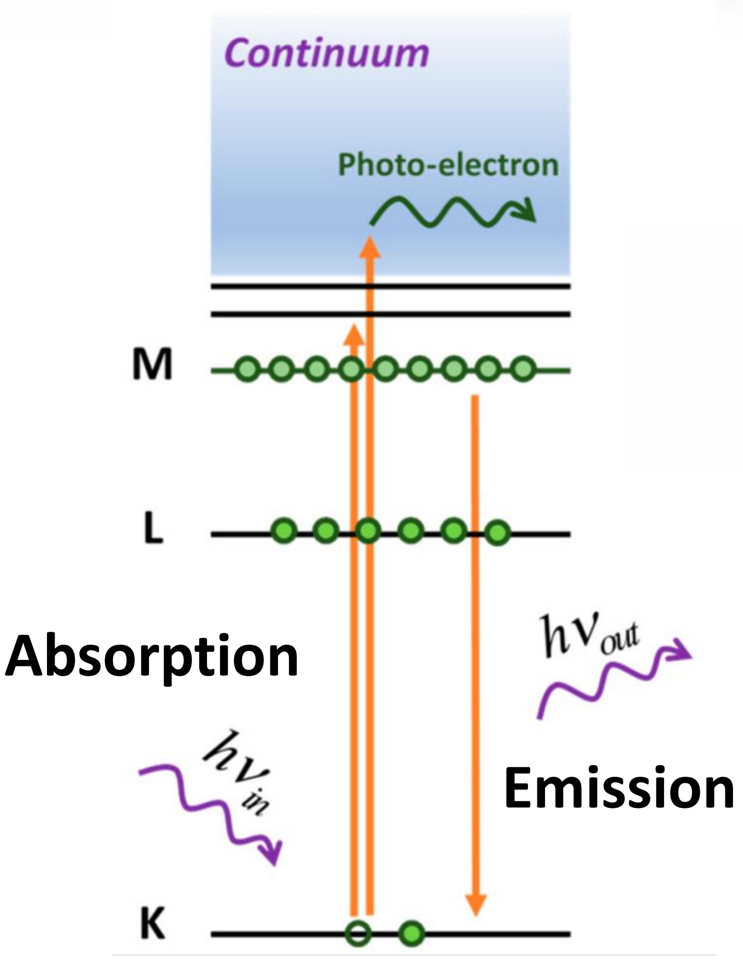
High energy resolution techniques

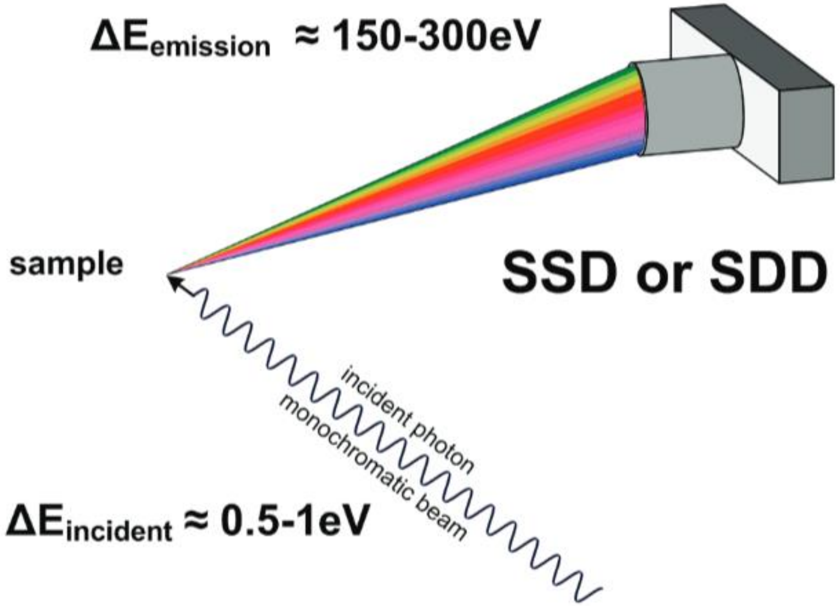
Denis Leshchev, ISS beamline scientist

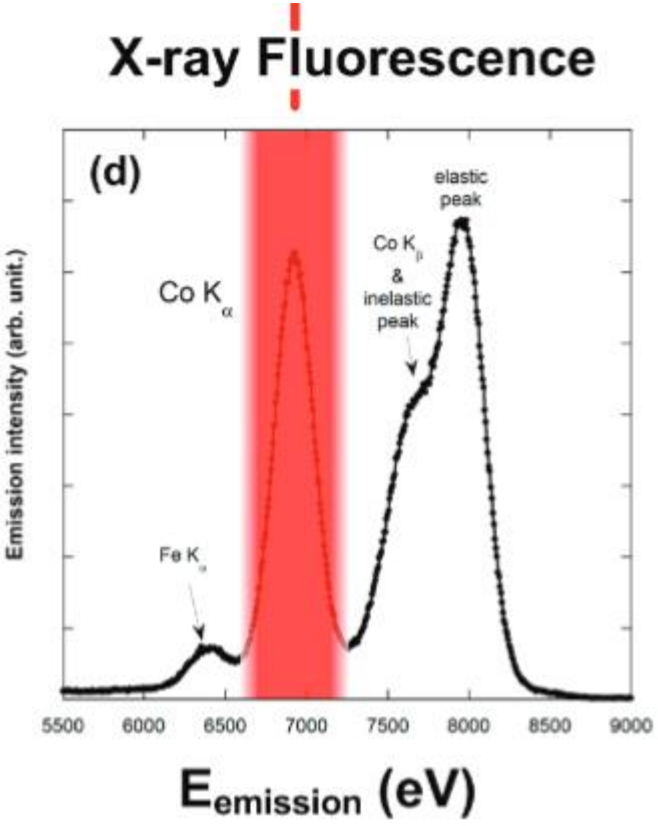
NSLS-II, BNL

XAS in fluorescence mode



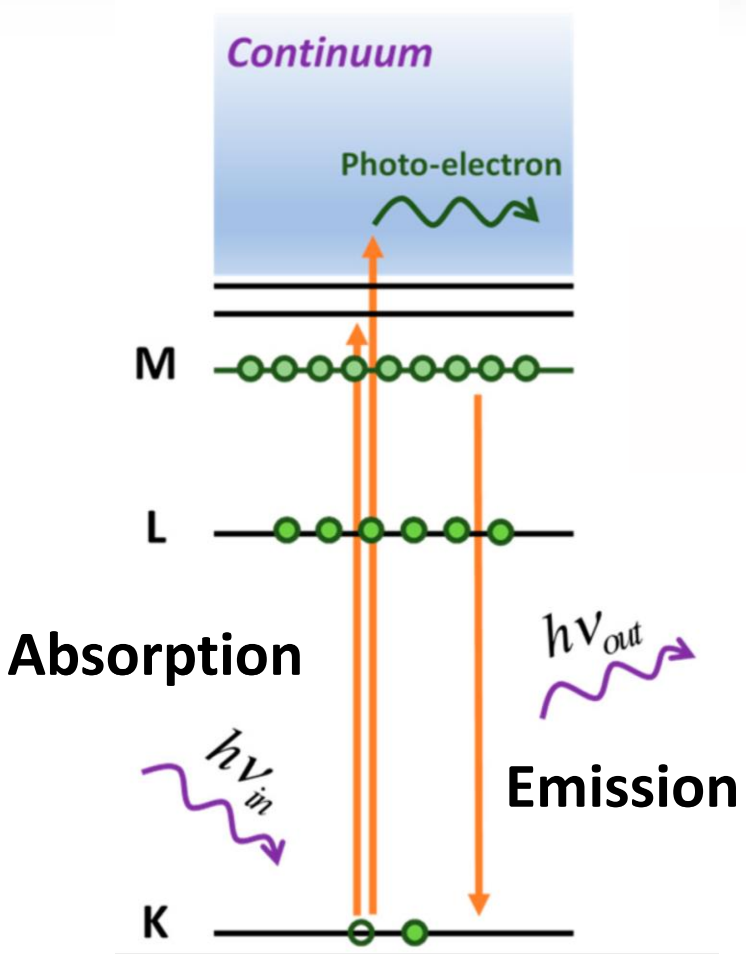
Biochimica et Biophysica Acta 1853 (2015) 1406–1415

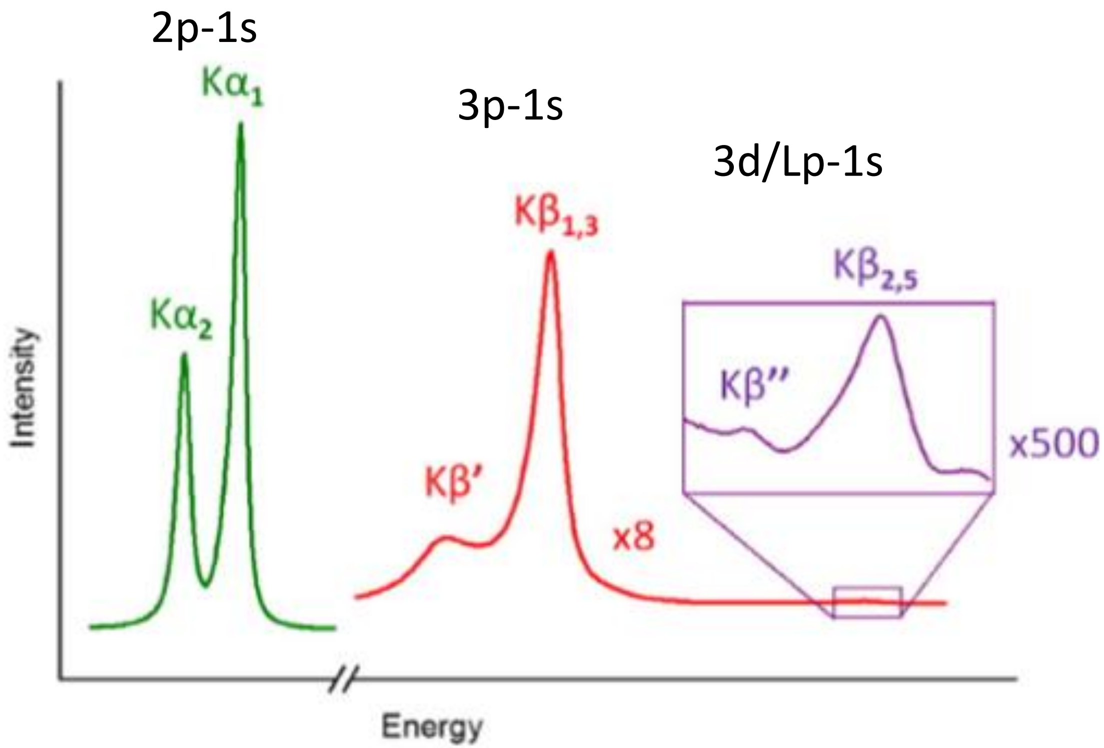




J. Environ. Qual. 46:1146–1157 (2017).

High-resolution analysis of emission



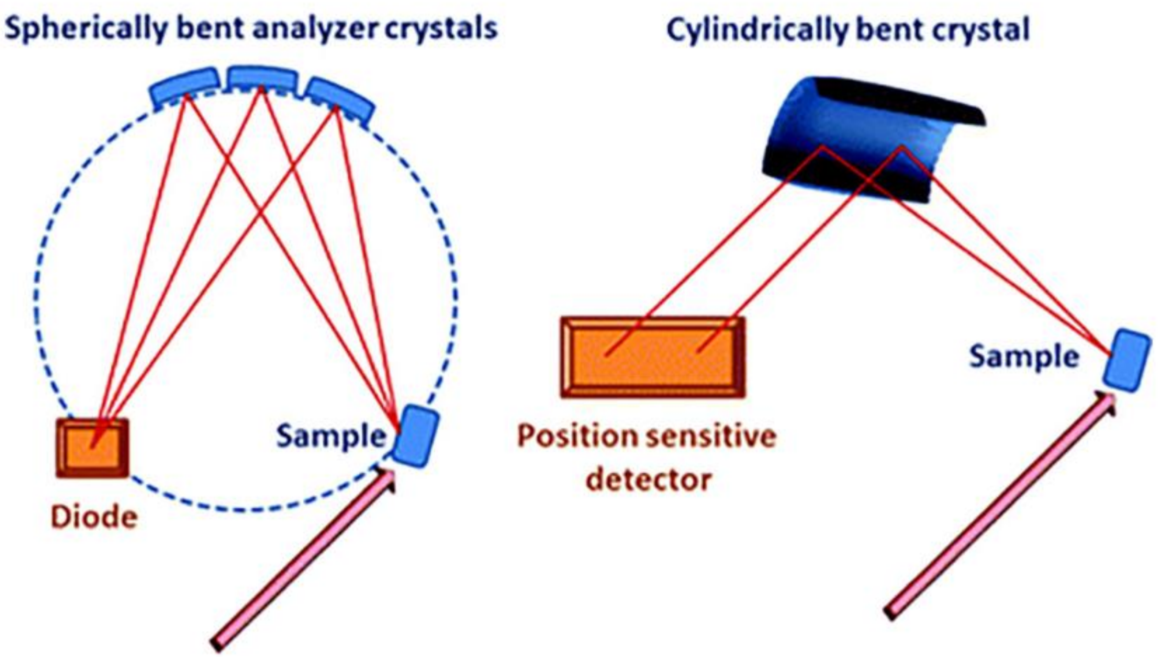


Biochimica et Biophysica Acta 1853 (2015) 1406–1415

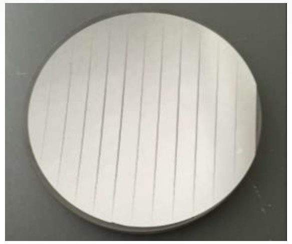
High-resolution hard x-ray spectroscopy

- Measure shapes of emission lines
- High resolution (~1 eV)

