XANES analysis and high energy resolution techniques

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@BrookhavenLab

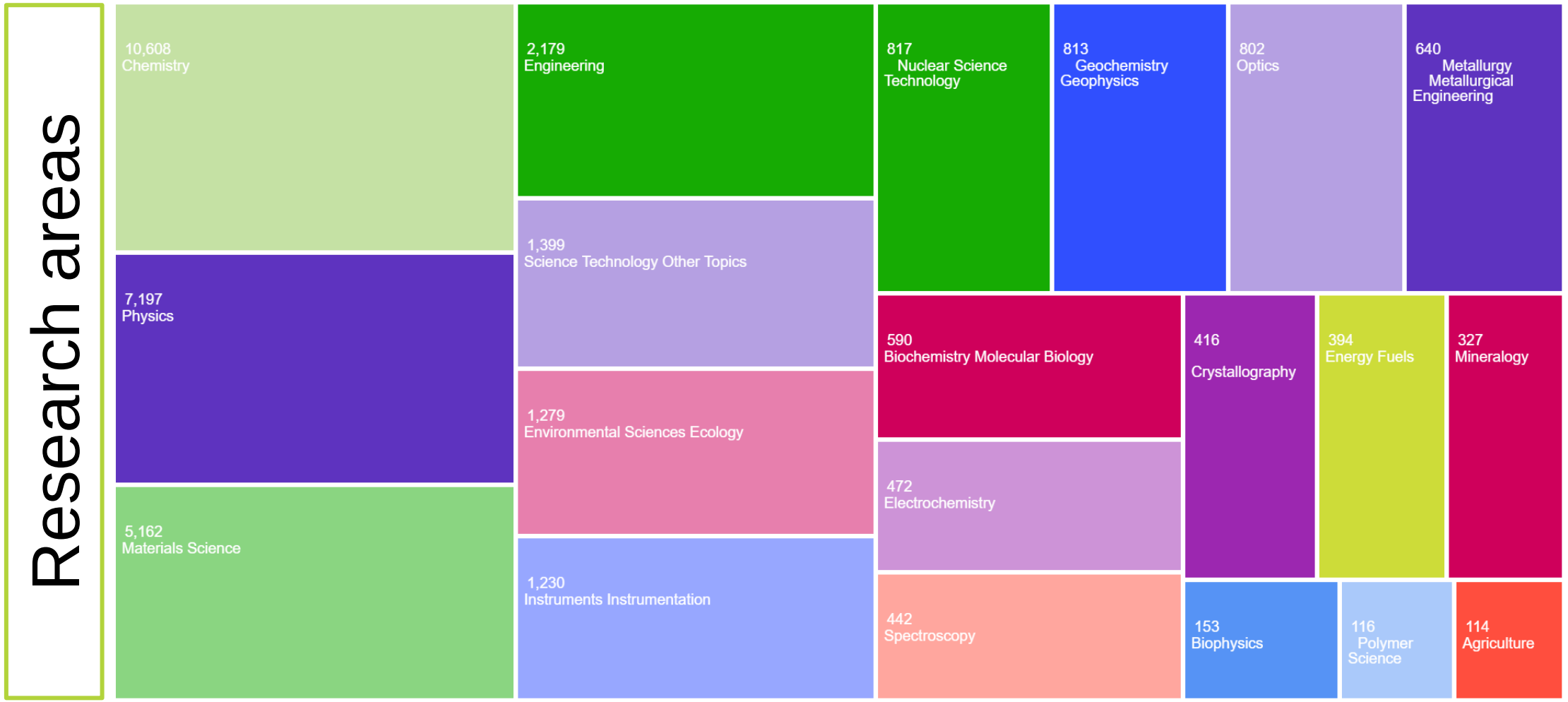
Agenda

- Fundamentals of XANES
- Relevance of the technique
- Interpretation of XANES
- High energy resolution techniques
- Data analysis

Acknowledgment

The following talk is heavily inspired by Denis Leshchev talks on XANES analysis and High-Resolution Spectroscopy talks at the 2024 NSLS-II EXAFS Workshop.

EXAFS in WoS
21,823 indexed entries and counting…



Source: Clarivate Web of Science. March 2025.

XANES in WoS
16,981 indexed entries and counting…

Source: Clarivate Web of Science. March 2025.

Fundamentals

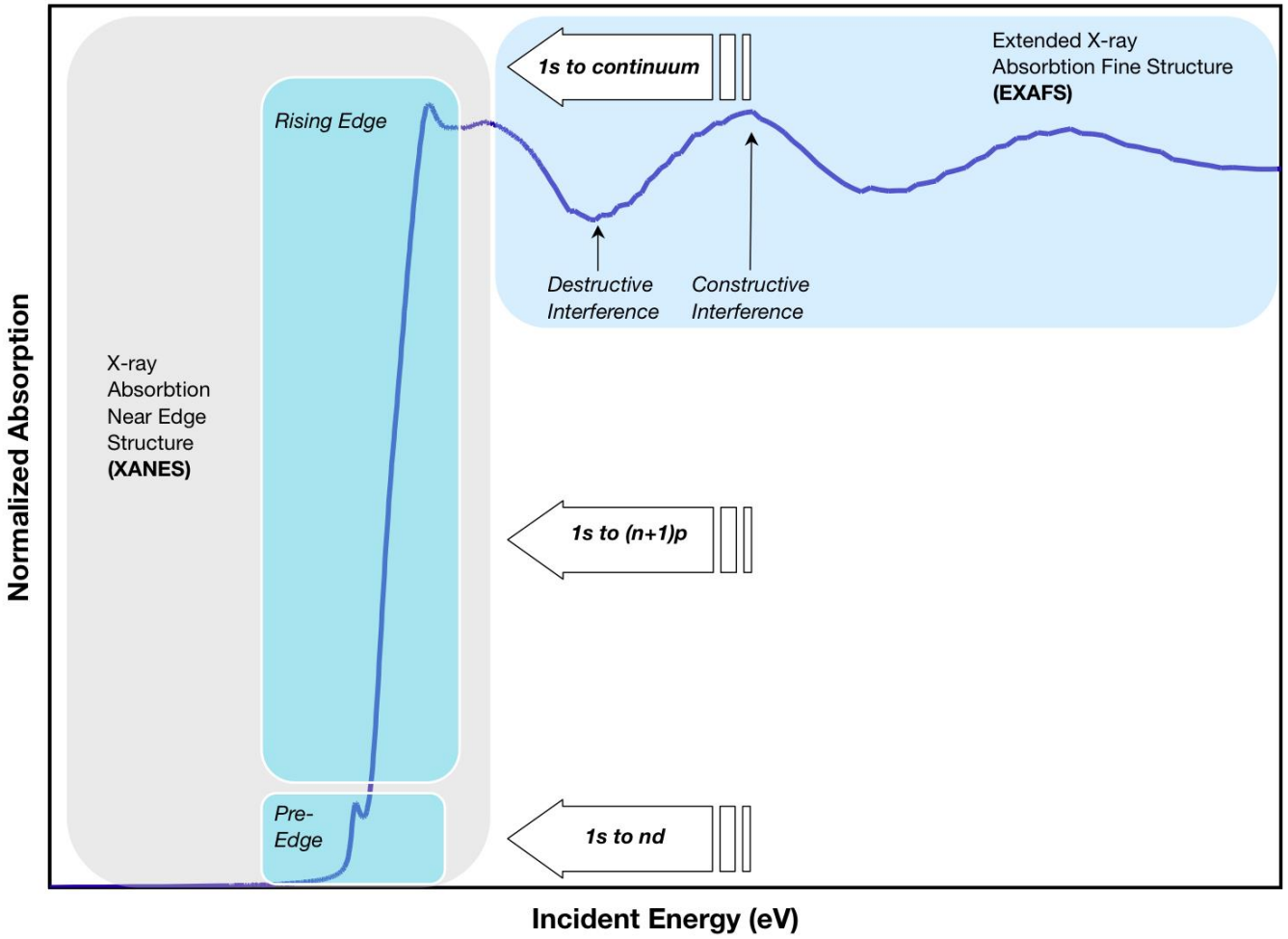
Relevance of XANES

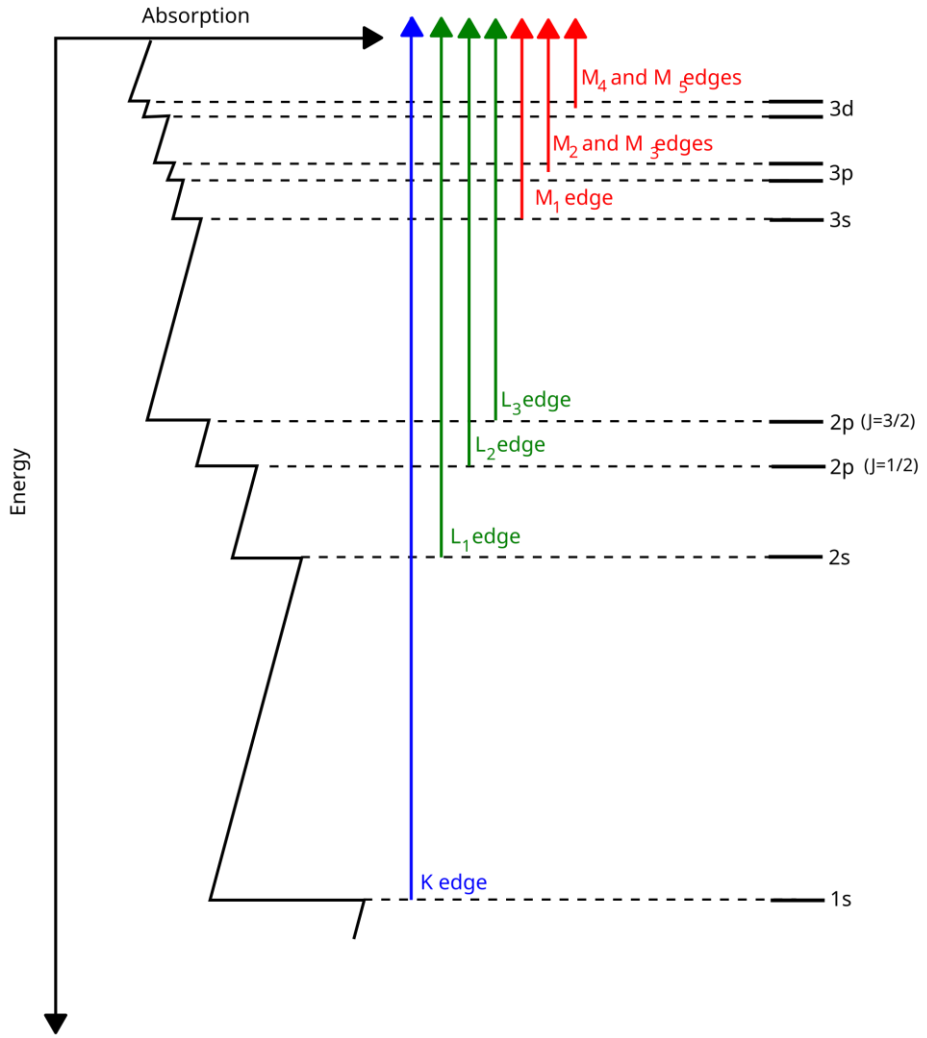
- On the pre-edge region:
  - Ligand field strength and geometry
  - Spin state
  - Centrosymmetry
  - Metal-ligand overlap and covalency

- On the rising-edge region:
  - Geometric structure
  - Metal-ligand overlap via shakedown transitions
  - Charge on the metal center
- Fast data acquisition, high signal to noise ratio, data integrity at high temperature.

Fundamentals

The XAFS Spectrum



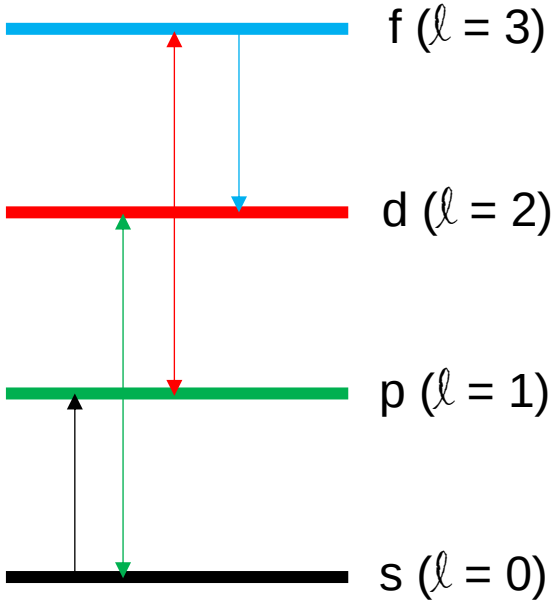


By Atenderholt and Muzarin at English Wikipedia, CC BY-SA 3.0.

