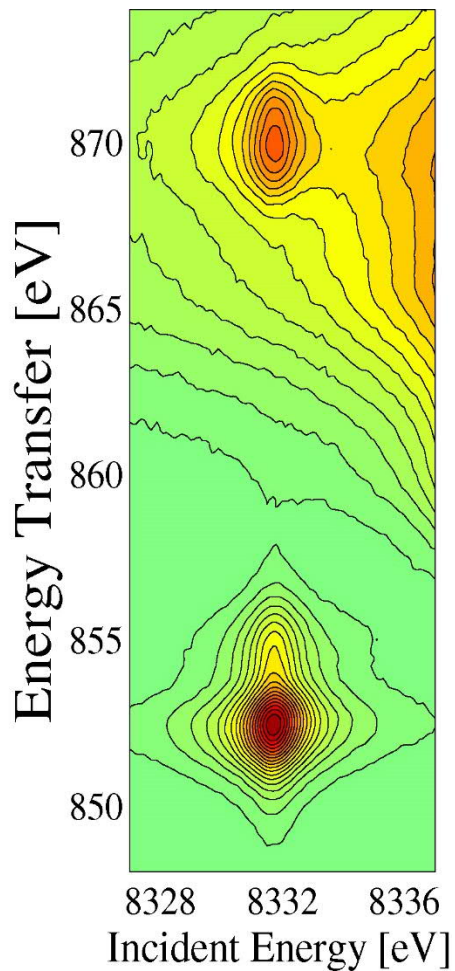




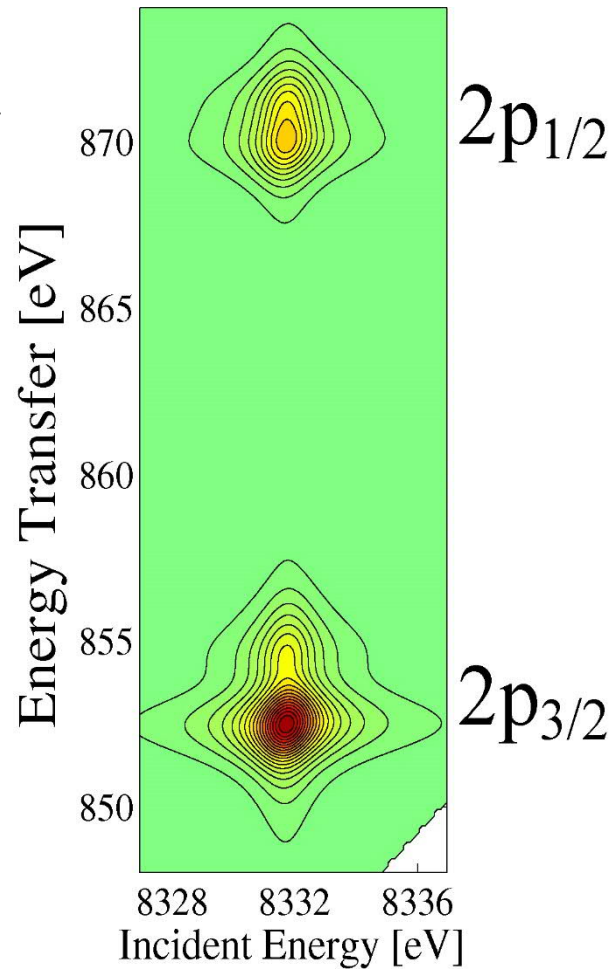
Experimental $1s2p_{3/2}$ RIXS spectrum, given as a contour plot with identical energy scales. The K main edge was subtracted in the plots on the right. The red (dark) area relates to the peak maximum. From top to bottom are, respectively, (a) FeAl_2O_4 , (b) Fe_2SiO_4 , (c) Fe_2O_3 , and (d) FePO_4 . *J. Phys. Chem. B* **2005**, *109*, 20751-20762