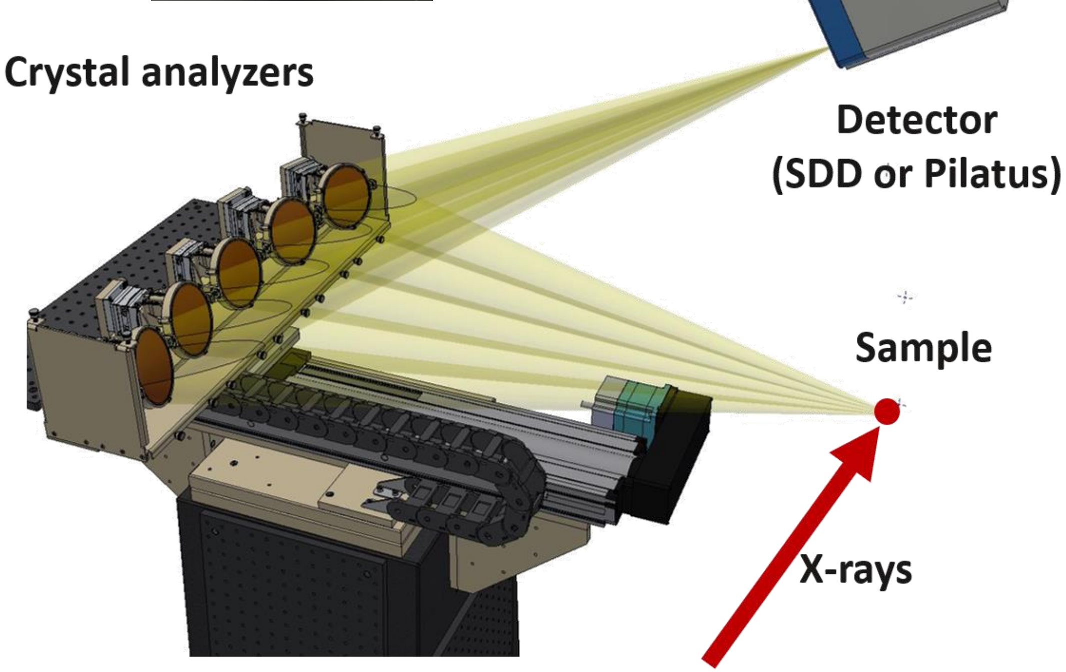
High-resolution instrumentation



P. Zimmermann et al. / Coordination Chemistry Reviews 423 (2020) 213466



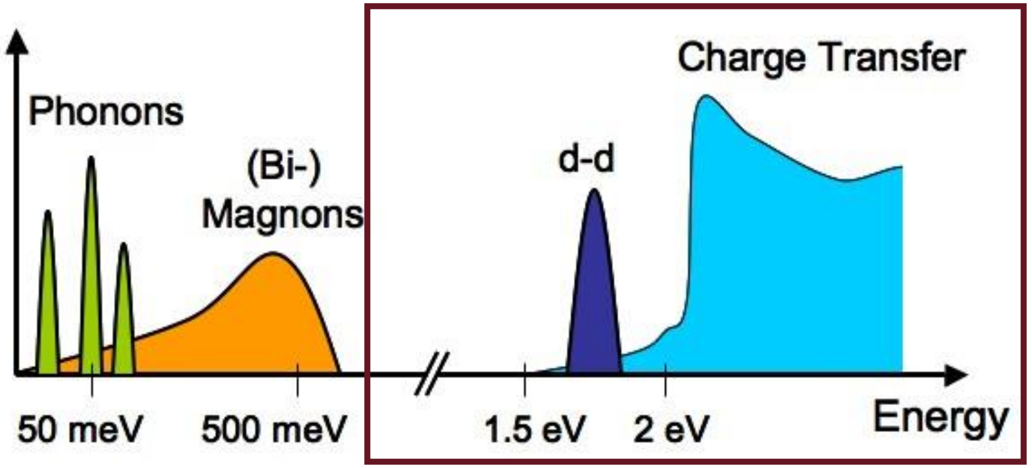
Si/Ge Analyzer crystals



What kind of problems we would like to solve at ISS?

- ISS aims to address problems in:
  - Chemistry
  - Catalysis
  - Materials science
  - Bioinorganic chemistry
  - Environmental sciences

We are here!

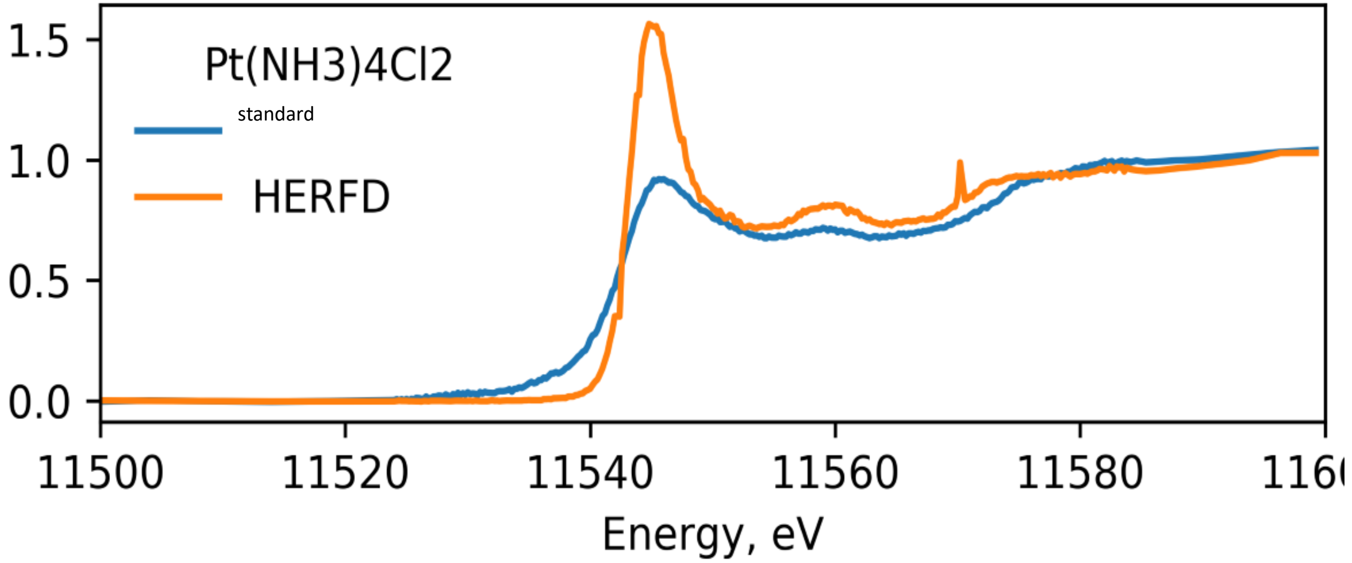


- Problems that are outside of the ISS scope:
  - Collective electronic excitations (magnetism, superconductivity, etc)
  - Polarization, momentum dependence

New flavors of X-ray spectroscopy

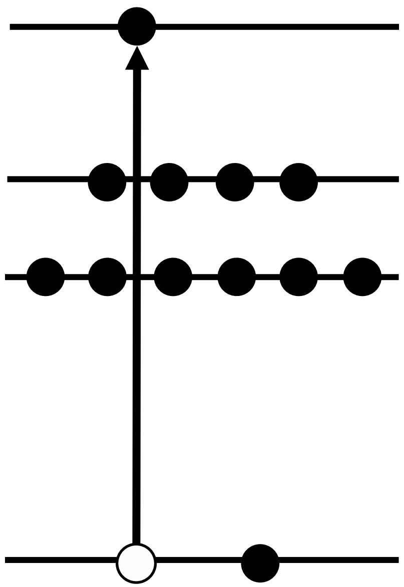
- HERFD XAS
- X-ray emission spectroscopy
- RIXS (RXES)

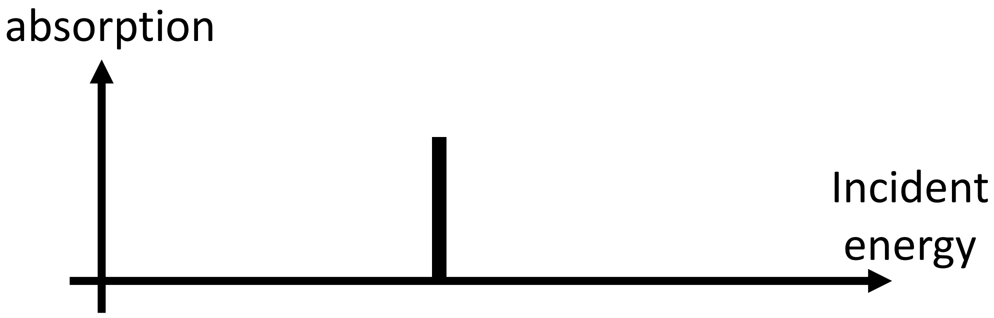
High-energy resolution fluorescence detected (HERFD) XAS



Helps to overcome core hole broadening!

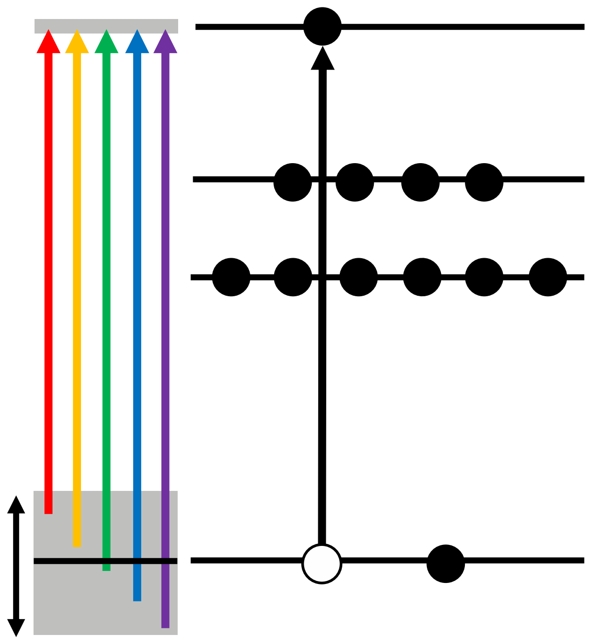
The core hole effect: unrealistic system with no broadening