Fundamentals

Nomenclature

- The XANES spectrum is governed by the dipole selection rule:
  - A photon has an angular momentum (ℓ) of 1, so the electron on the absorbing atom must undergo $\Delta\ell = \pm 1$ to conserve momentum.
  - Dipole forbidden but quadrupole allowed transitions ($\Delta\ell = \pm 2$) may be present but much weaker

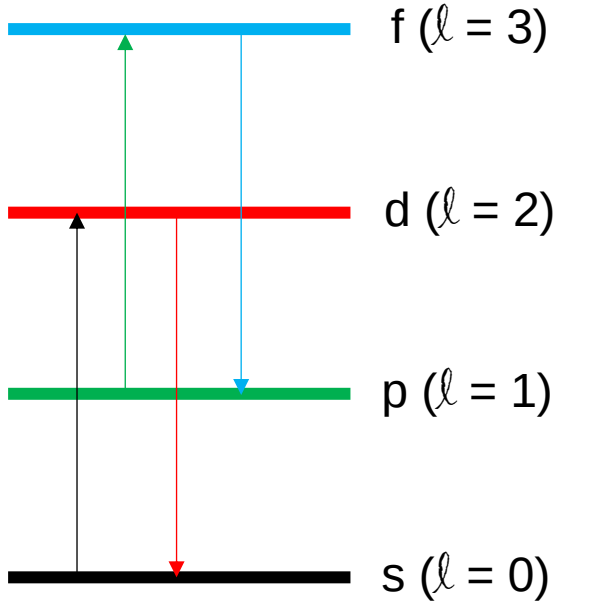


Dipole allowed transitions

Dipole allowed transitions:

- s → p
- p → s, d
- d → p, f

<u>For K-edge:</u>
1s to p (unoccupied)
<u>For L1-edge:</u>
2s to p (unoccupied)
<u>For L2-edge:</u>
$2p_{1/2}$ to d (unoccupied)
<u>L3-edge:</u>
$2p_{3/2}$ to d (unoccupied)

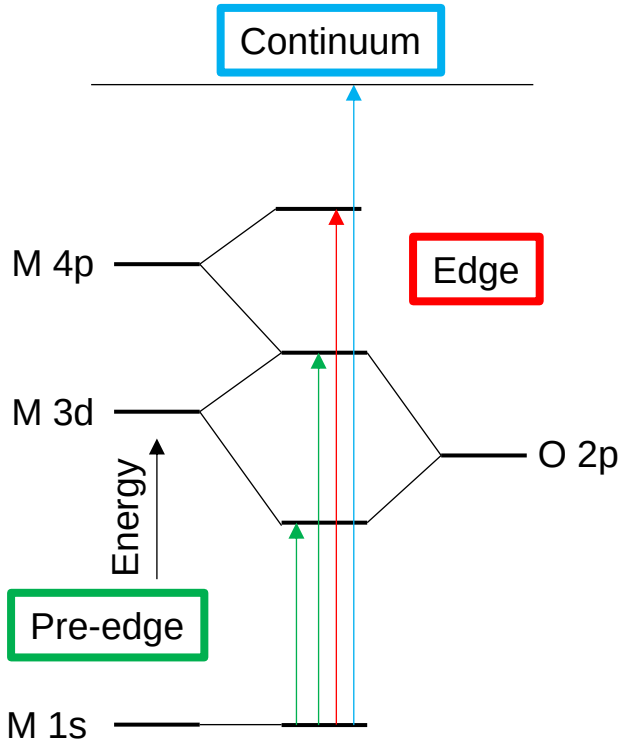


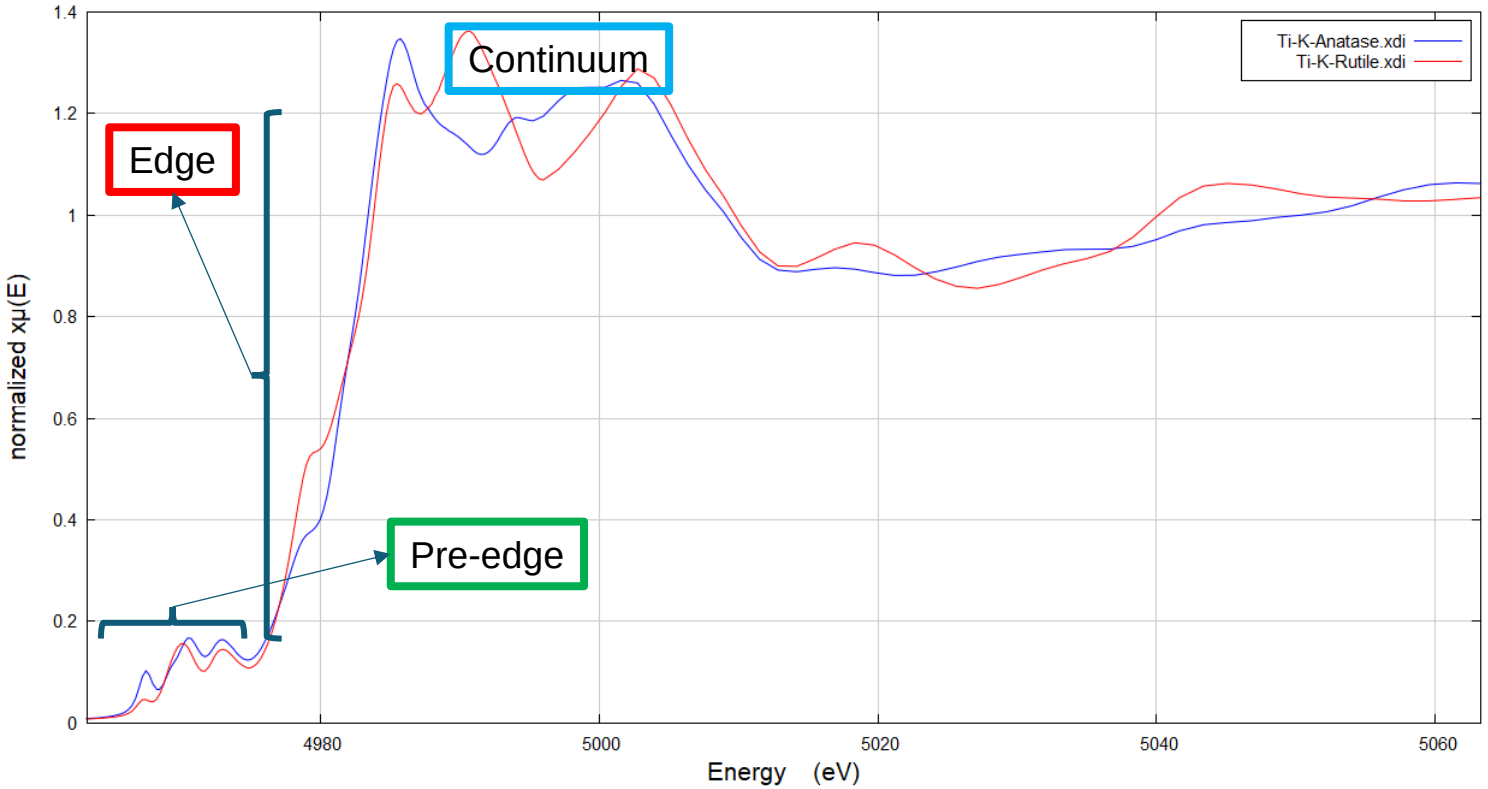
100x weaker

Quadrupole allowed transitions

Fundamentals

Metal K-edge XANES





Metal K-pre-edge absorptions arise due to quadrupole-allowed dipole-forbidden 1s to 3d excitation ($\Delta\ell = \pm 2$, week)

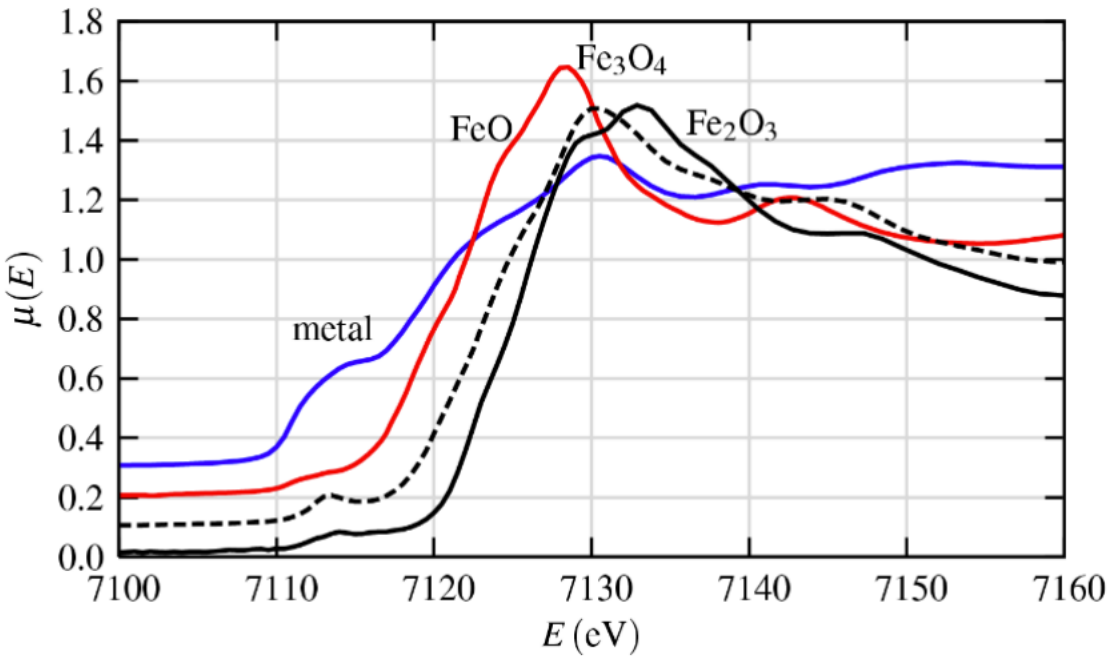
Metal K-rising-edge absorptions are dielectric dipole allowed 1s to 4p excitation ($\Delta\ell = \pm 1$, strong)

Interpretation of XANES

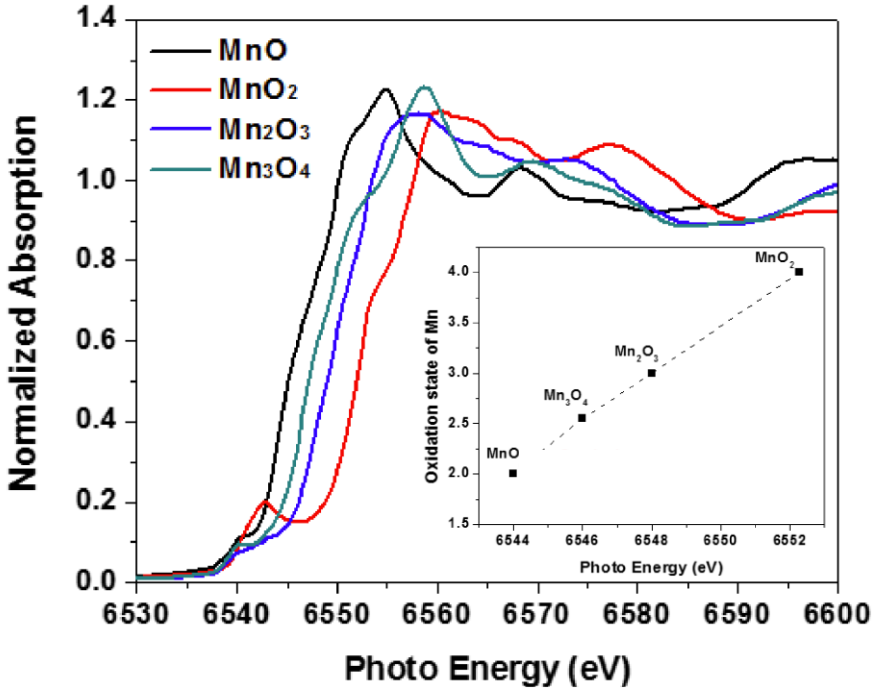
Sensitivity to electronic structure

Interpretation of XANES

Selectivity to oxidation state



Fundamentals of XAFS, Matt Newville



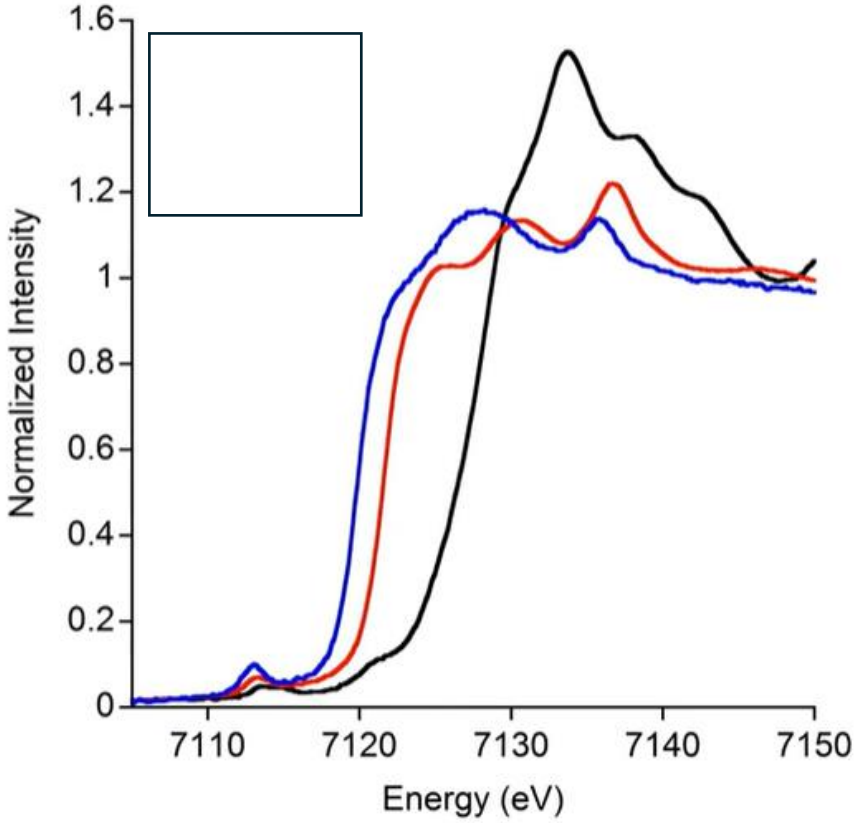
Chem. Commun. 51(2015)5951

- Rising edge and white line maxima shift to higher energy with increase of oxidation state*