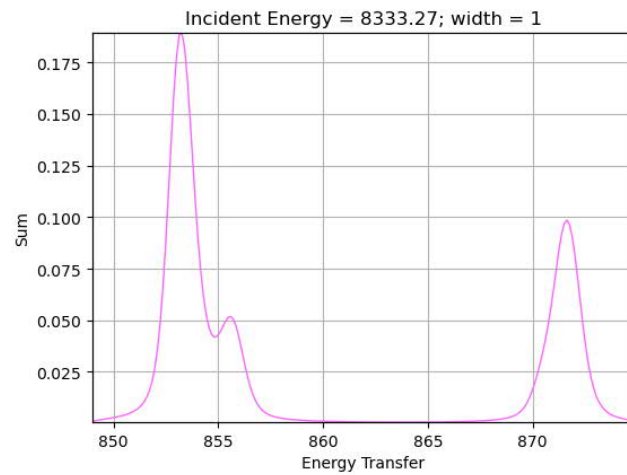
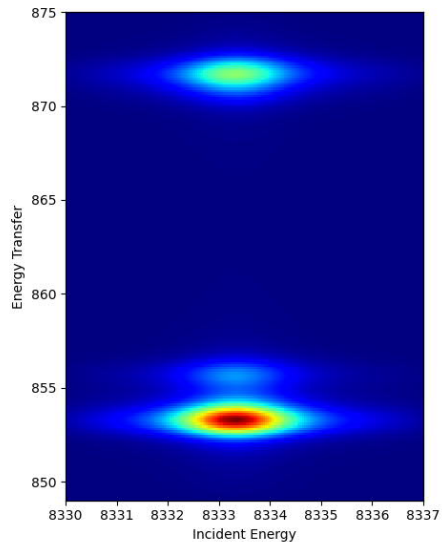
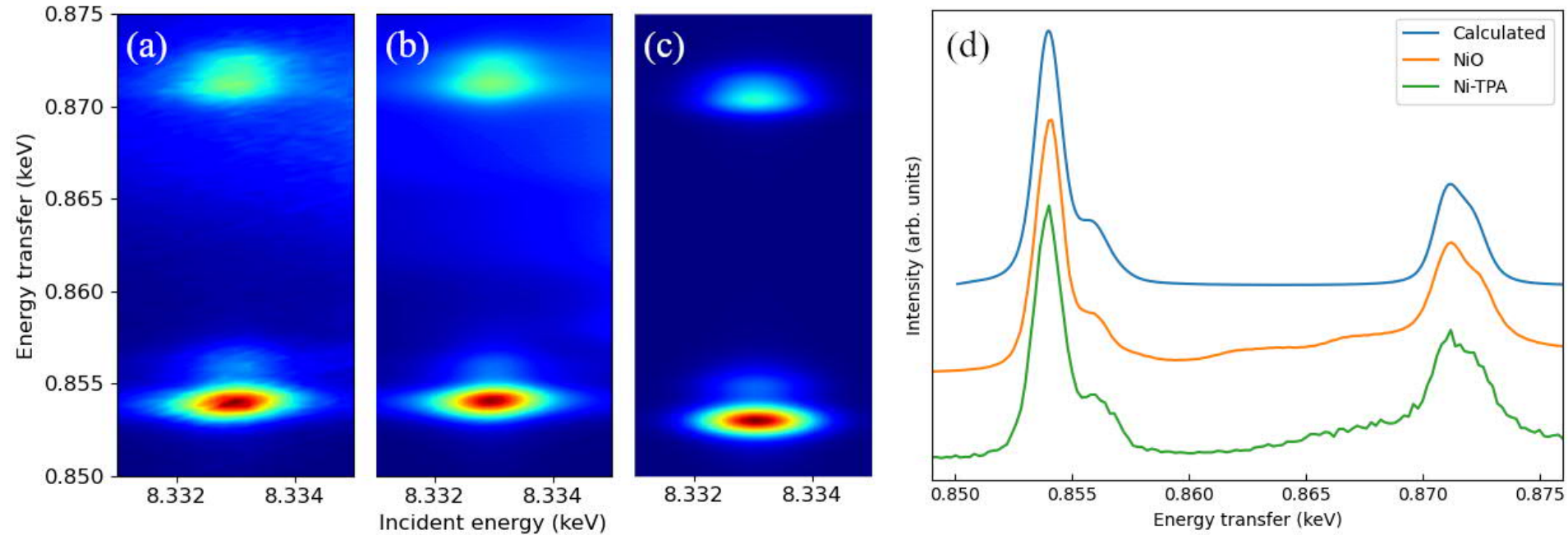
Experiment



Theory



NICKEL LOCAL COORDINATION



Thank you!
Questions?