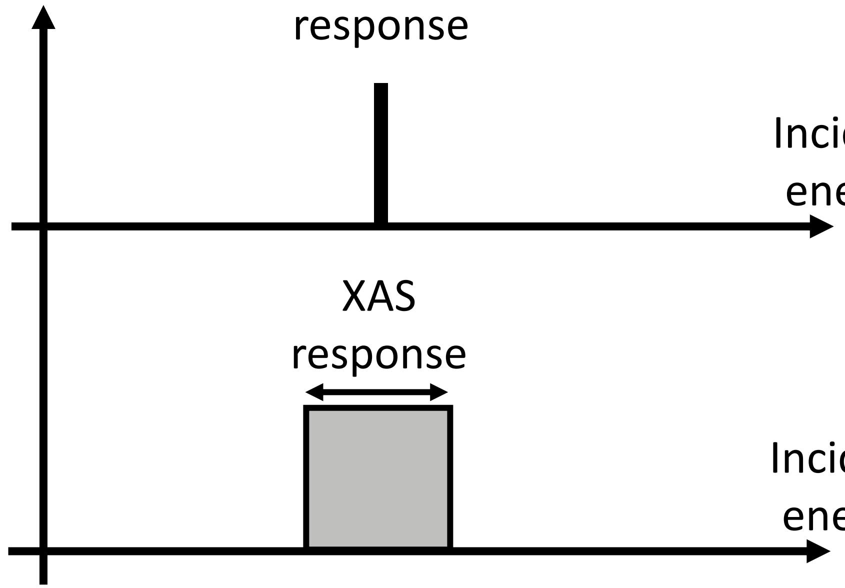


The core hole effect: unrealistic system with unrealistic broadening

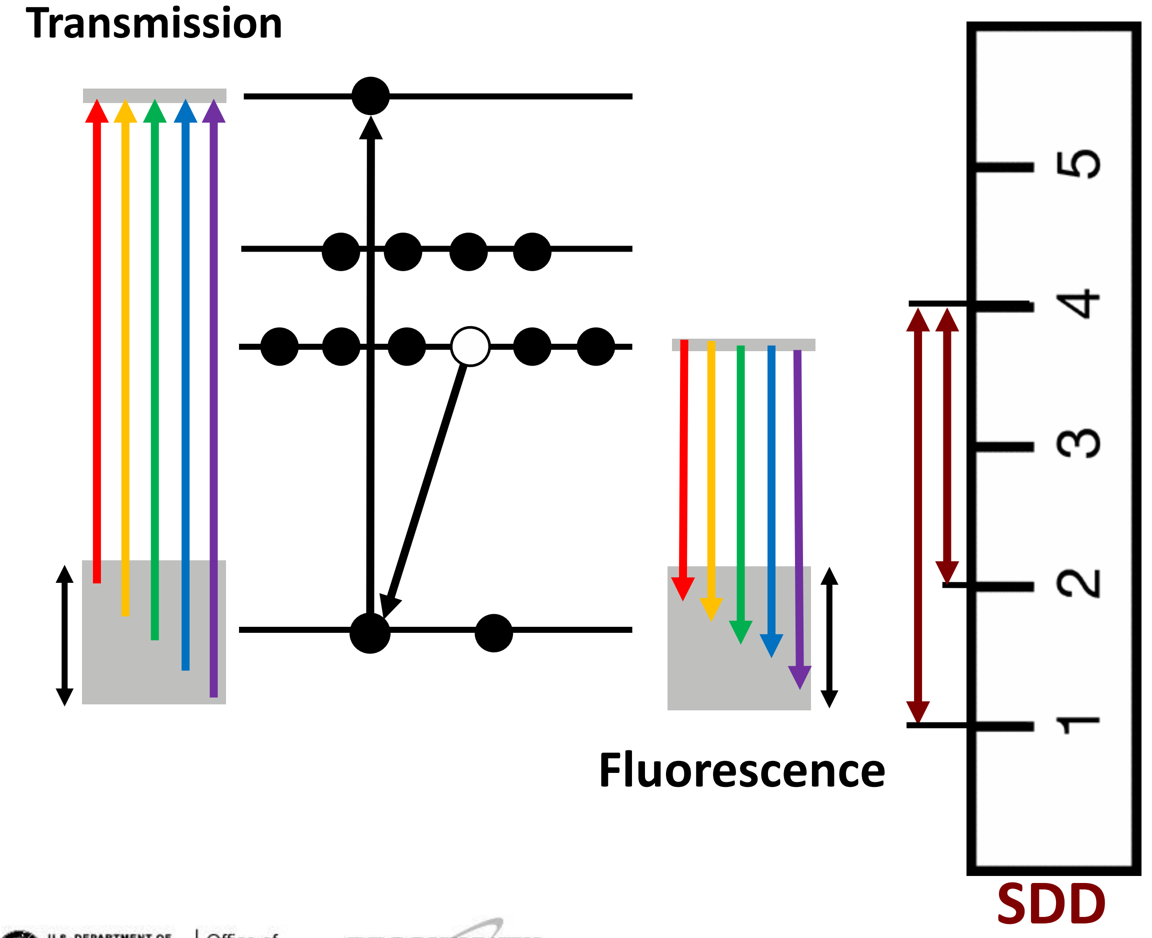
Transmission

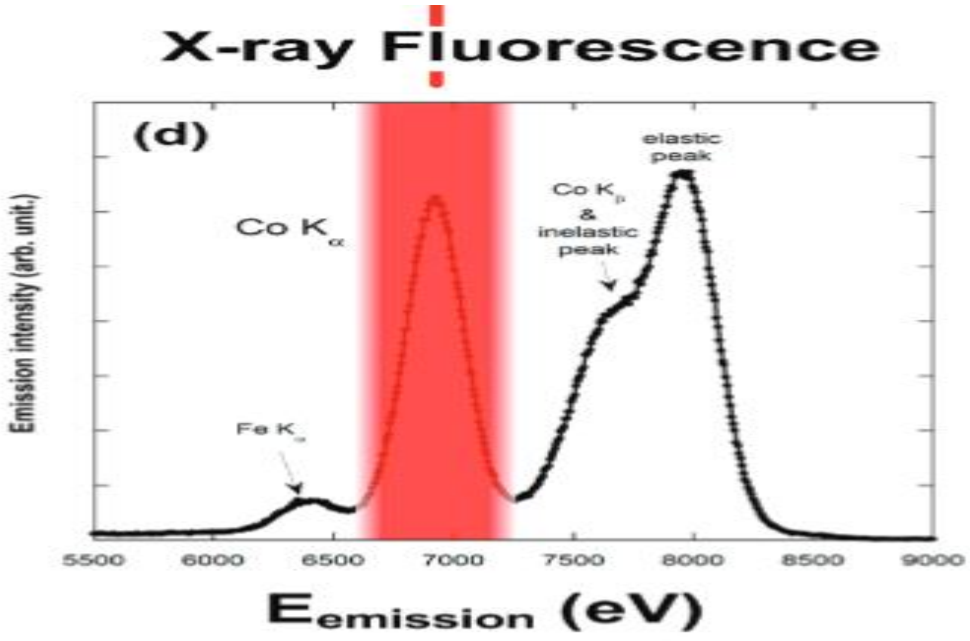


Finite core hole lifetime results in the energy broadening of the level



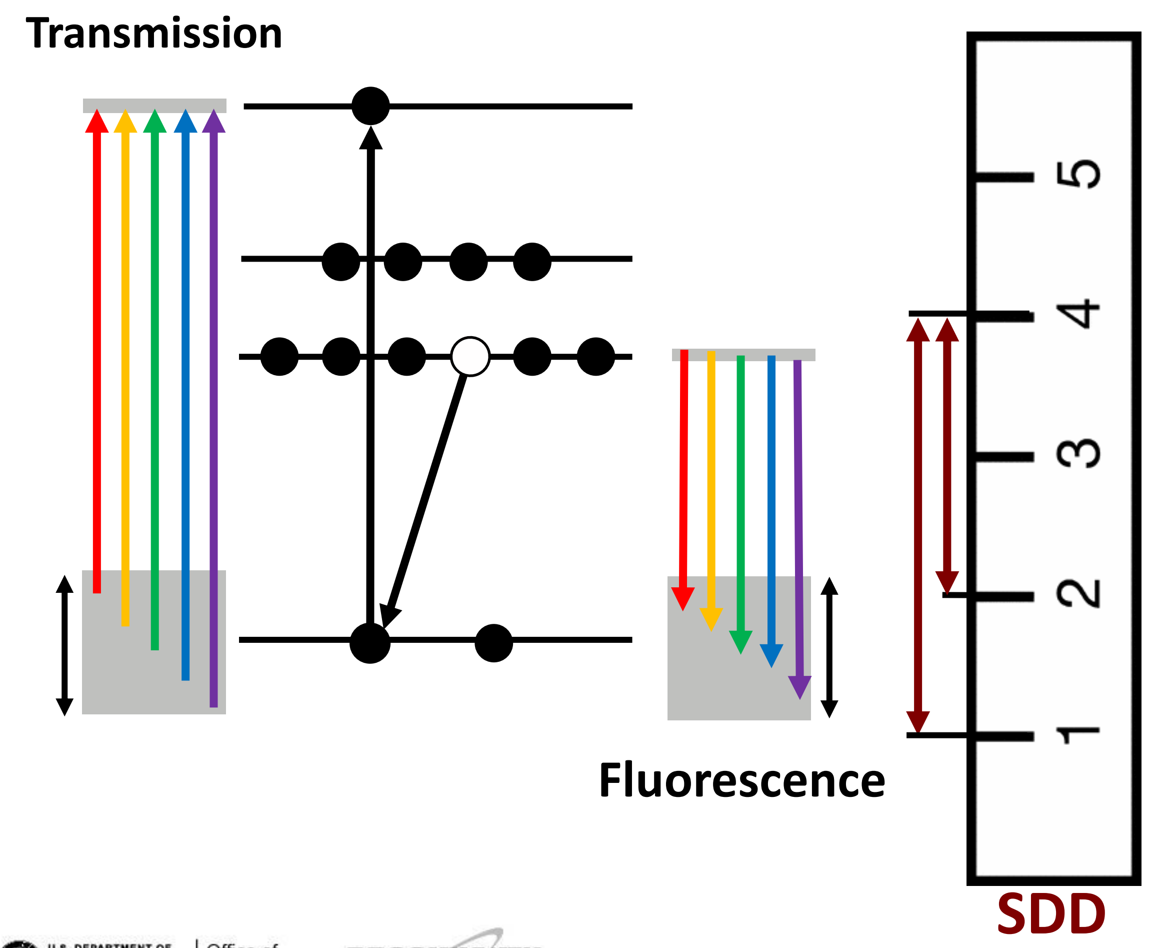
The core hole effect: unrealistic system with unrealistic broadening

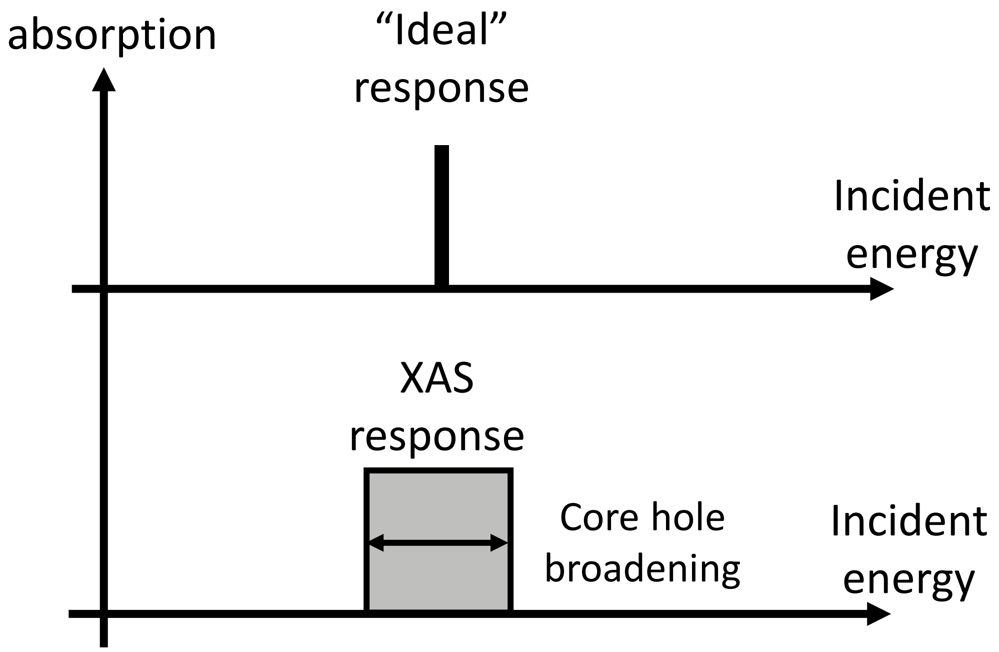




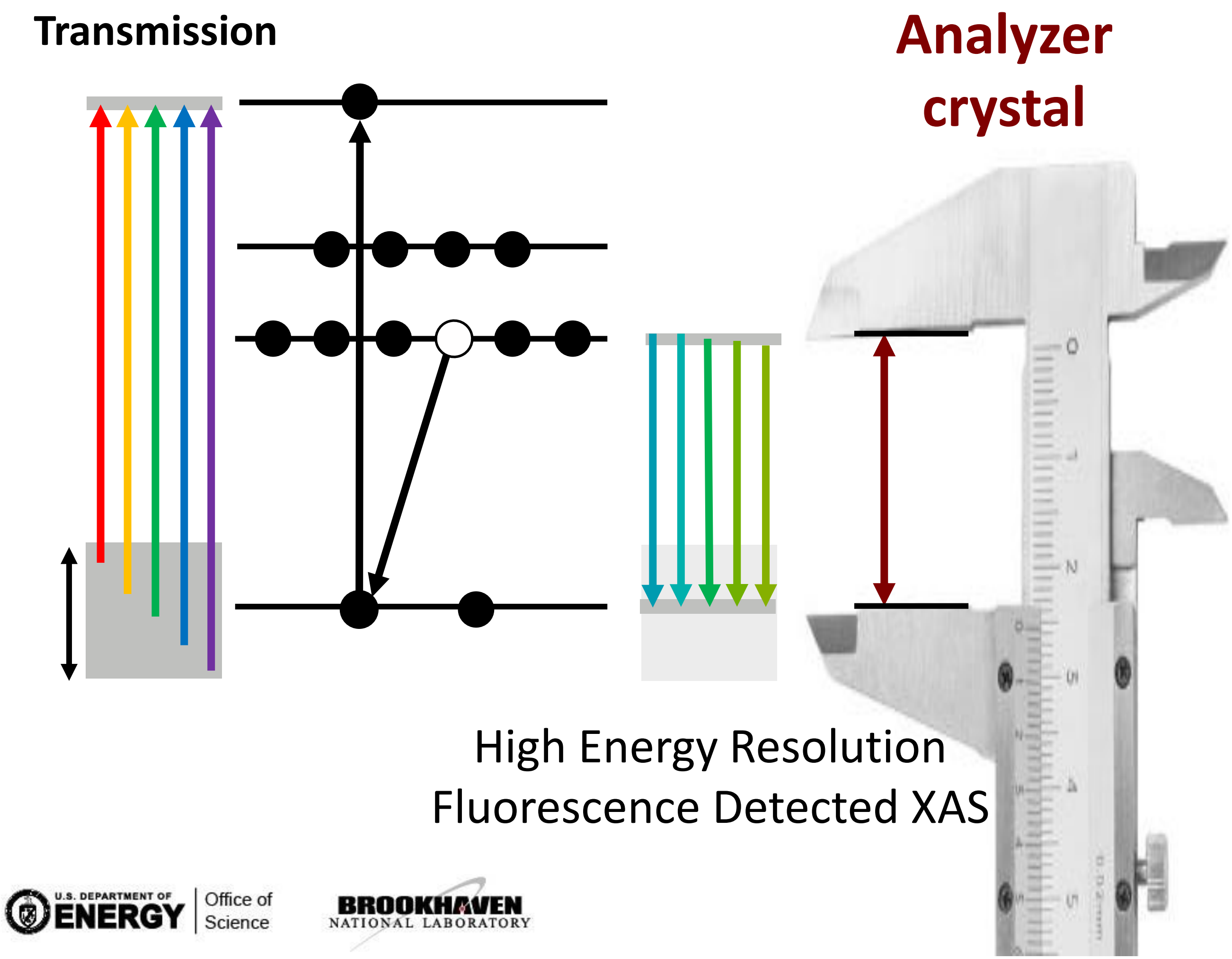
SDD filters out Elastic, Compton, background
Measures fluorescence intensity