*Special considerations apply

Interpretation of XANES

Selectivity to bonding



Chris Pollock, Fundamentals of X-ray Absorption Spectroscopy

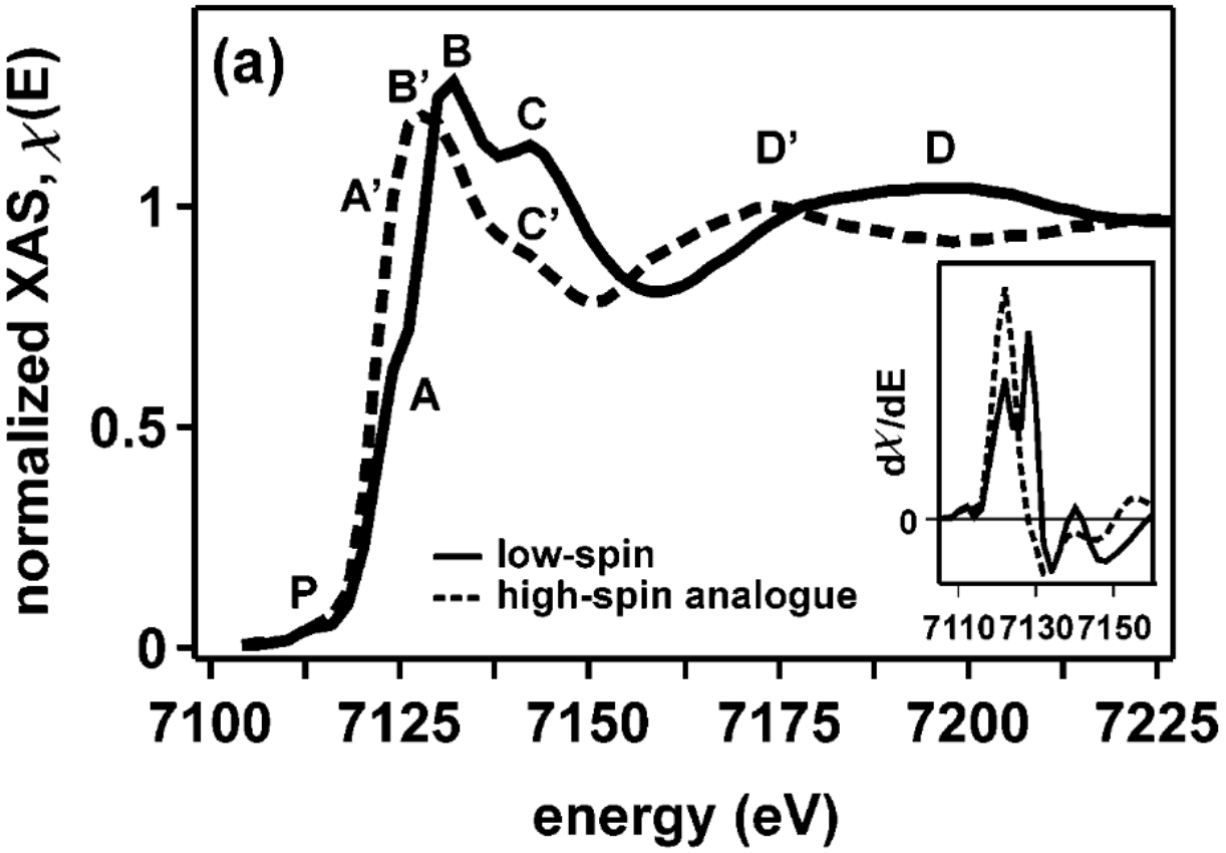
Electronegativity of bounded halogens change the core energy level of Fe 1s electrons

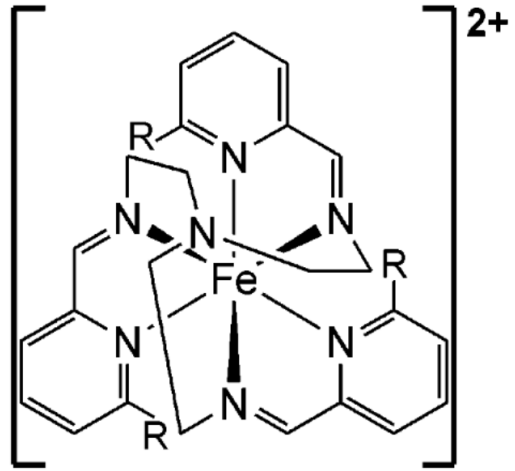
Increase in electronegativity pulls electrons from Fe making look more oxidized

In general, heavier atoms push the edge lower in energy

Interpretation of XANES

Local structure



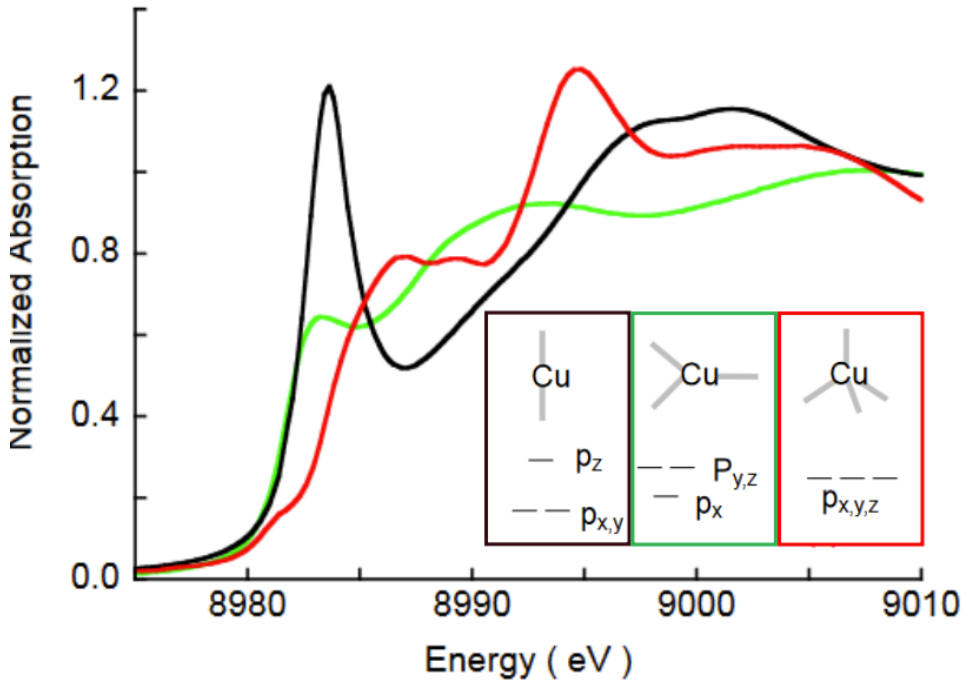


- Same oxidation state (Fe^{2+}) but different spin shift

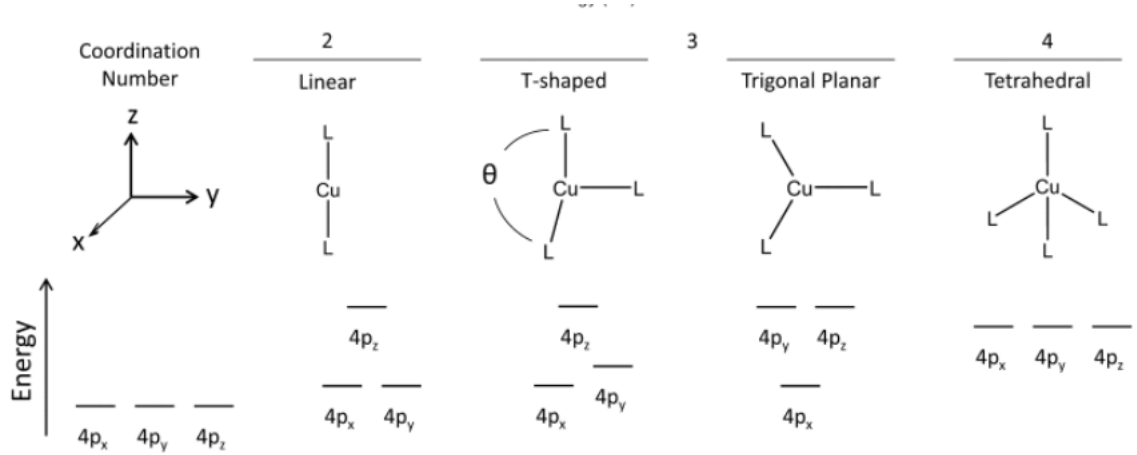
J. Phys. Chem. A 110 (2006) 38

Interpretation of XANES

Local symmetry



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



1s → 4p transition and its energy and intensity depend on the ligand environment around the Cu(I) centers

J. Phys. Chem. A 110 (2006) 38

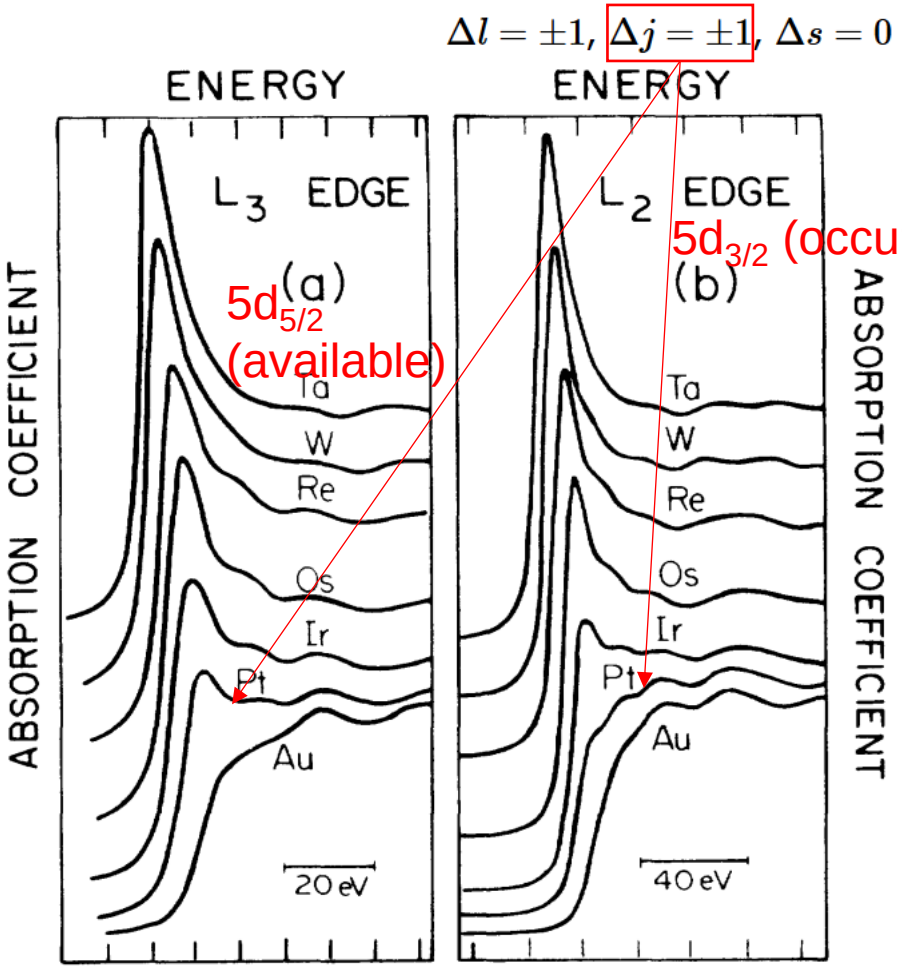
Interpretation of XANES

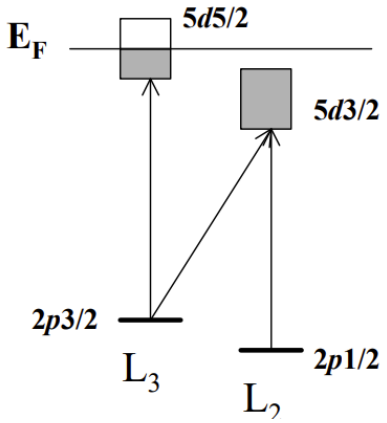
L2 and L3 edges for 5d metals

For L2 and L3 edges - Number of holes in the 5d orbital (2p – 5d) determines the white line intensity