The core hole effect: unrealistic system with unrealistic broadening

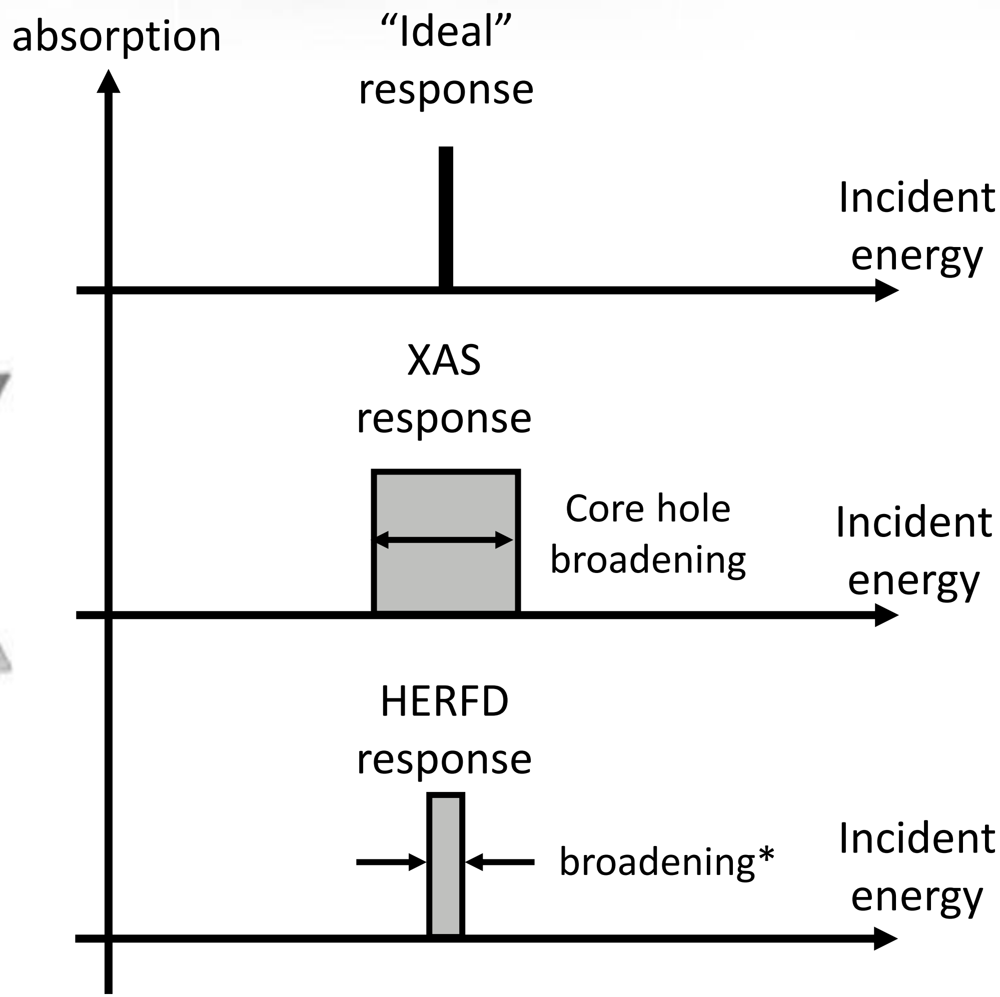




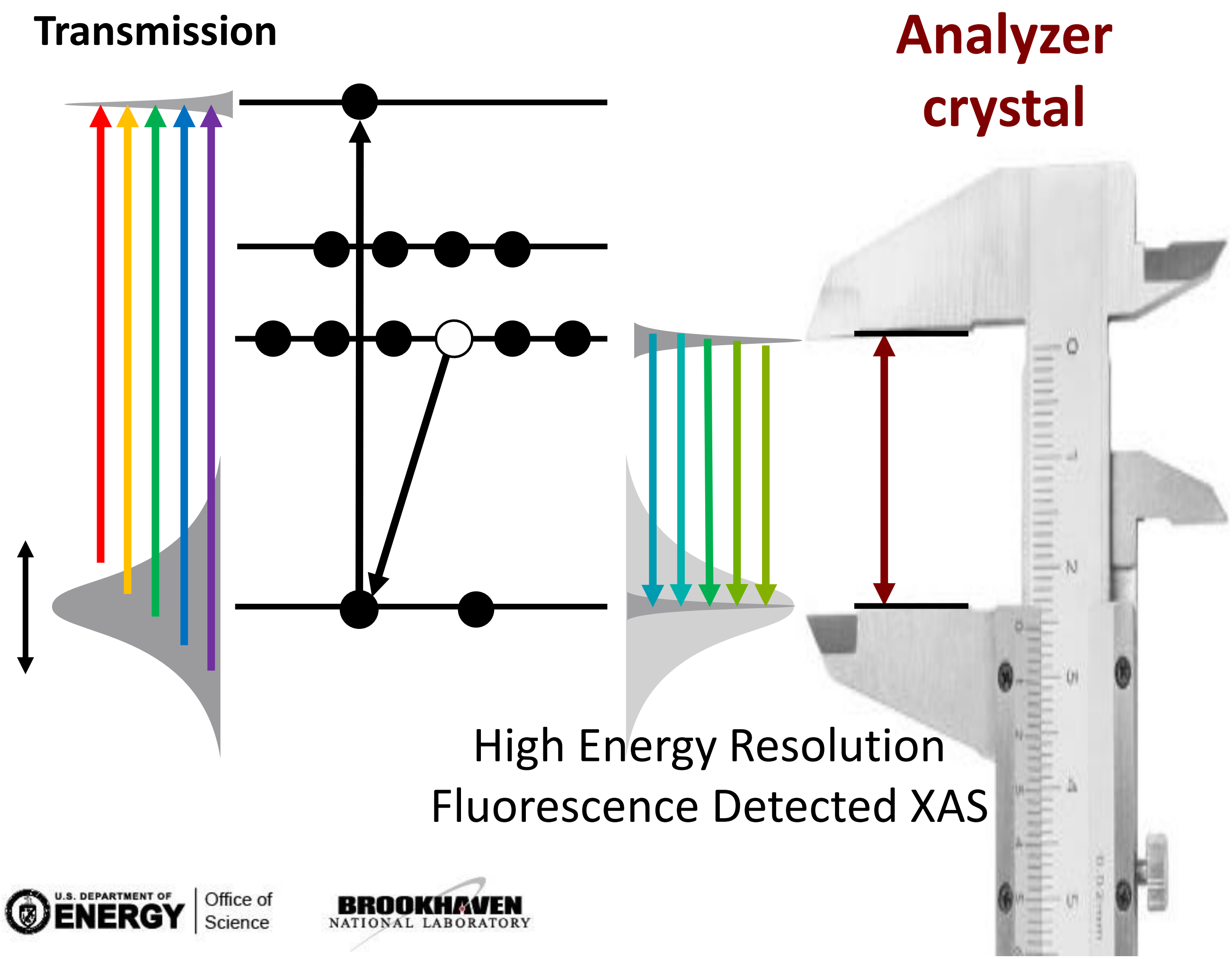
The core hole effect: unrealistic system, broadening, HERFD

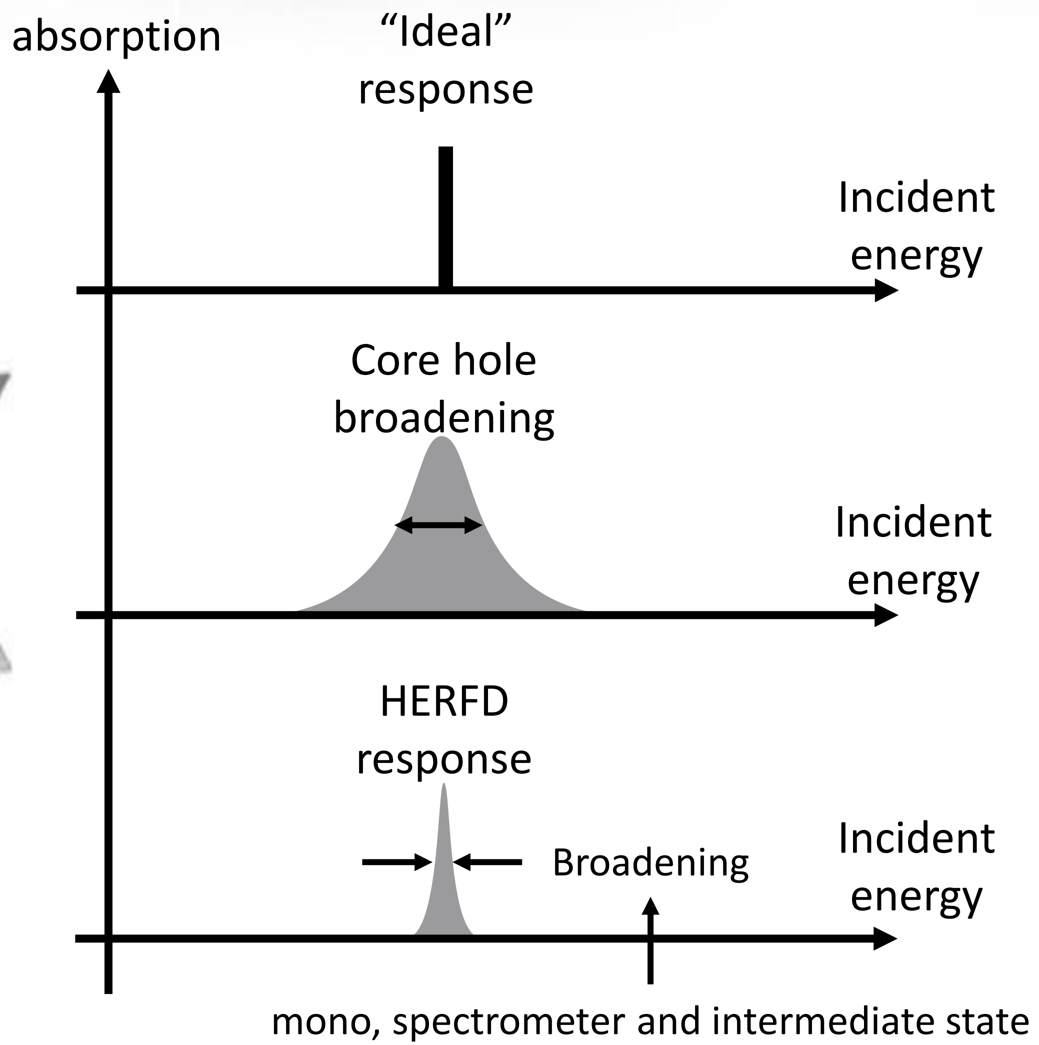


High Energy Resolution
Fluorescence Detected XAS



The core hole effect: slightly more realistic system, broadening, HERFD

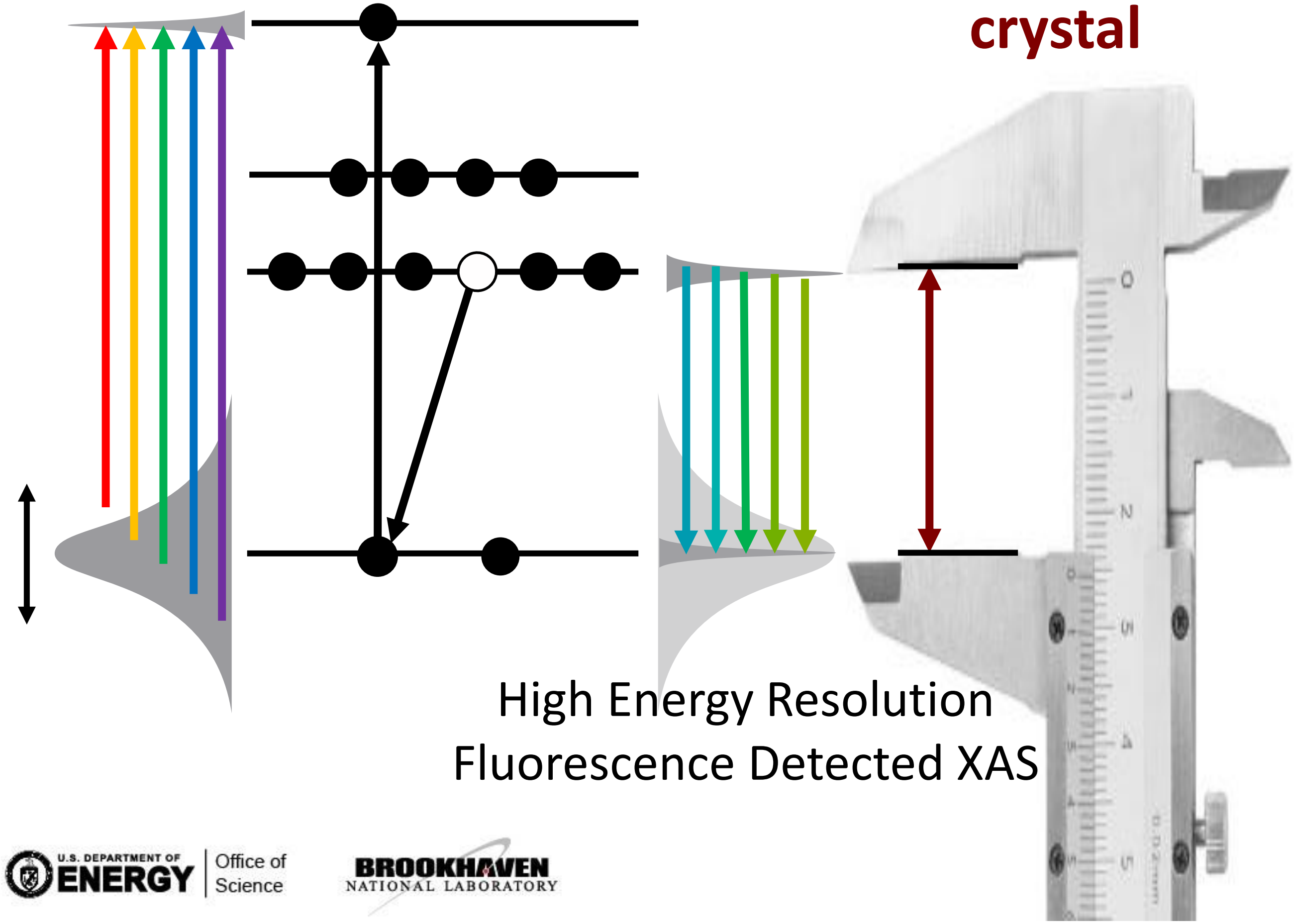




The core hole effect: slightly more realistic system, broadening, HERFD

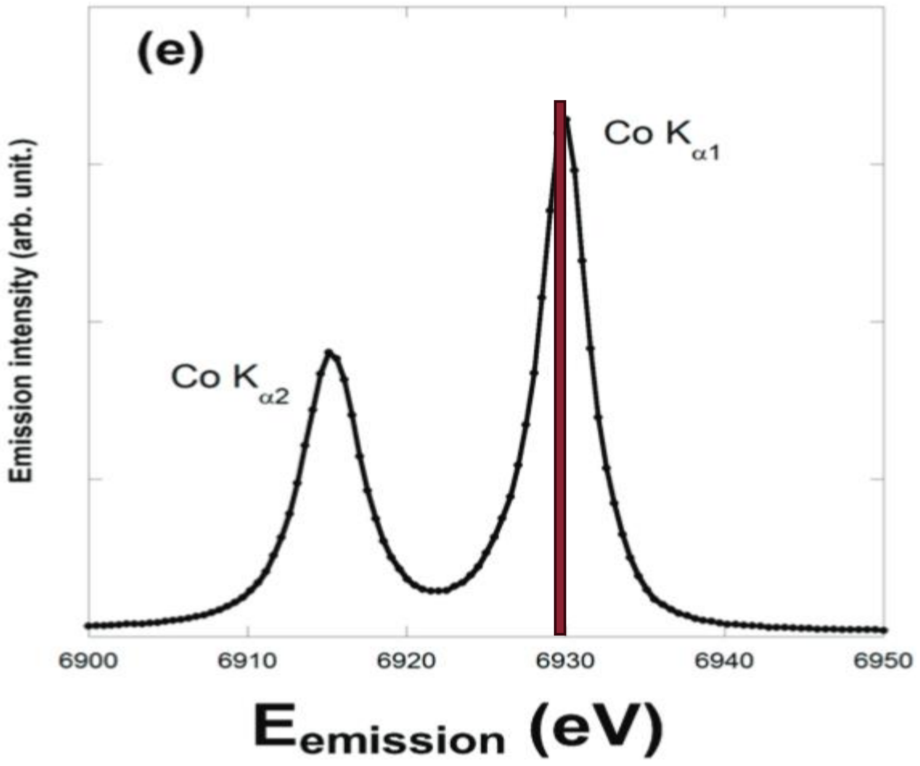
Transmission

Analyzer crystal



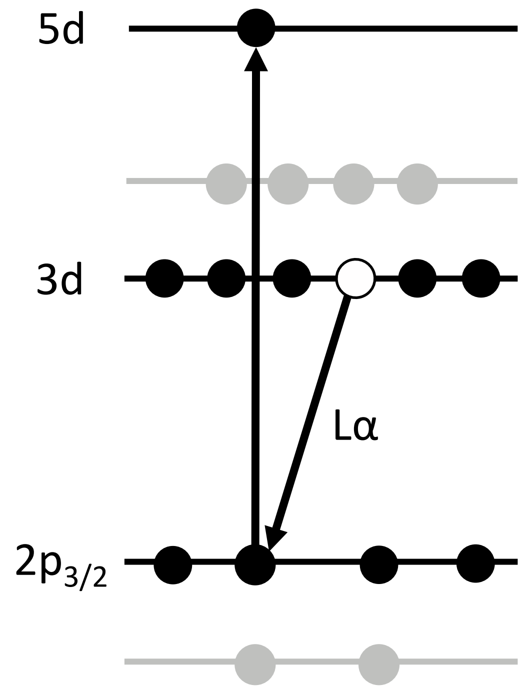
High Energy Resolution
Fluorescence Detected XAS

What HERFD does in practice



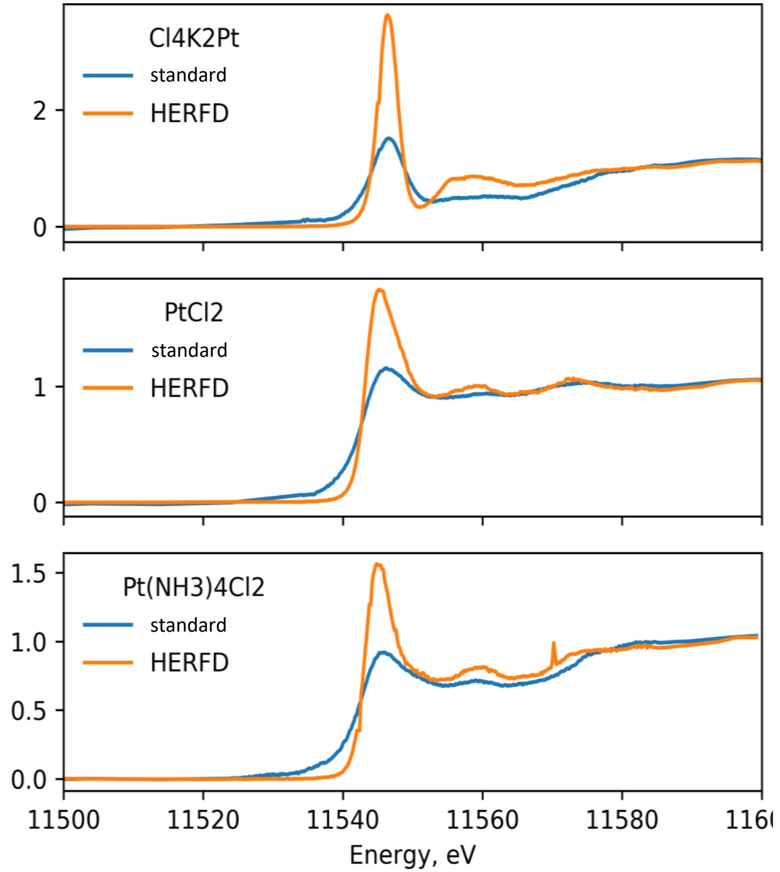
Instrument IRF and intermediate state

HERFD Examples: 5d metals



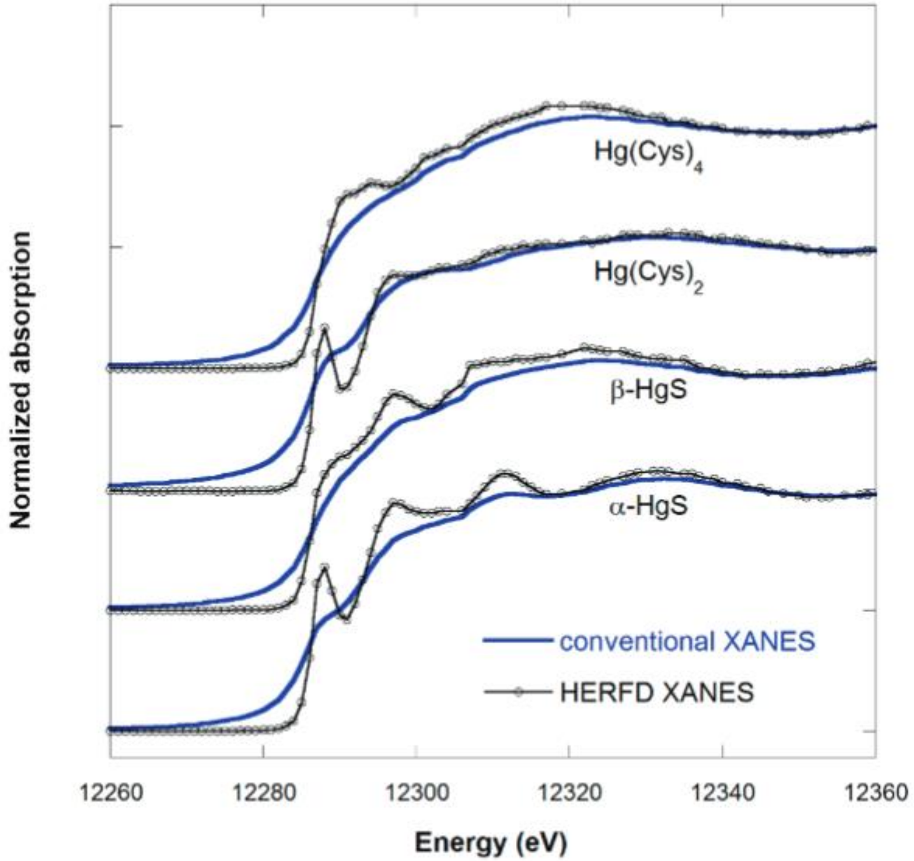
5d metals core-hole broadening can reach 6-8 eV