White line absent in gold because of full 5d shell

Absence of white line in Au-L3 and Pt-L2 edges frequently used to determine formation of intermetallic Au-X and Pt-X systems by charge transfer contribution to white line





Phys Rev Lett, 36̄ (1987) 2972

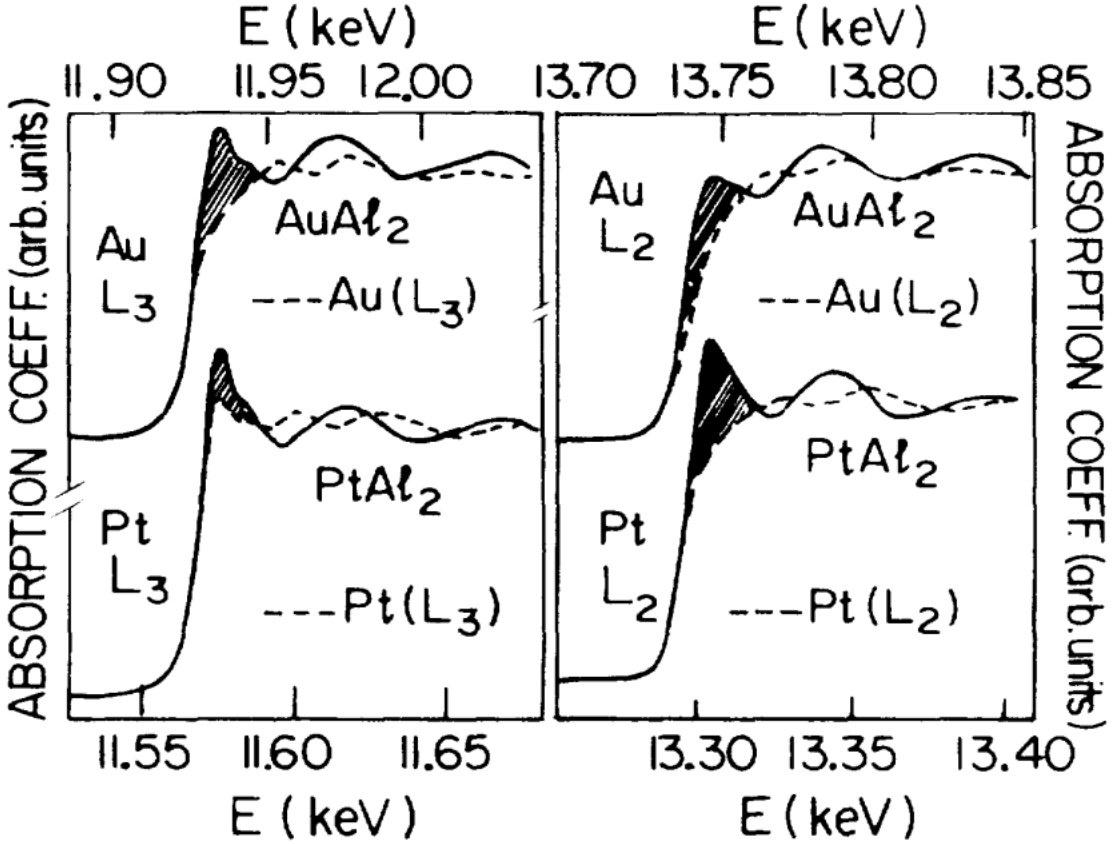
Interpretation of XANES

L2 and L3 edges for 5d metals

For L2 and L3 edges - Number of holes in the 5d orbital (2p – 5d) determines the white line intensity

White line absent in gold because of full 5d shell in L3-edge

Absence of white line in Au-L3 and Pt-L2 edges to determine formation of intermetallic $AuAl_2$ and $PtAl_2$ systems by charge transfer contribution to white line



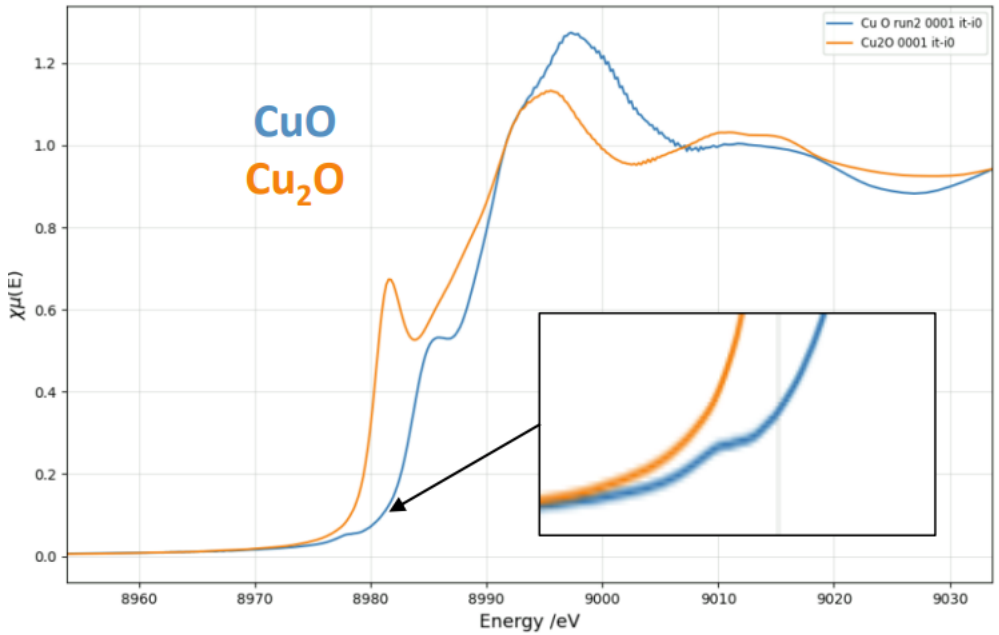
Phys Rev Lett, 36 (1987) 2972

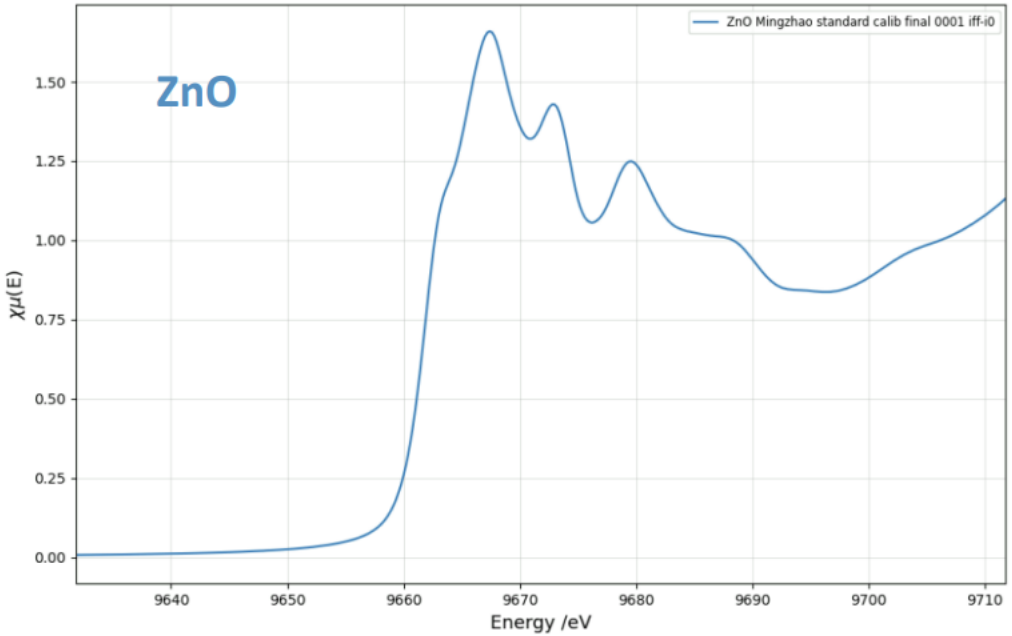
Interpretation of XANES

Pre-edge

Interpretation of XANES

Pre-edge features





Cu_2O, ZnO - d^{10} systems - do not have any pre-edge

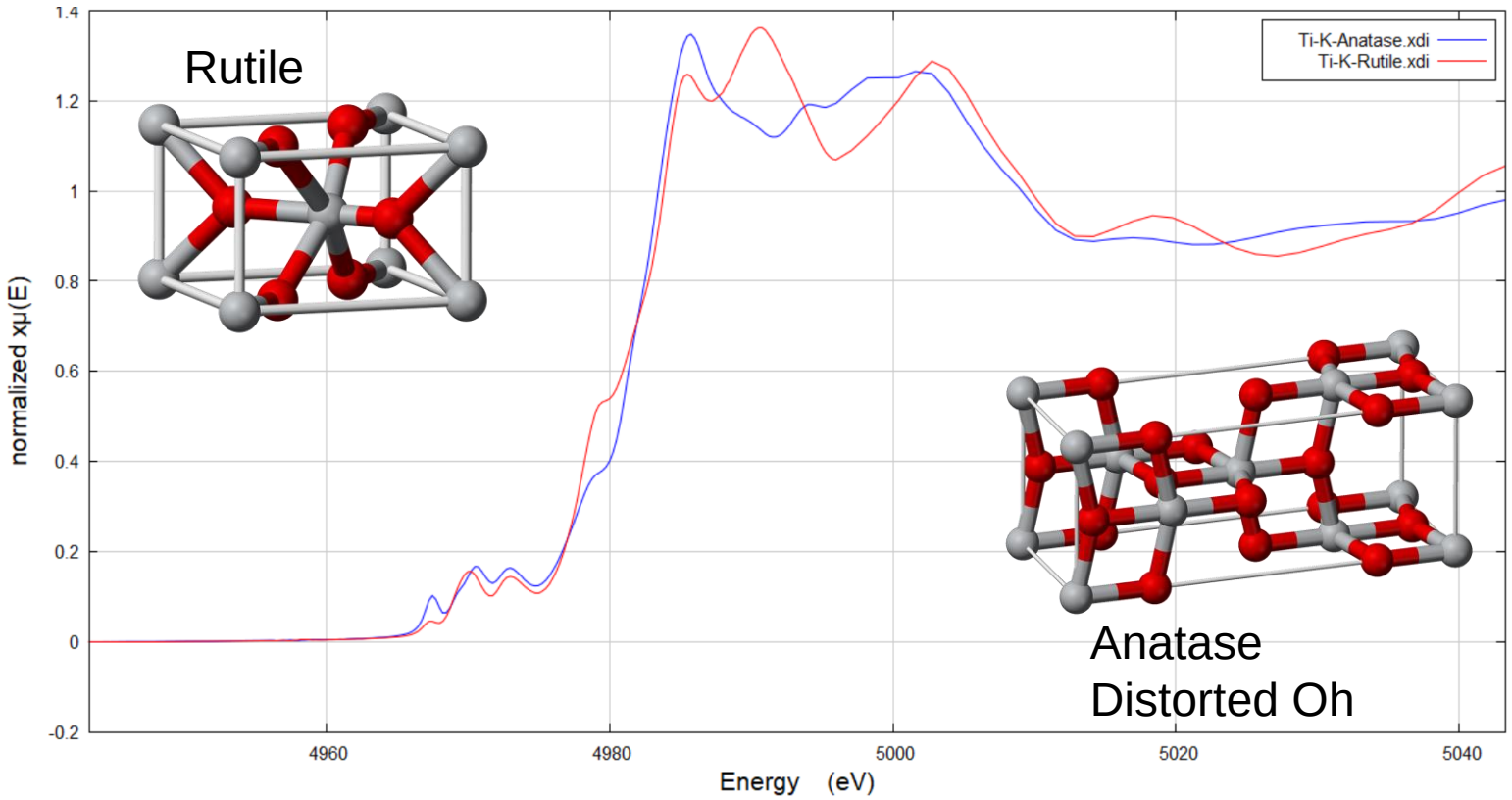
CuO – d^9 system – has one!

Interpretation of XANES

Pre-edge features

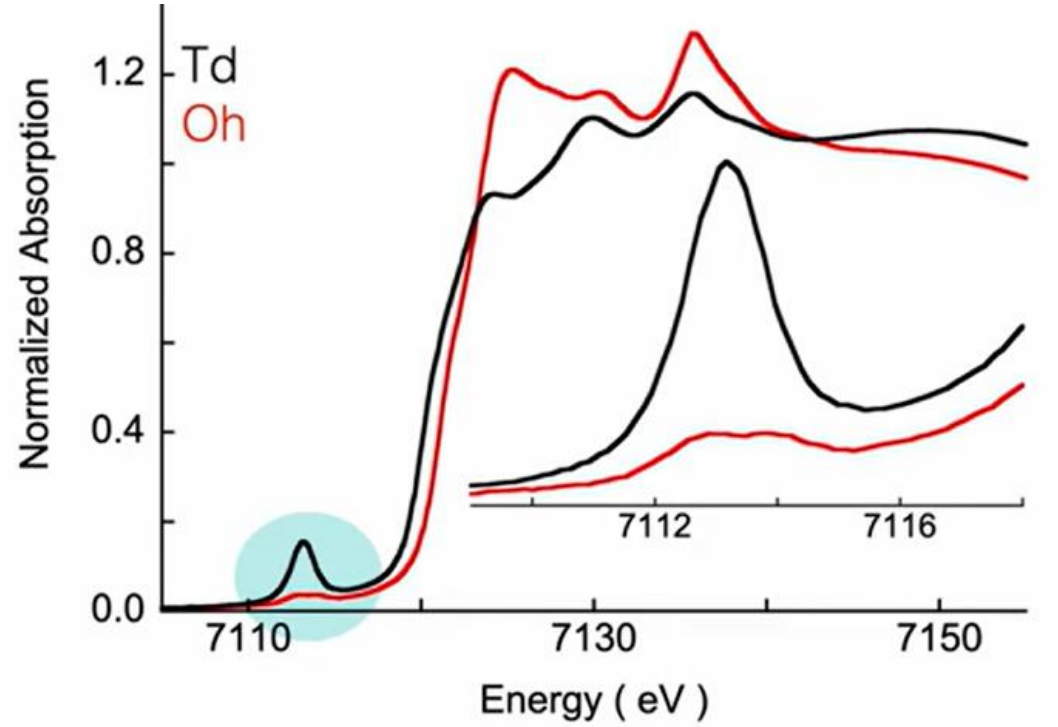
Rutile and anatase: Both TiO2 with Oh coordination and same oxidation state

Deviation from centrosymmetric geometry increase intensity of pre-edge features



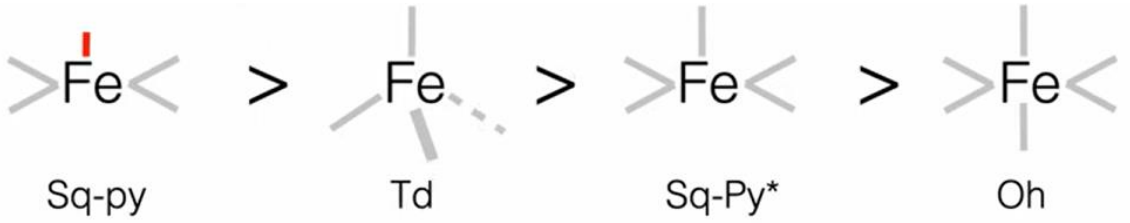
Interpretation of XANES

Pre-edge features



Ritimukta Sarangi, Electronic Structure Interpretation from XANES

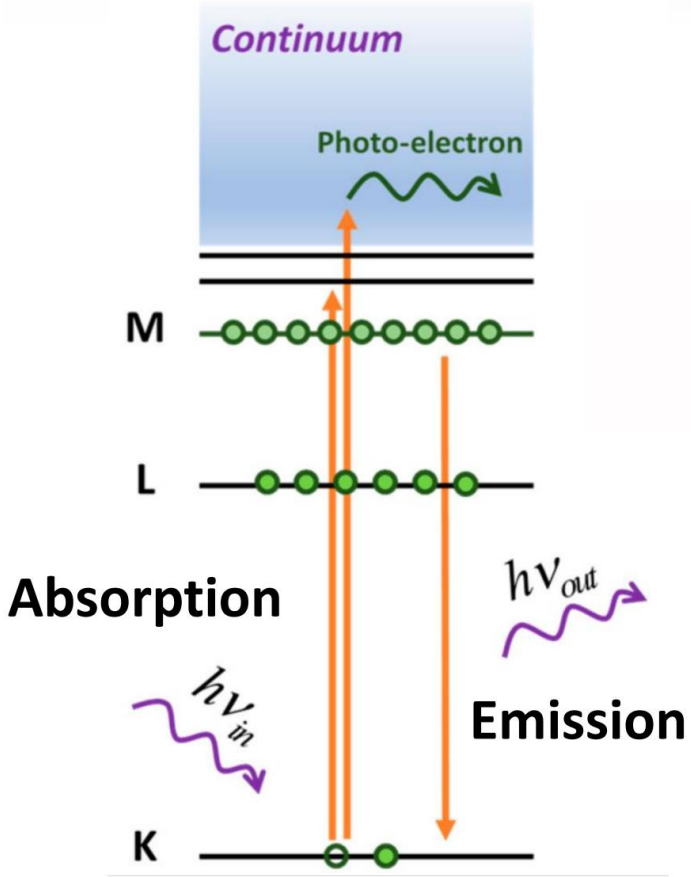
- Pre-edge intensity proportional to deviation from centrosymmetry (metal 3d-4p mixing)



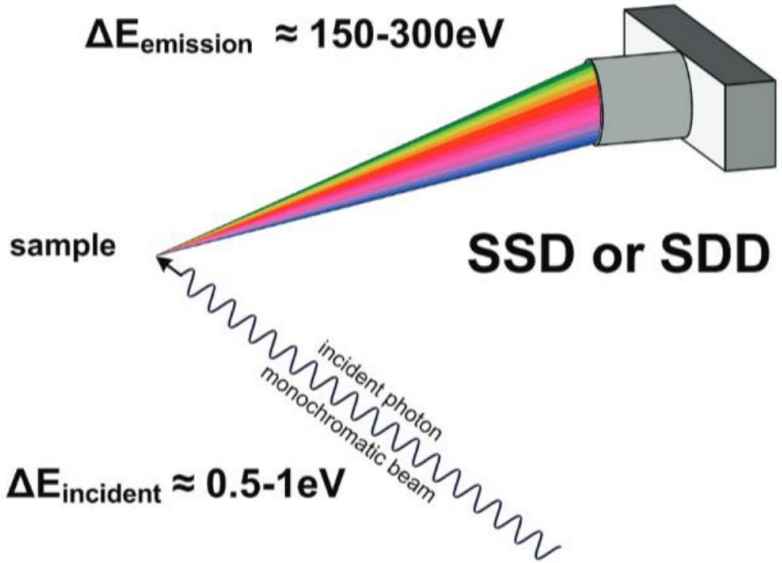
High energy resolution techniques

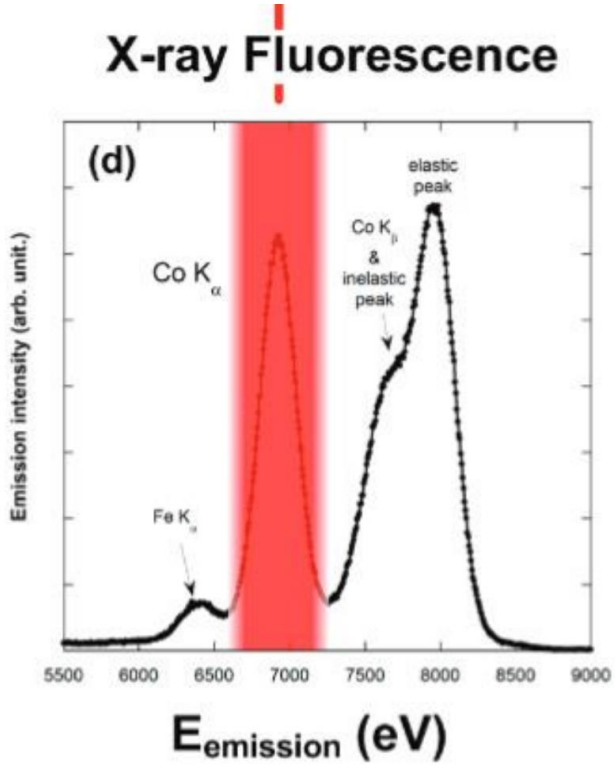
A brief introduction

XAS with fluorescence detection



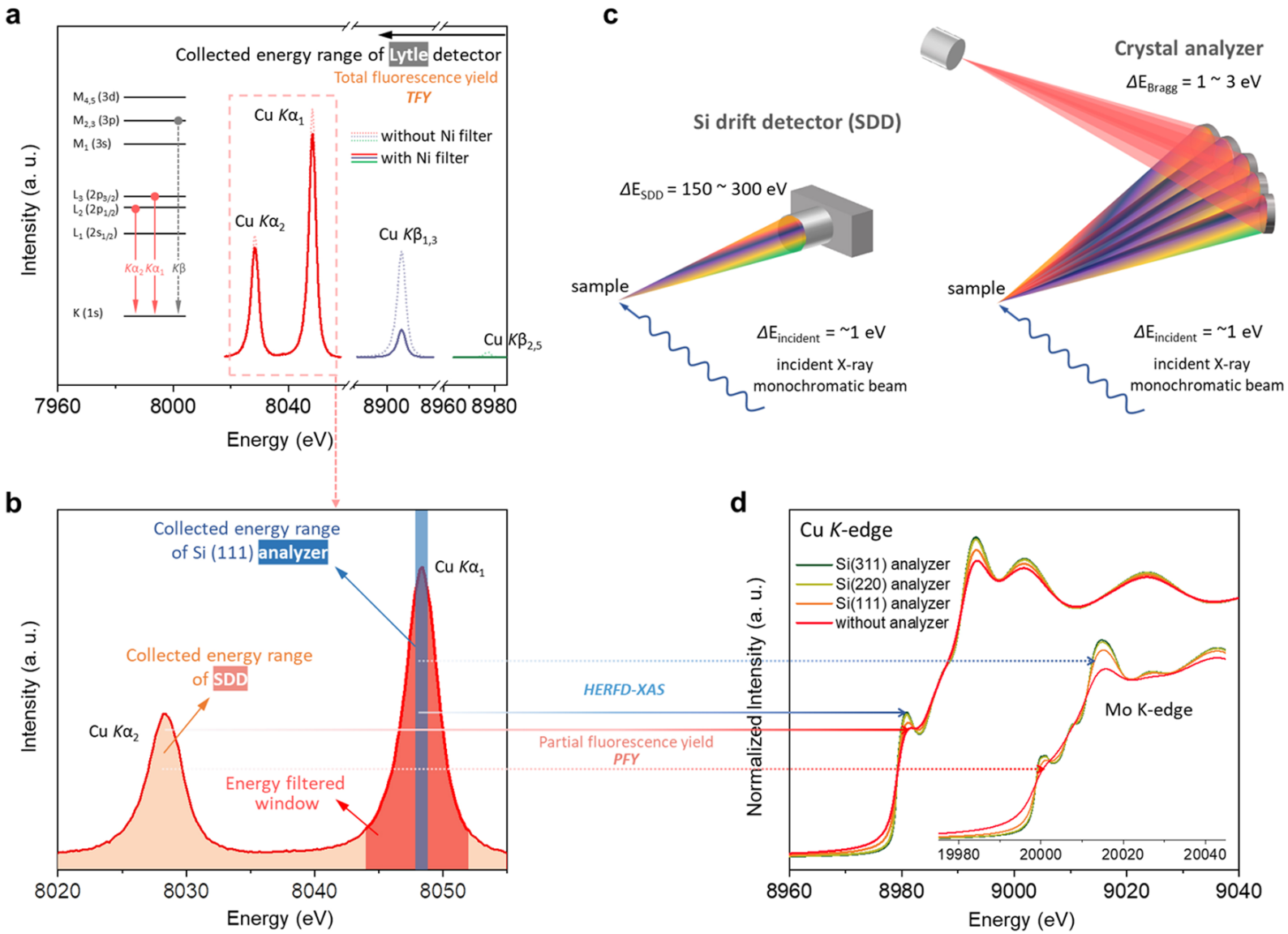
Biochimica et Biophysica Acta 1853 (2015) 1406–1415