Pt L3-edge HERFD



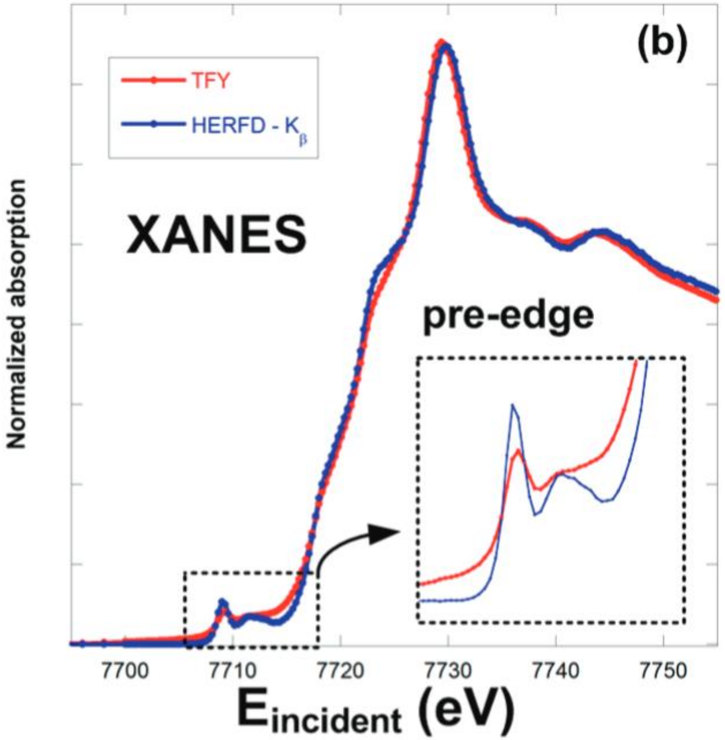
ISS data
Samples from Bruce

Hg L3-edge HERFD



J. Environ. Qual. 46:1146–1157 (2017).

HERFD Examples: 3d metals



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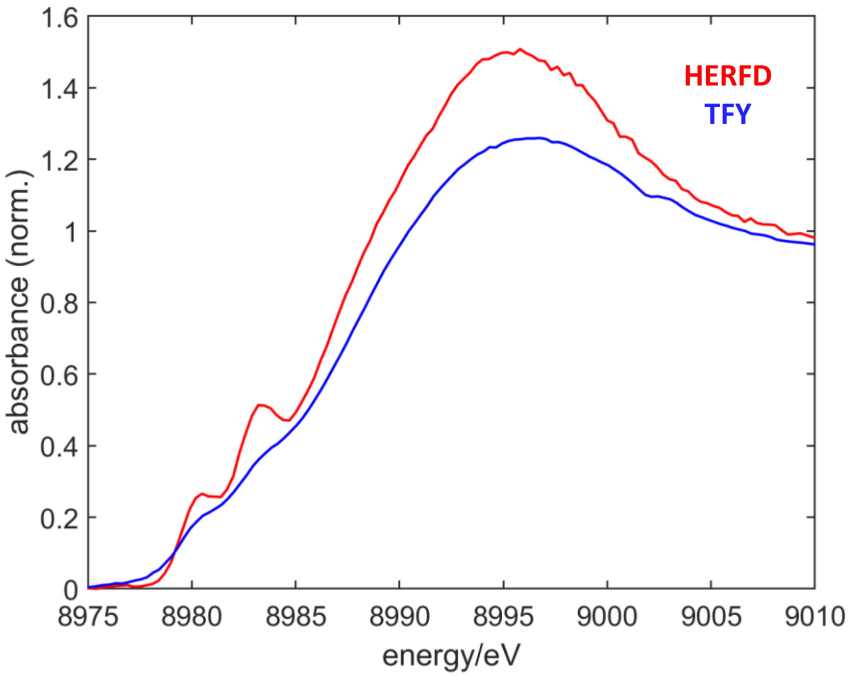
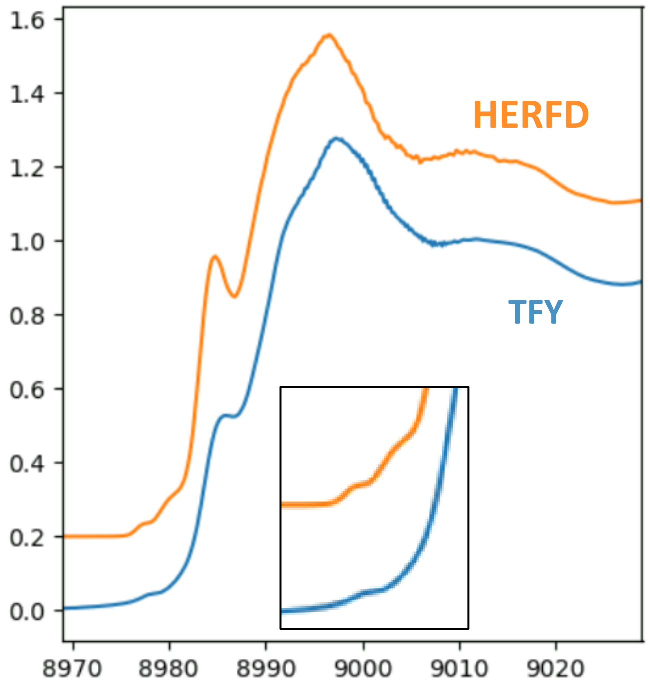
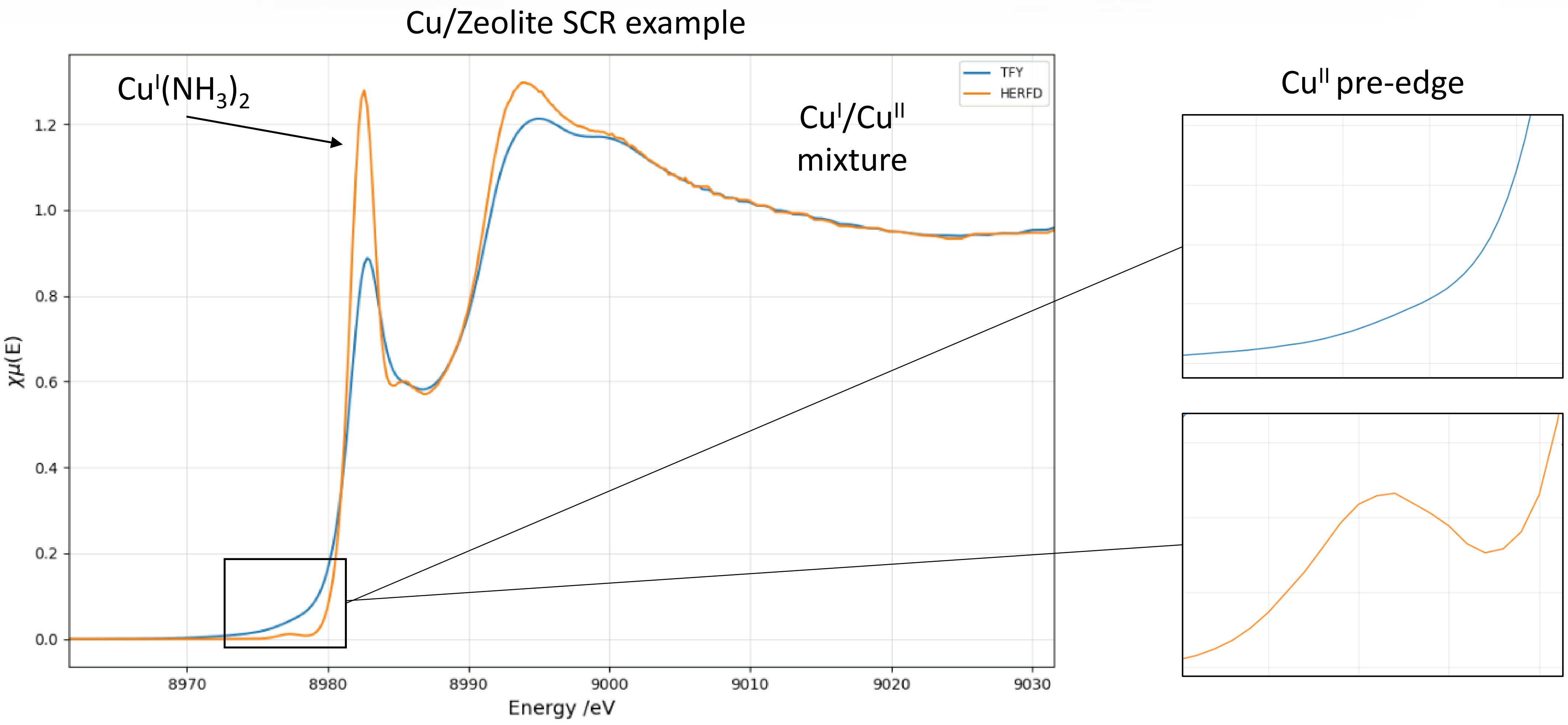


Cu organometallic complex



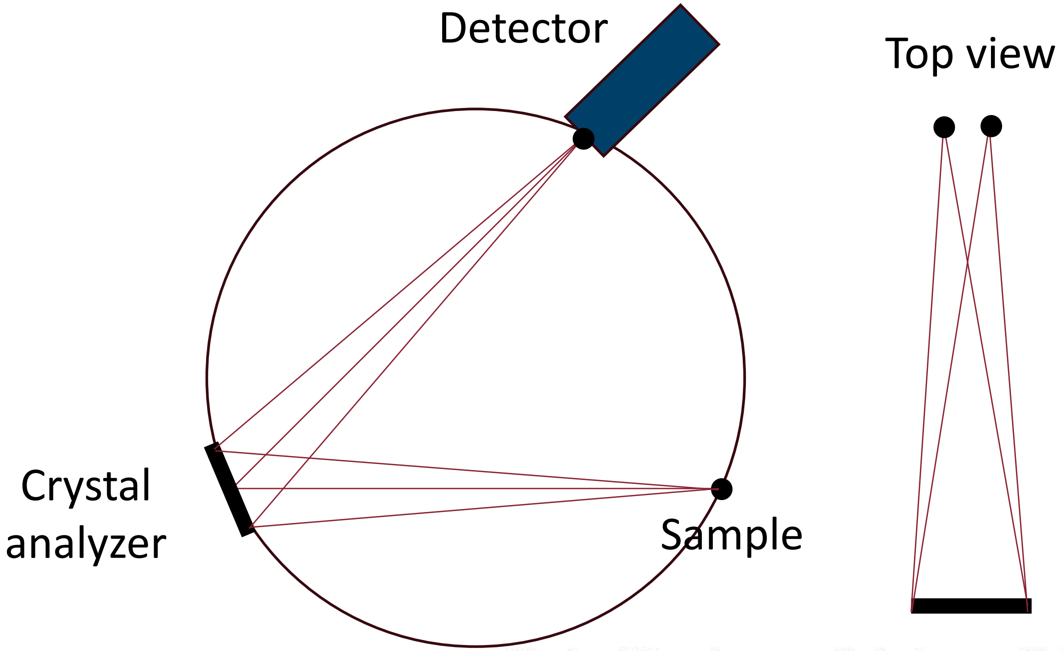
CuO sample

HERFD Examples: 3d metals, continued



Other applications of HERFD spectroscopy

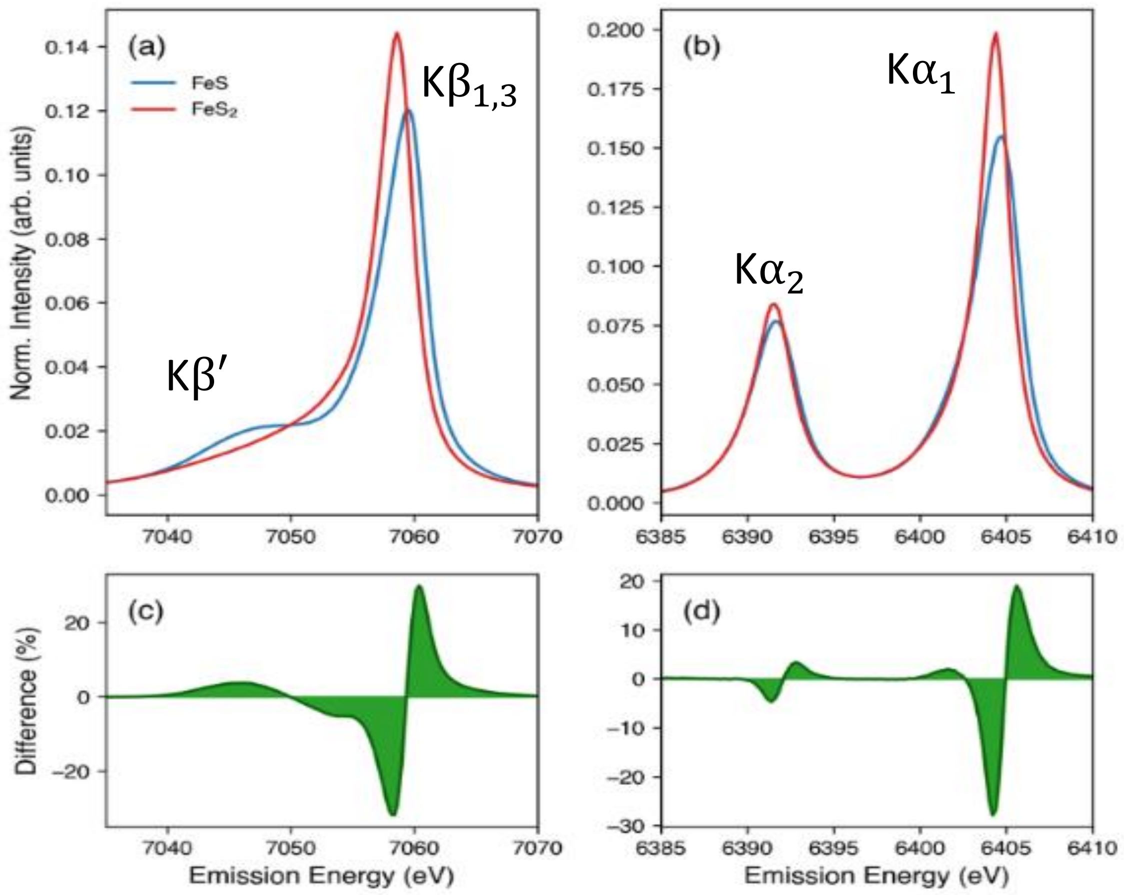
- Poor contrast between element of interest and the rest of the sample/environment
  - Low loading Fe or Co in Fe-rich environment
  - Pt/Zn and Ir/Cu measurements
  - High background (due to diffraction)
- Limited EXAFS due to edge overlap
- Position sensitivity



X-ray emission spectroscopy: a spin probe

- Fix E_{in} well above the edge (100-150 eV), scan E_{out}
- Kα (2p → 1s) and Kβ (3p → 1s) lines are sensitive to spin state of the absorbing atom (3d/2p and 3d/3p exchange interaction)

$\Delta S = 2$



Inorg. Chem.2020, 59, 12518−12535

X-ray emission spectroscopy: spin, covalency

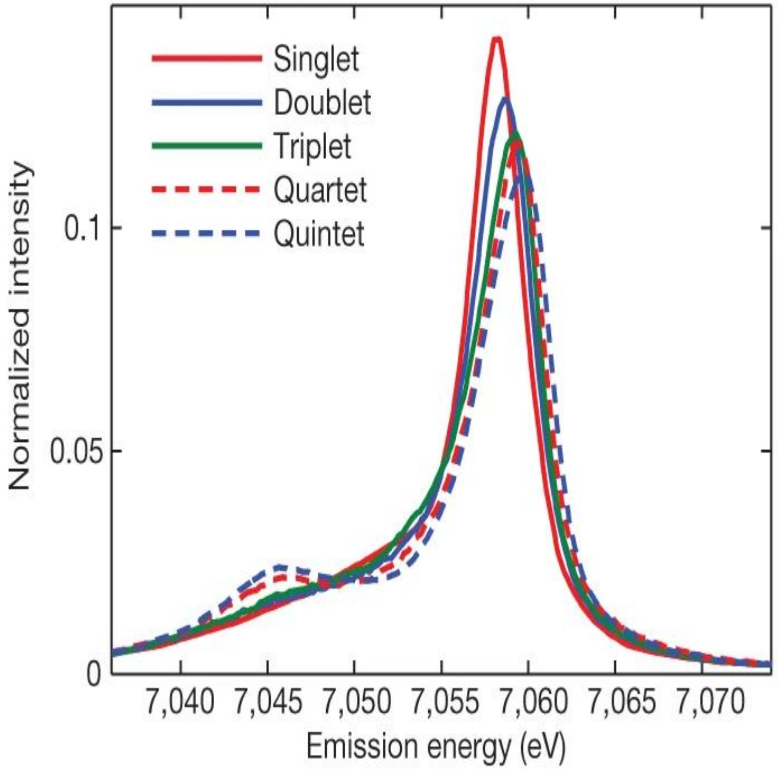
Semi-empirical exchange energy:

$$\Delta E_{\text{exch}} = \kappa\left(\frac{2}{15}G_{\text{pd}}^{1} + \frac{21}{245}G_{\text{pd}}^{3}\right)(2S_{\text{d}} + 1)$$

covalency (↑ κ) d shell spin (↑ S_d)

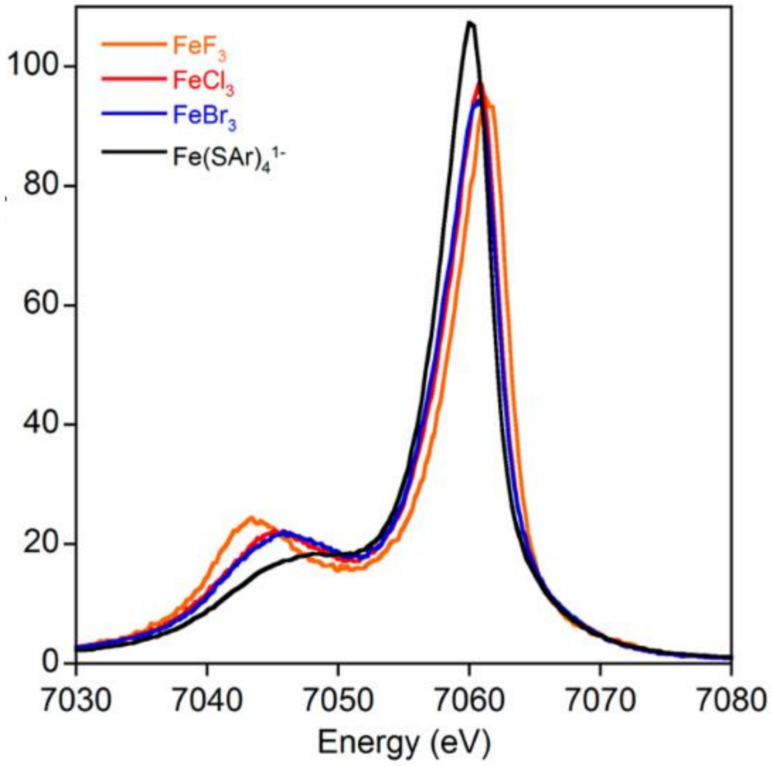
Inorg. Chem.2020, 59, 12518−12535

Nature **509,** 345–348 (2014)



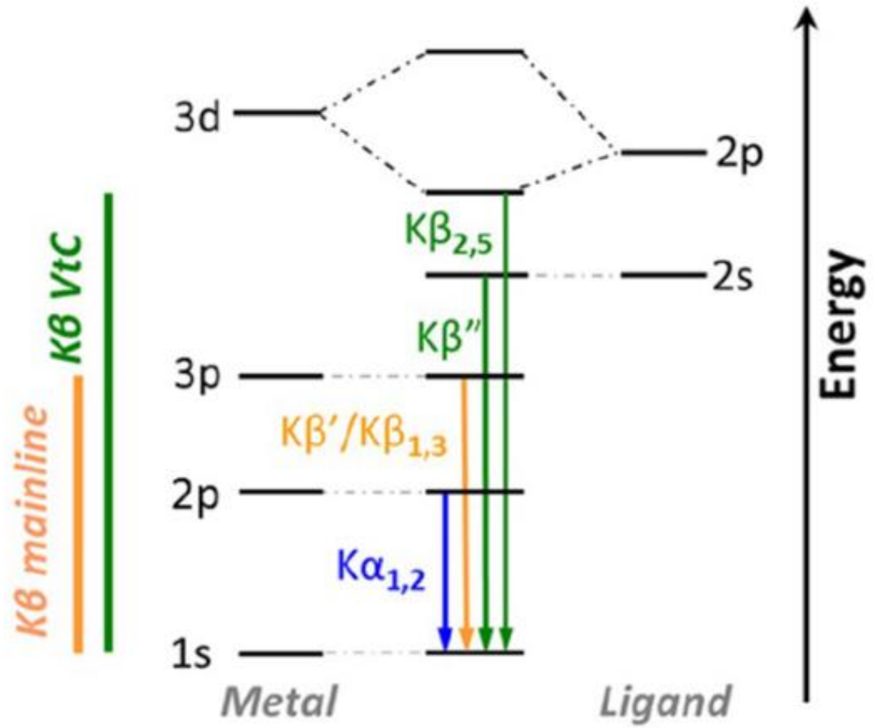
All Fe-N_6, different spins

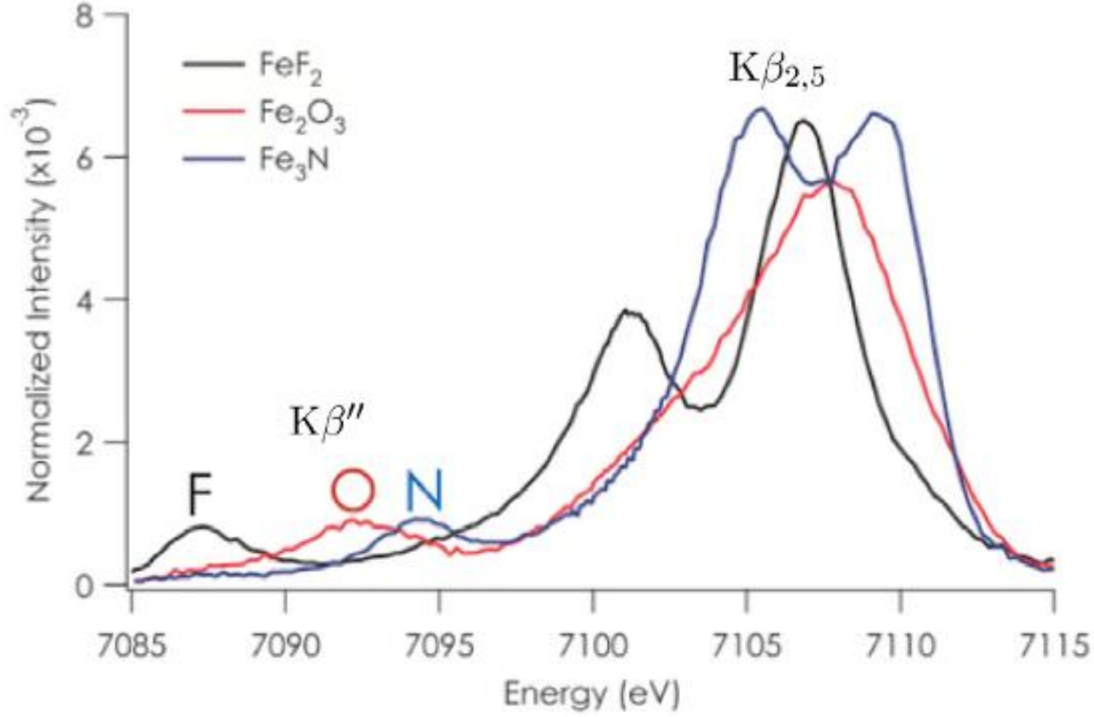
J.Am.Chem.Soc.2014, 136, 9453−9463



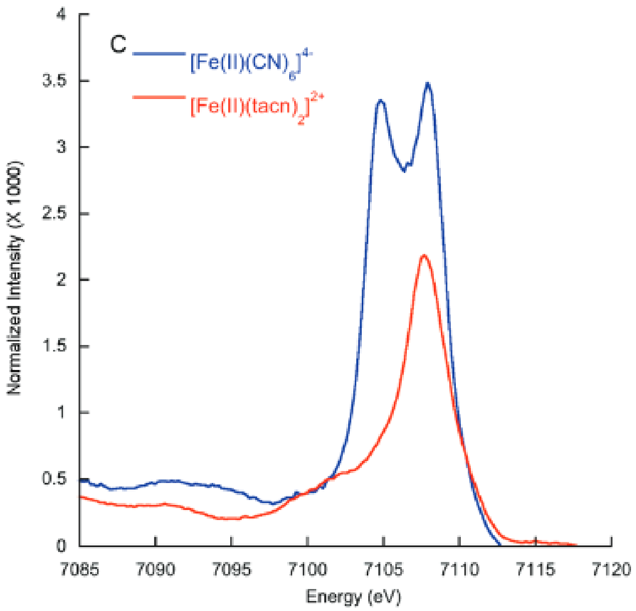
All Fe(III) HS, different covalency

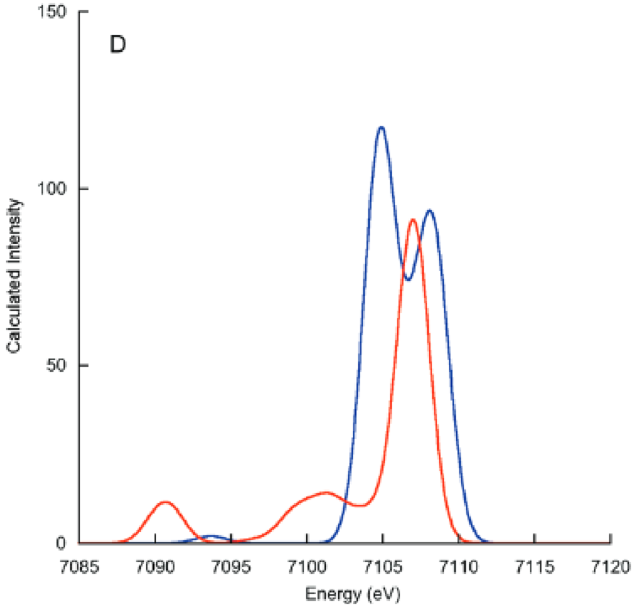
X-ray emission spectroscopy: valence-to-core

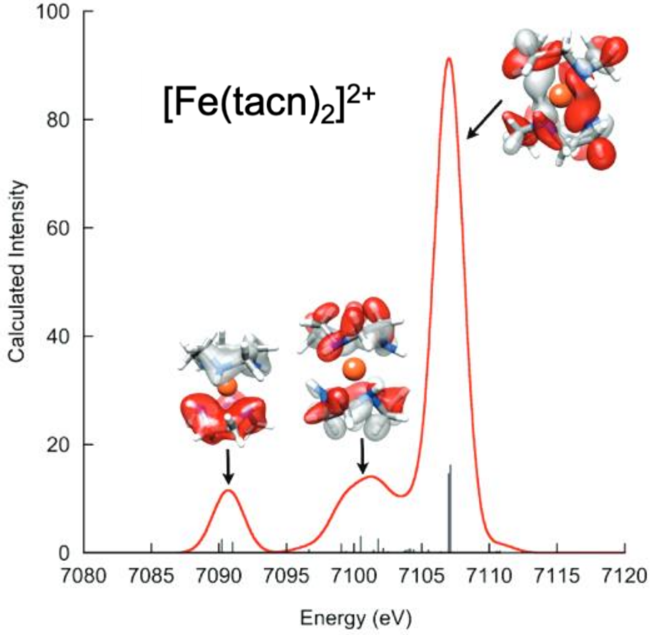




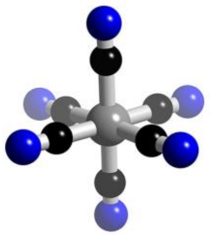
X-ray emission spectroscopy is amicable to DFT

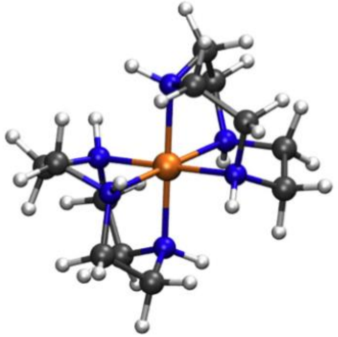






Fe(CN)6

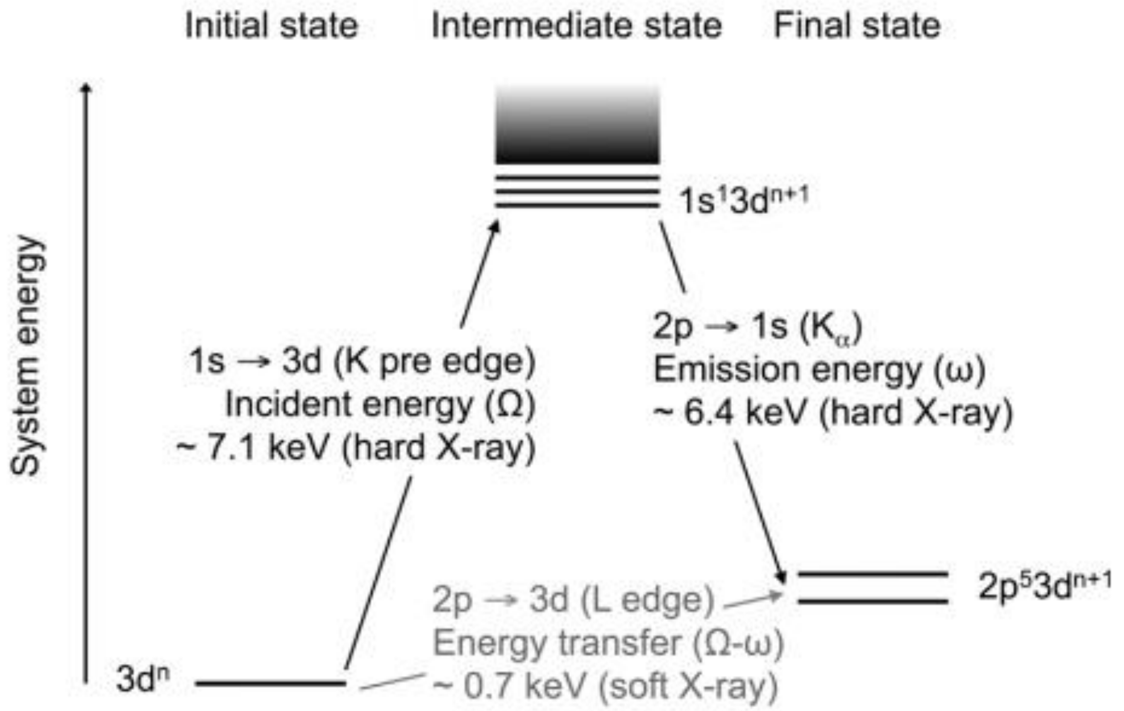




$[Fe(tacn)_2]^{2+}$

Resonant Inelastic X-ray Scattering

- Resonant inelastic x-ray scattering (resonant X-ray emission)
- Scan E_{in} across pre-edge region, scan E_{out} along emission line
- Covalency, oxidation state