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

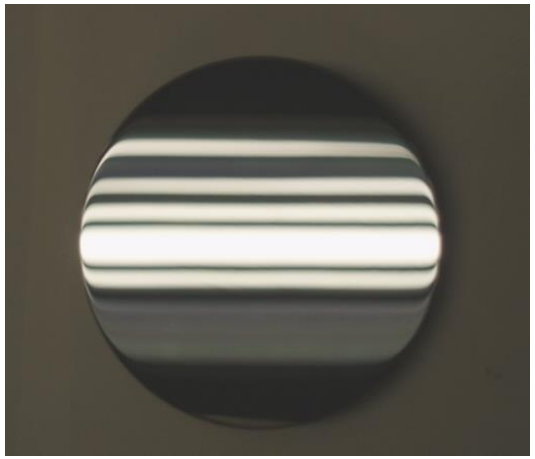
High energy resolution techniques

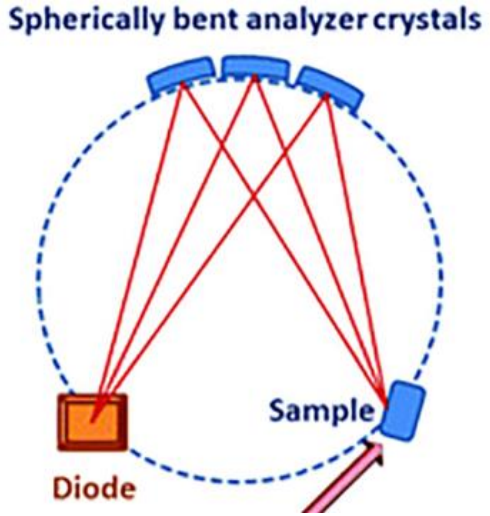


Nature Communications 14 (2023) 6576C

High energy resolution techniques

Detection with narrow bandwidth (lower than core hole lifetime broadening).
Fluorescence photons emitted from the sample are dispersed using curved Si/Ge crystals



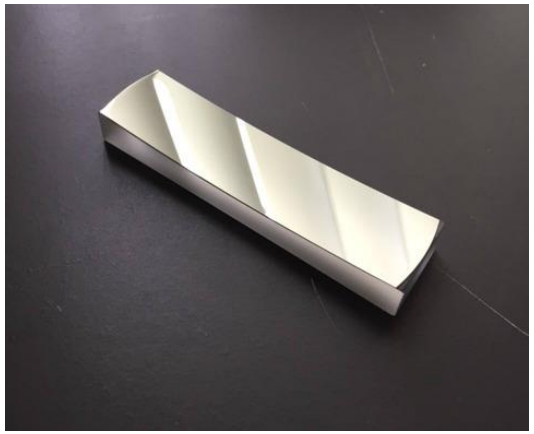


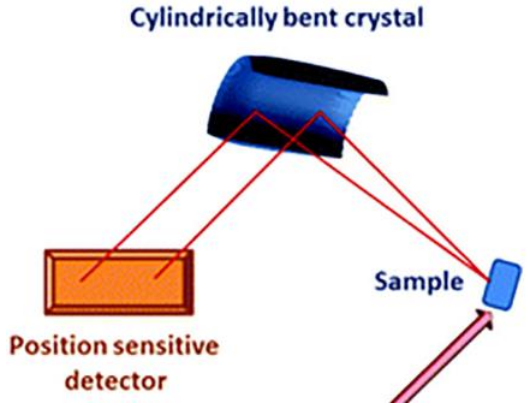
Johann geometry

- Focusing geometry
- Spherical crystal curvature
- Dilute samples

von Hamos geometry

- Dispersive geometry
- Full emission line in 1 image
- Cylindrical curvature
- Concentrated samples
- Fast

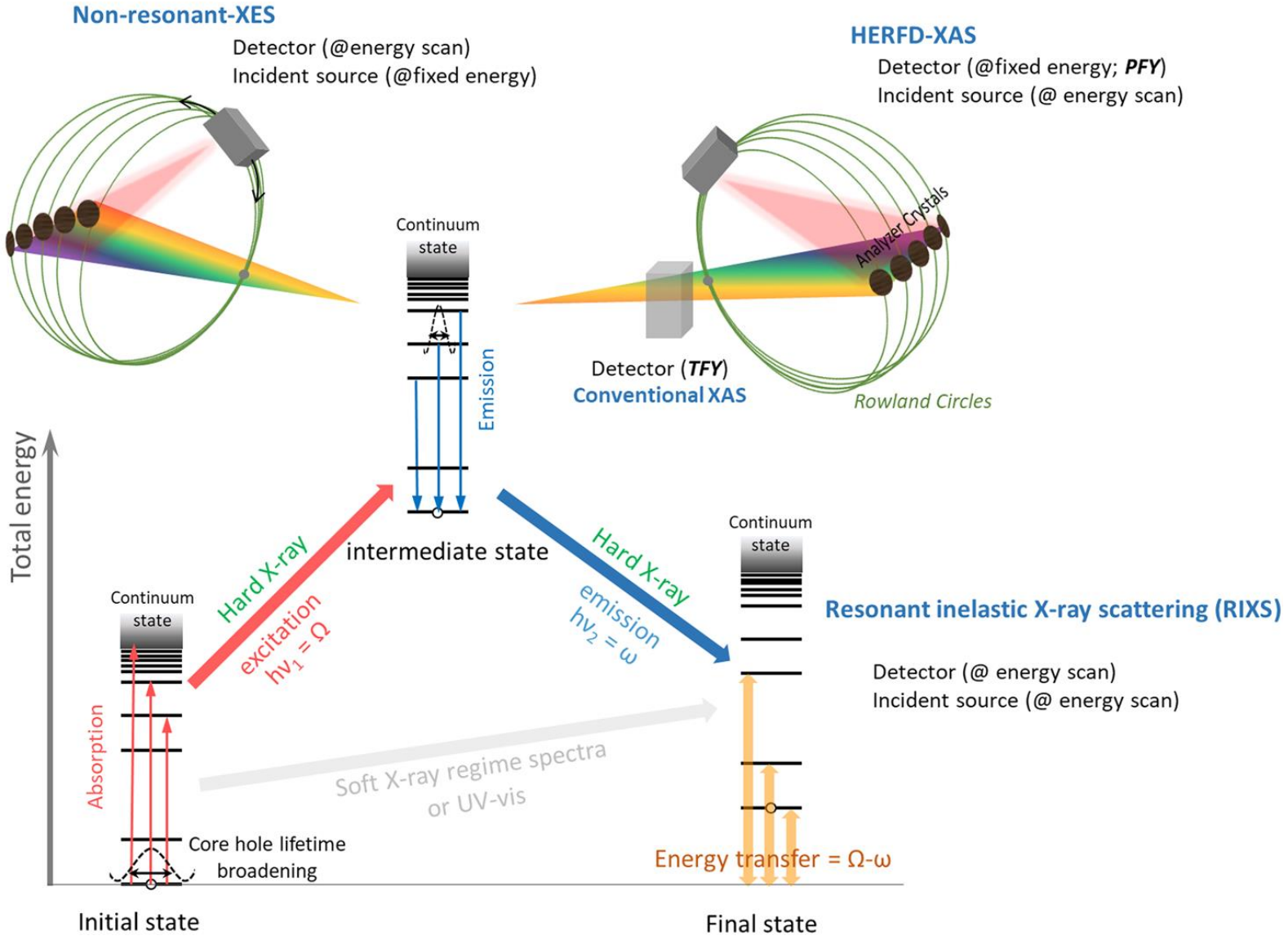




Nature Communications 14 (2023) 1370
Coordination Chemistry Reviews 417 (2020) 213466

High energy resolution techniques

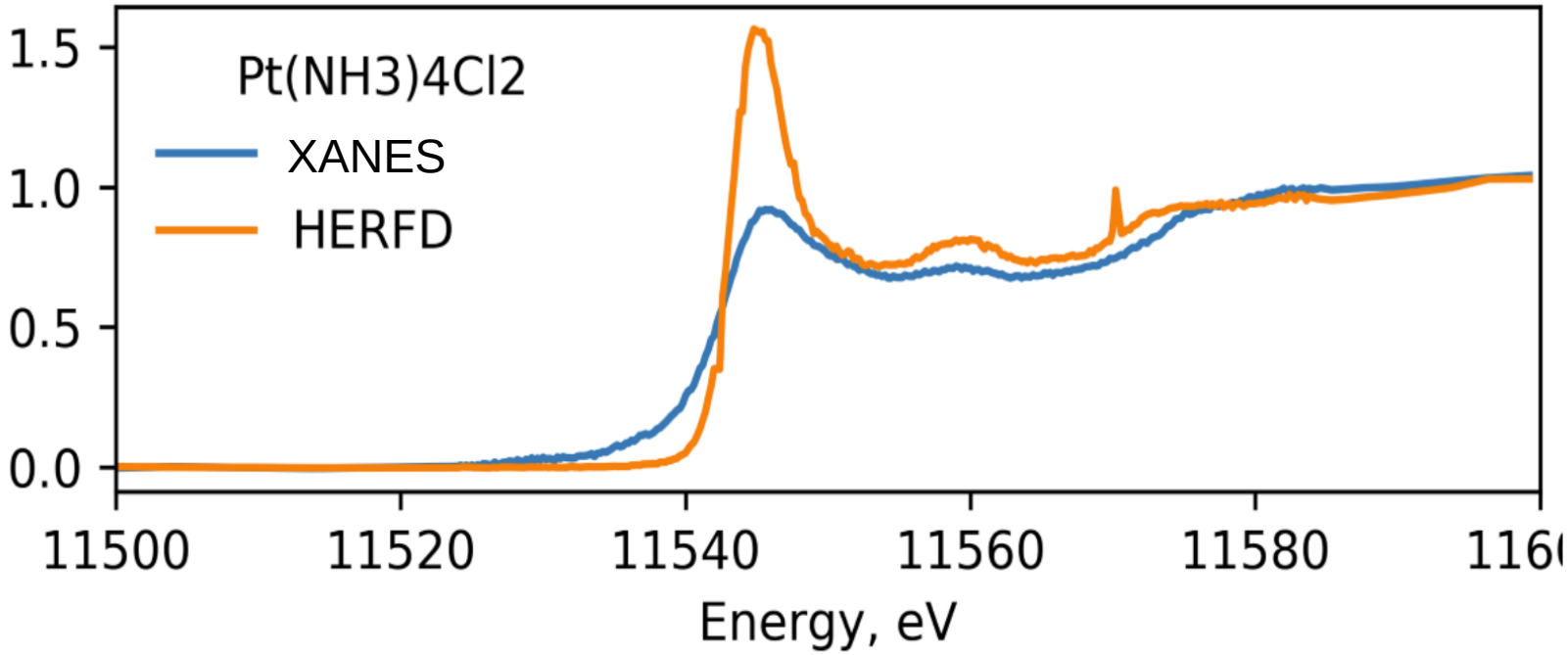
Total energy schemes for various X-ray photon-in (Ω) and photon-out (ω) spectroscopies, accompanied with their brief fundamentals and experimental schemes.



Nature Communications 14 (2023) 6576C

High energy resolution techniques

High-energy resolution fluorescence detected (HERFD) XAS

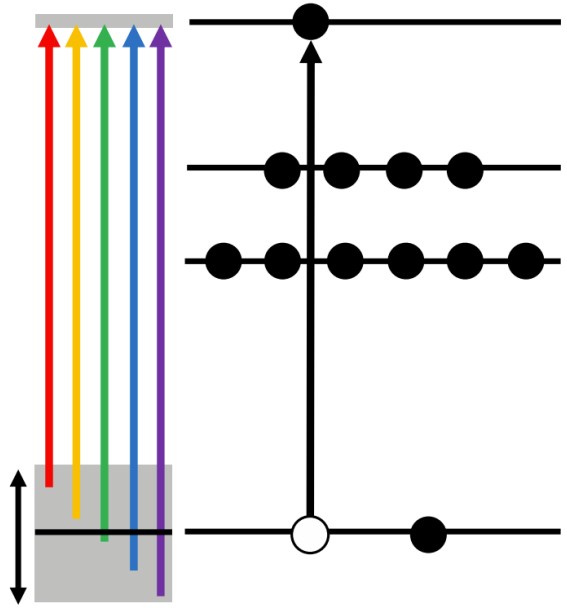


Helps to overcome core hole broadening!

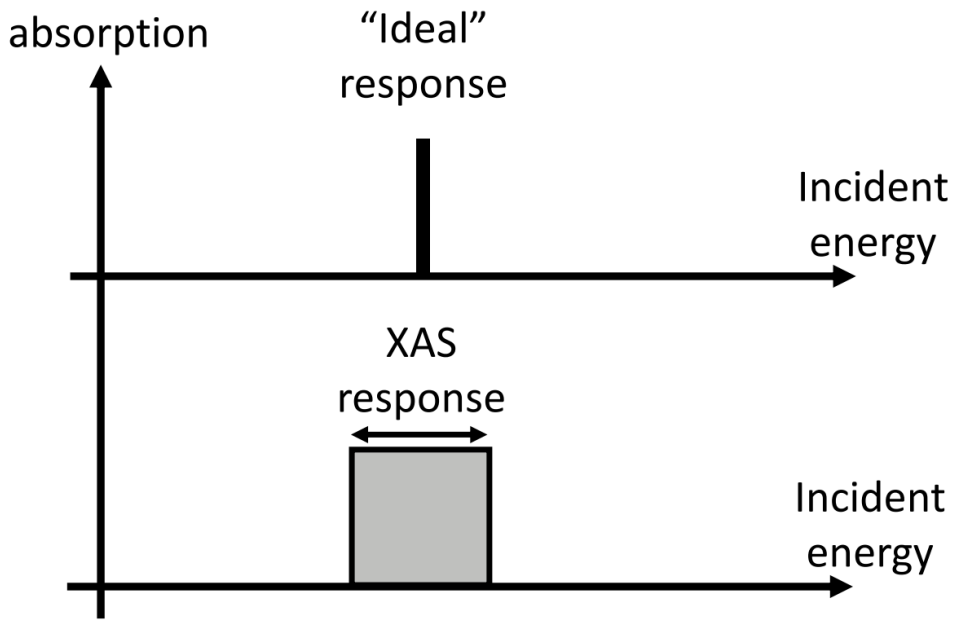
High energy resolution techniques

High-energy resolution fluorescence detected (HERFD) XAS

Transmission

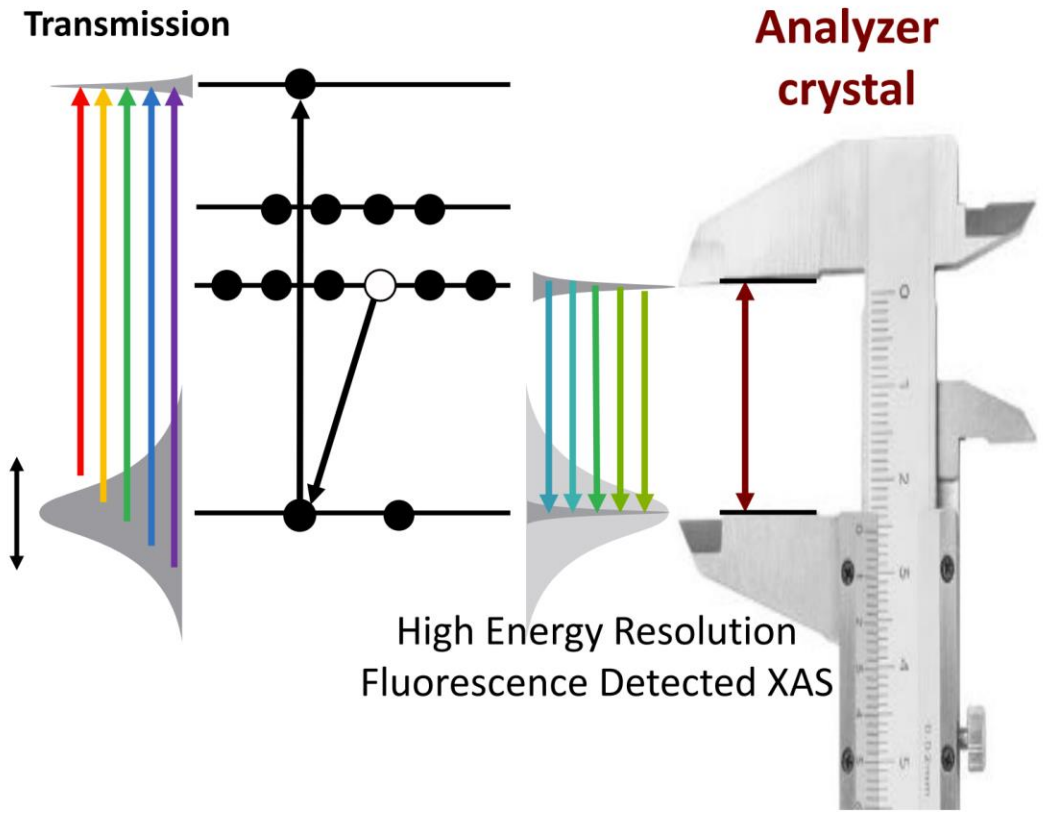


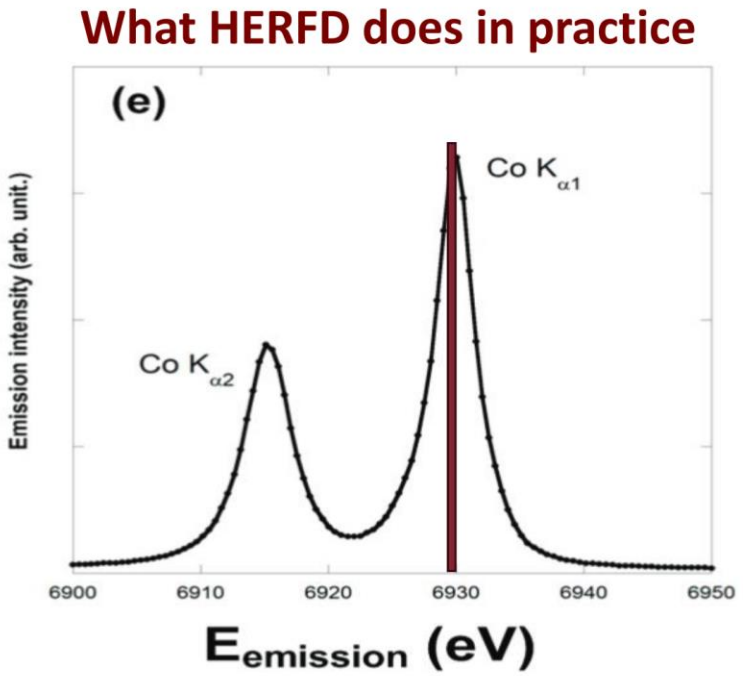
Finite core hole lifetime results in the energy broadening of the level



High energy resolution techniques

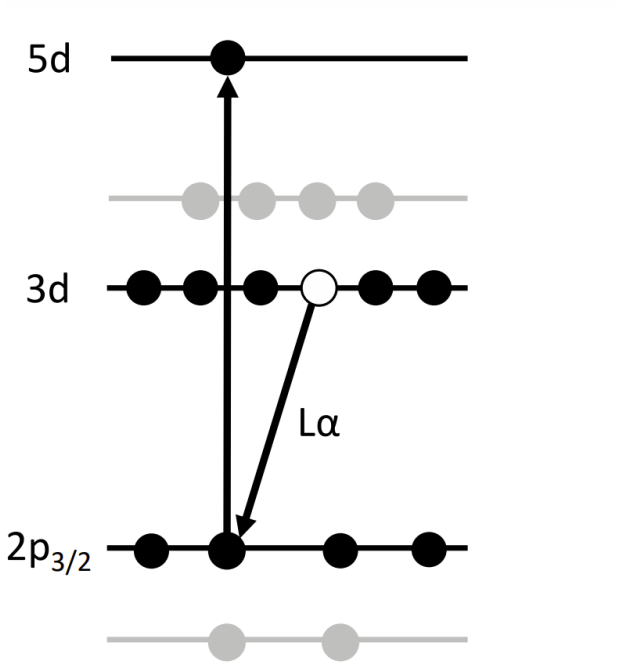
High-energy resolution fluorescence detected (HERFD) XAS





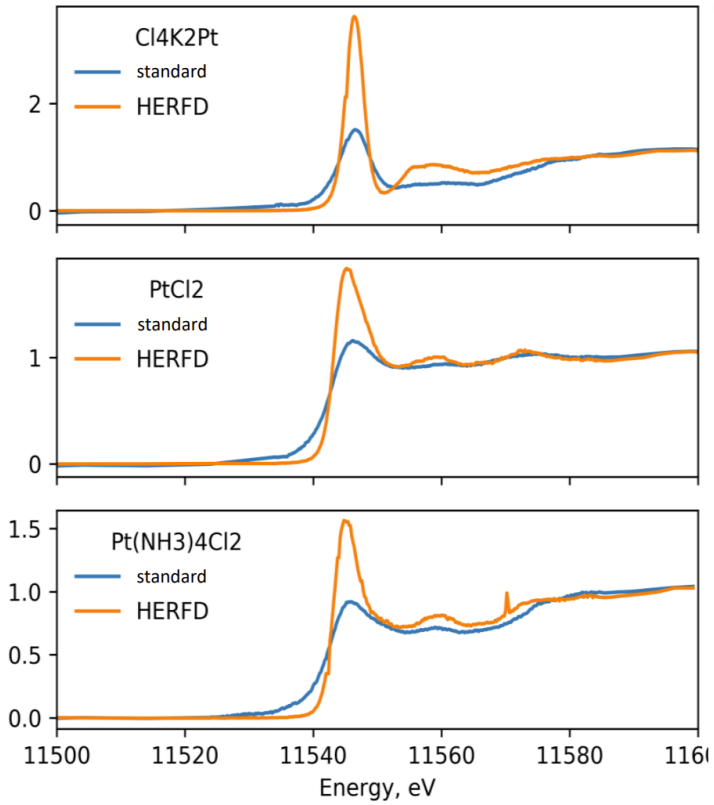
High energy resolution techniques

HERFD Examples: 5d metals



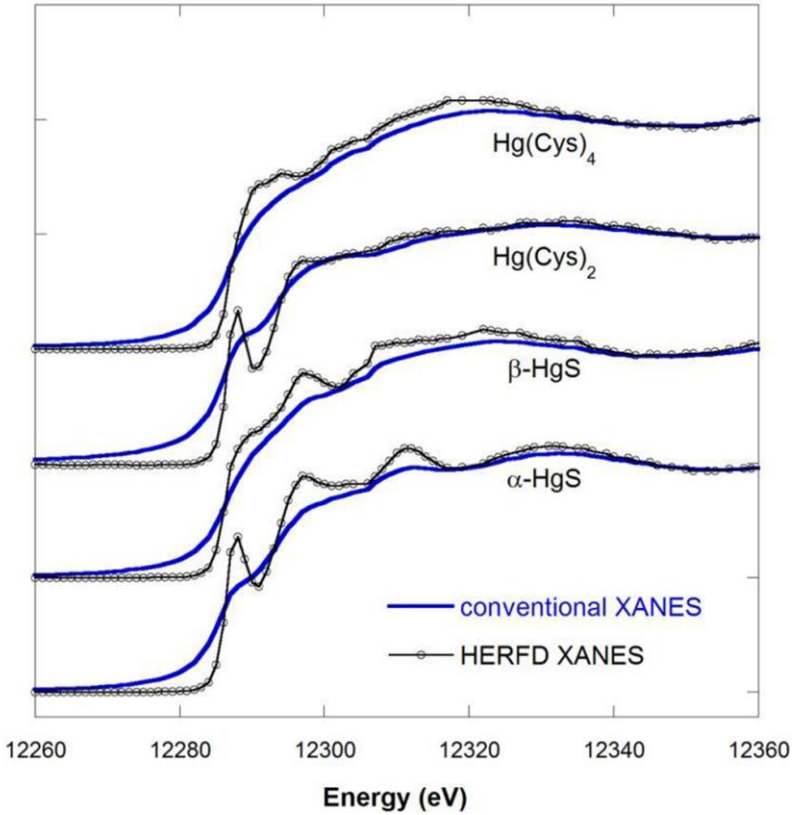
5d metals core-hole broadening can reach 6-8 eV