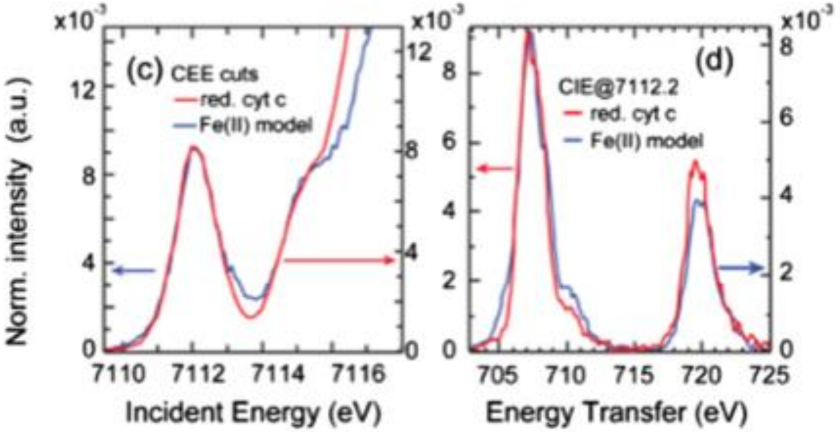


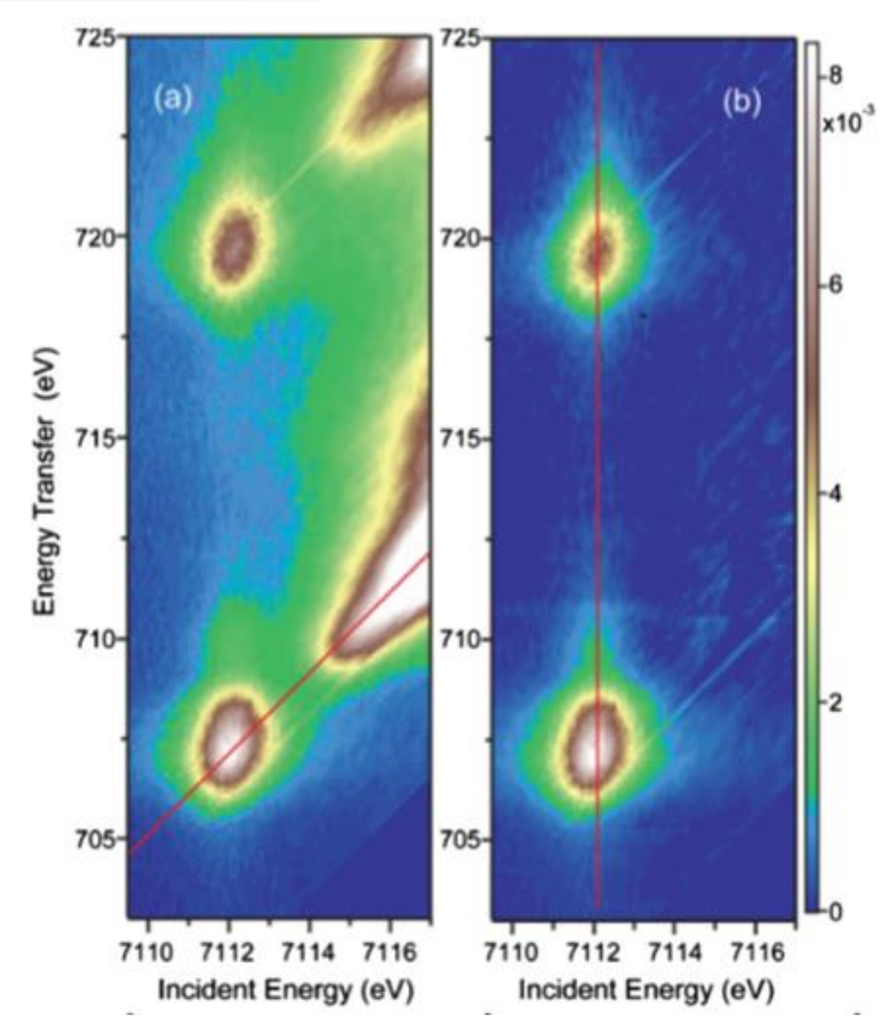
Coordination Chemistry Reviews 345 (2017) 182–208

RIXS: examples

Fe 1s2p RIXS
L-edge like data
(ferrous cyt *c*)

- Cuts through pre-edge 1s2p RIXS give L-edge like data
- Differential covalency and bonding

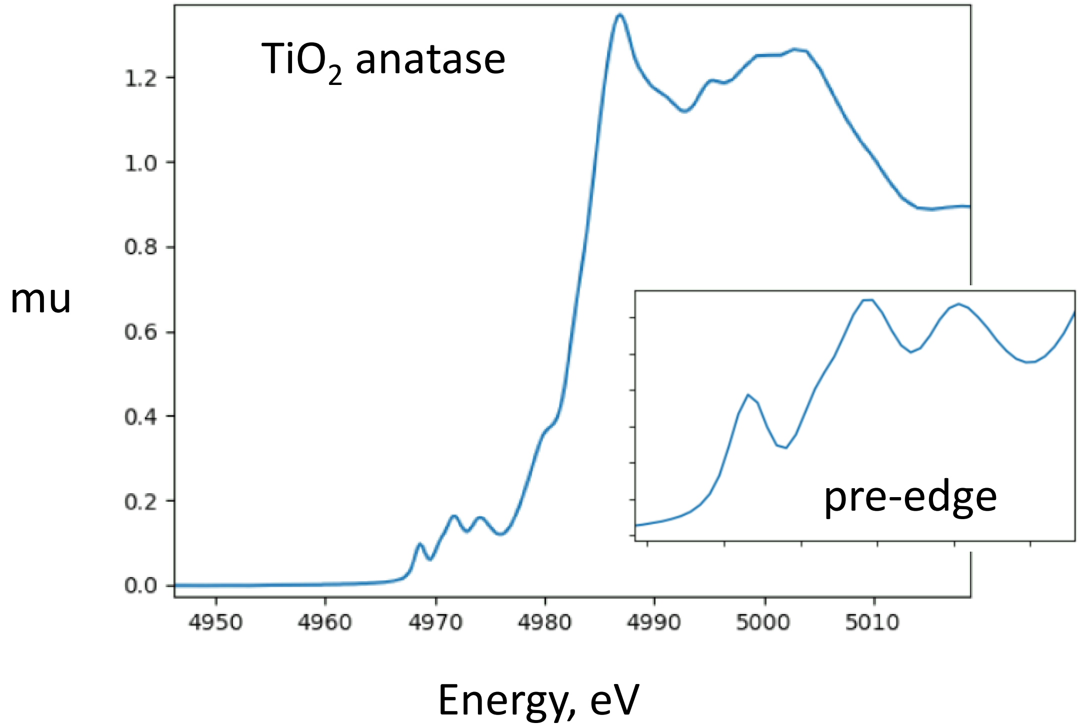


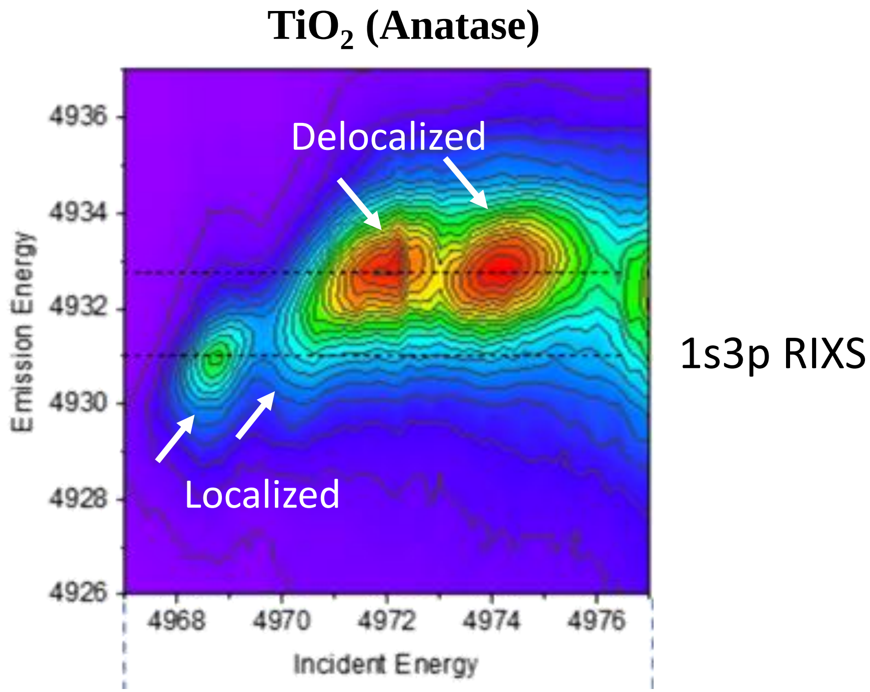


M.L. Baker et al. / Coordination Chemistry Reviews 345 (2017) 182–208

RIXS: examples

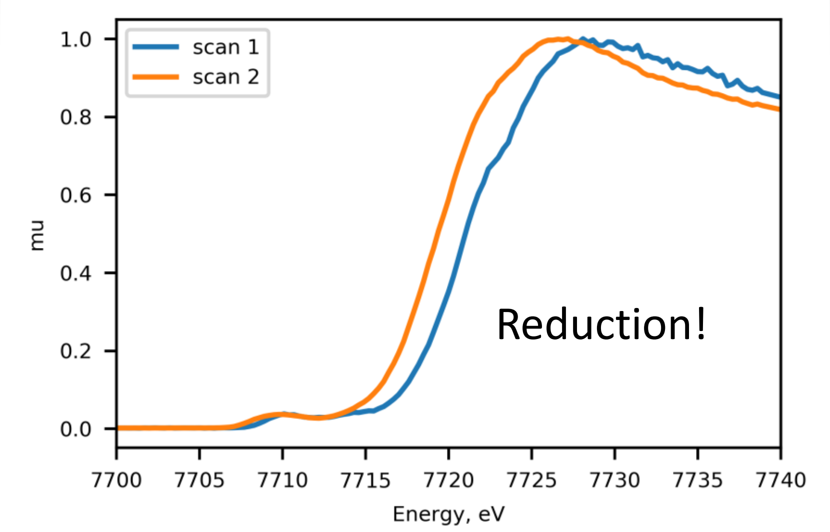
- Localized/delocalized orbitals in TiO_2

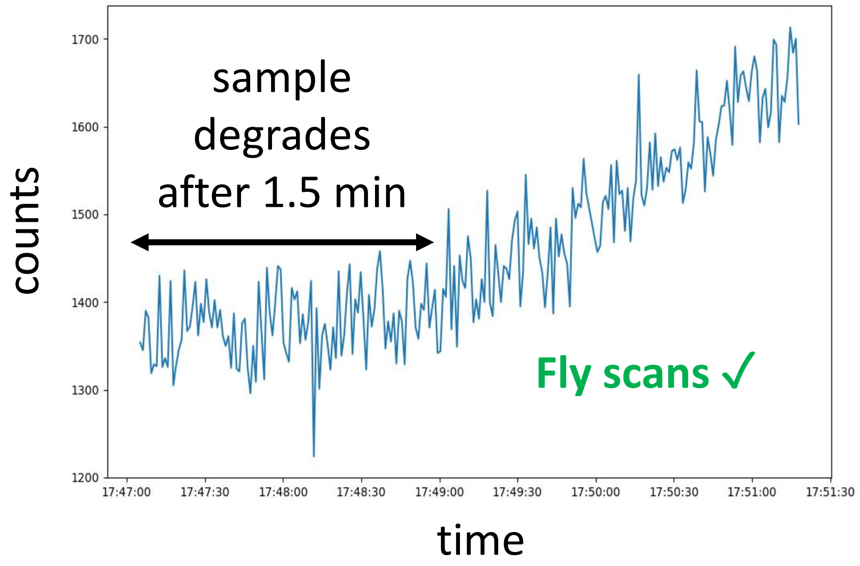


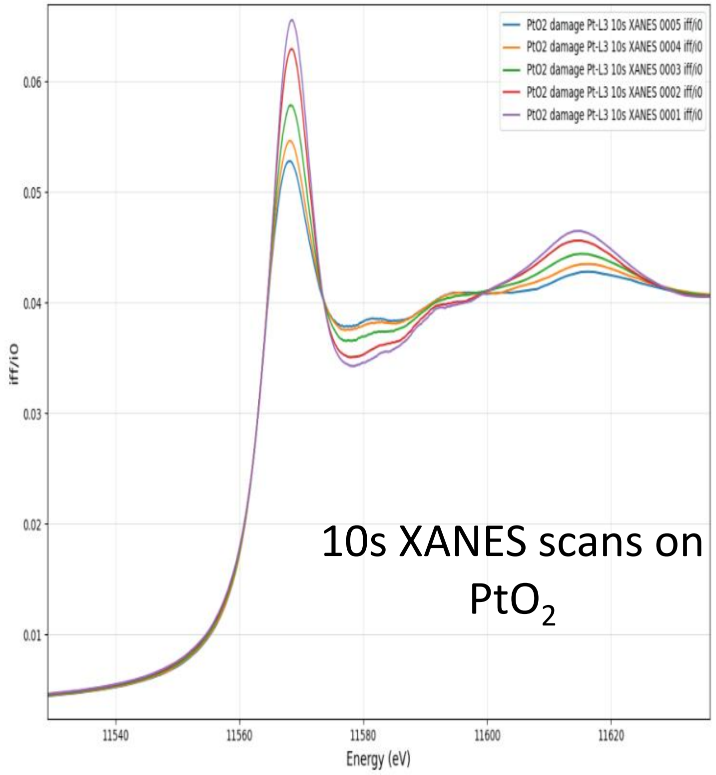


Challenge: Sample damage

- High flux density (~10^{13} ph/s in 0.1×0.1 mm^2) cause sample to degrade
- Need to check every sample for degradation
- Cryo-environment, liquid jets, raster scanning
- Ensure you have enough spots on the sample to measure







Conclusions

- HR spectroscopy (HERFD-XAS, XES, RIXS) provides complementary insights into electronic structure of materials
- HERFD-XAS: cleaner data, enhanced sensitivity
- XES: spin, ligand speciation
- RIXS: covalency, bonding