Pt L3-edge HERFD



ISS data
Samples from Bruce

Hg L3-edge HERFD

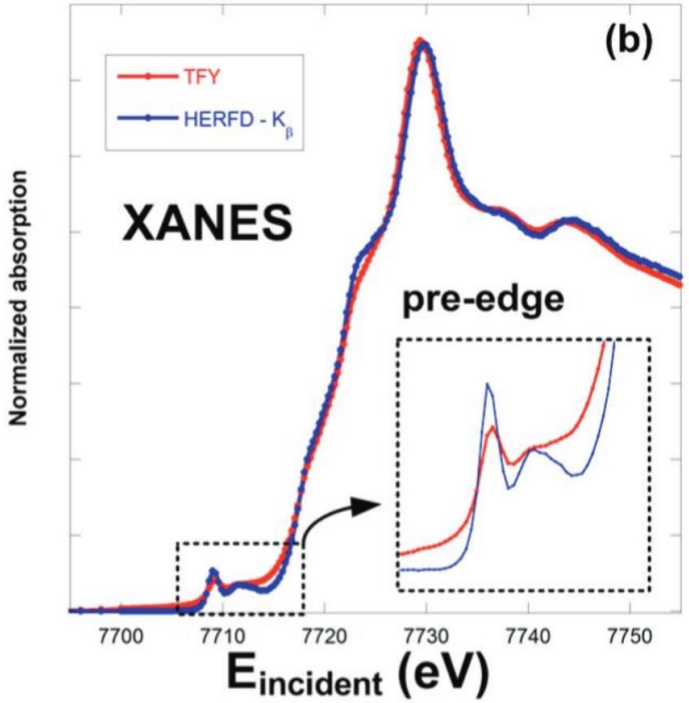


J. Environ. Qual. 46:1146–1157 (2017).

High energy resolution techniques

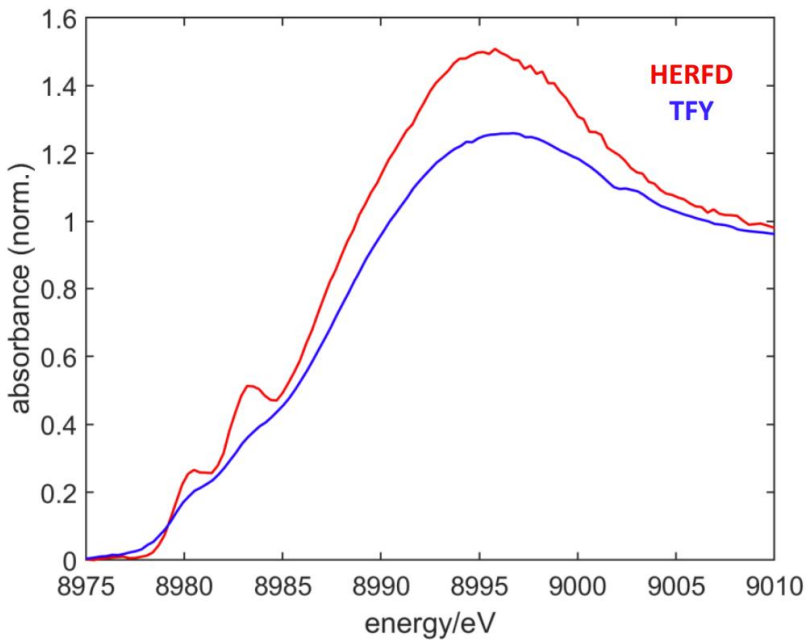
HERFD Examples: 3d metals

Co K-edge HERFD



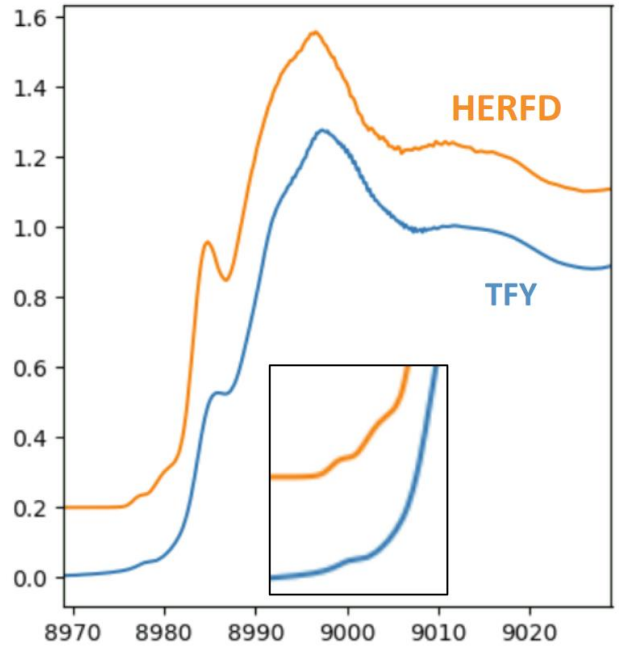
J. Environ. Qual. 46:1146–1157 (2017).

Cu K-edge HERFD



Cu organometallic complex

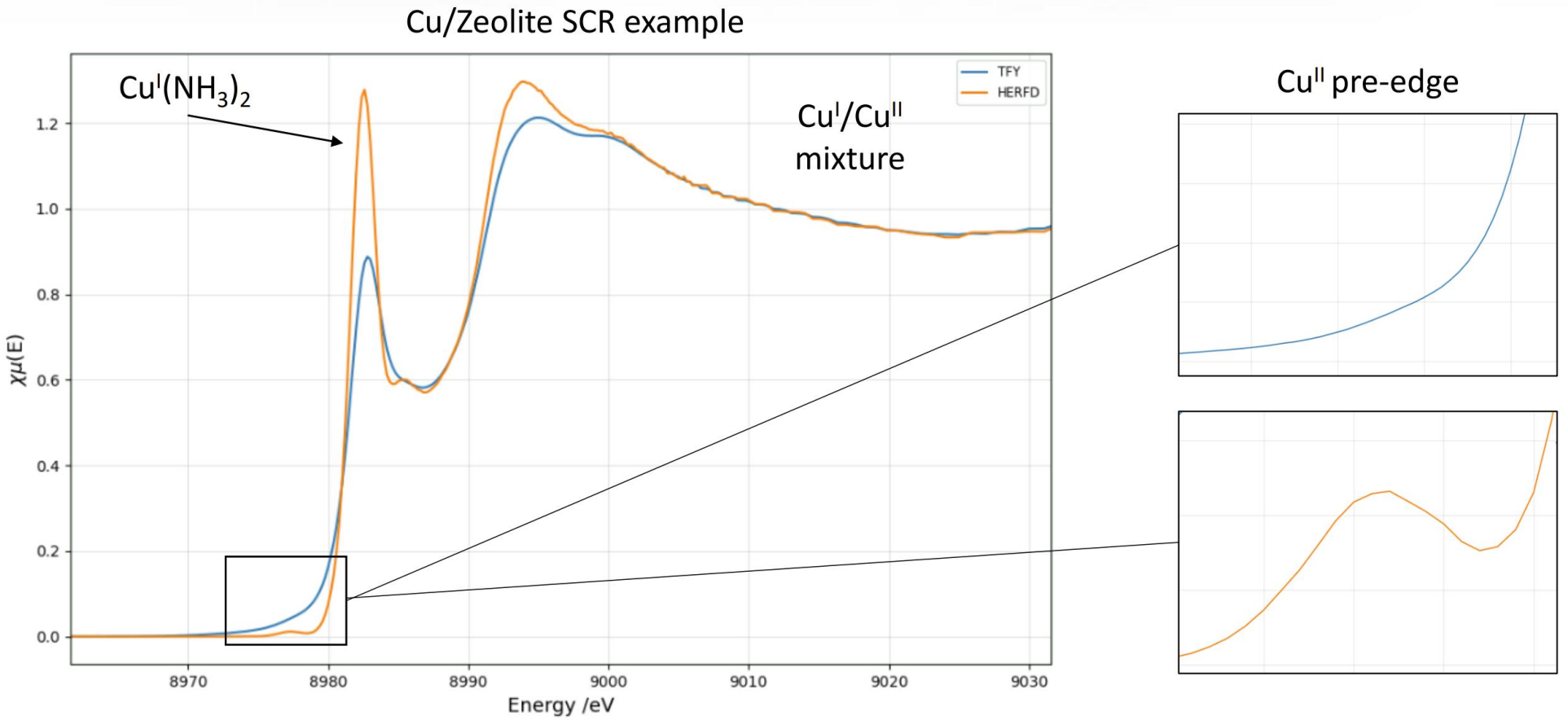
CuO K-edge HERFD



CuO sample

High energy resolution techniques

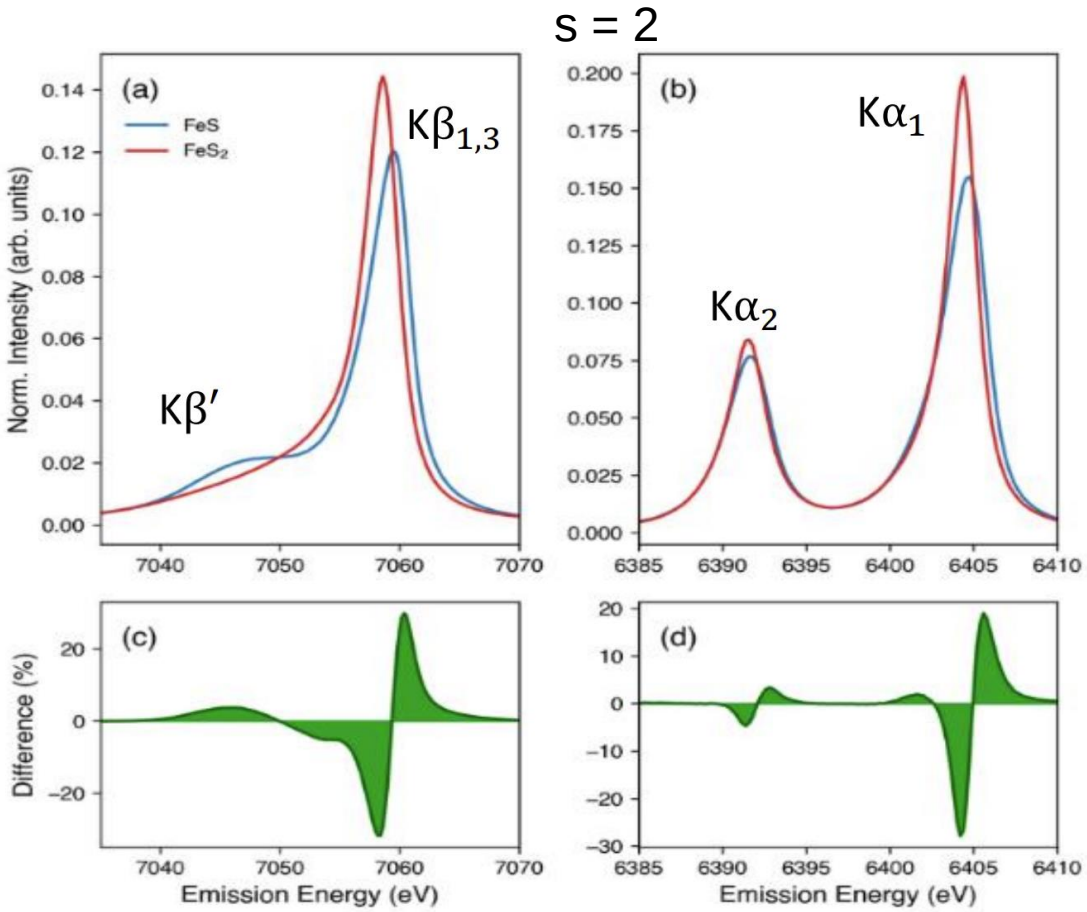
HERFD Examples: 3d metals



High energy resolution techniques

X-ray emission spectroscopy: a spin probe

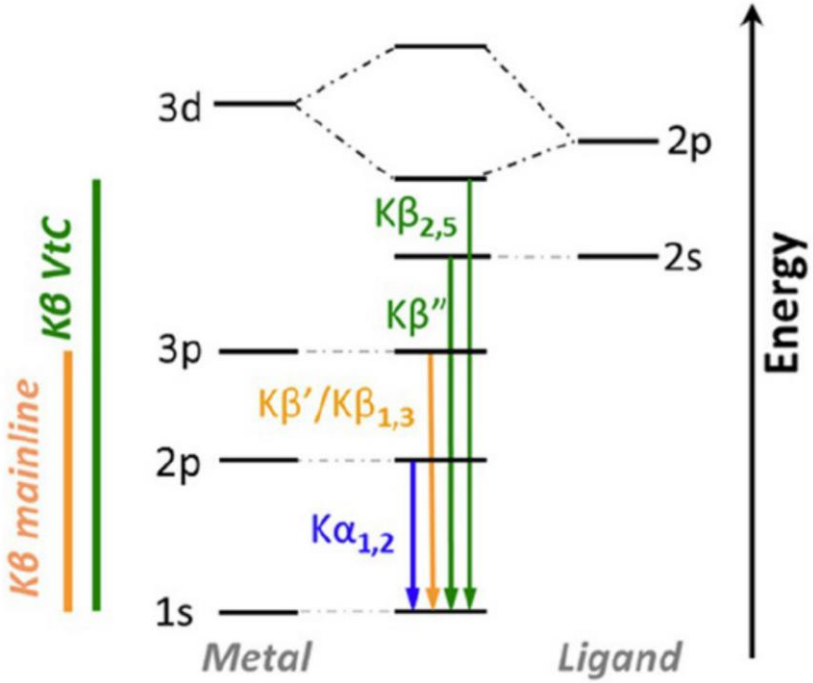
- Fix E_{in} well above the edge (100-150 eV), scan E_{out}
- Kα (2p → 1s) and Kβ (3p → 1s) lines are sensitive to spin state of the absorbing atom (3d/2p and 3d/3p exchange interaction)

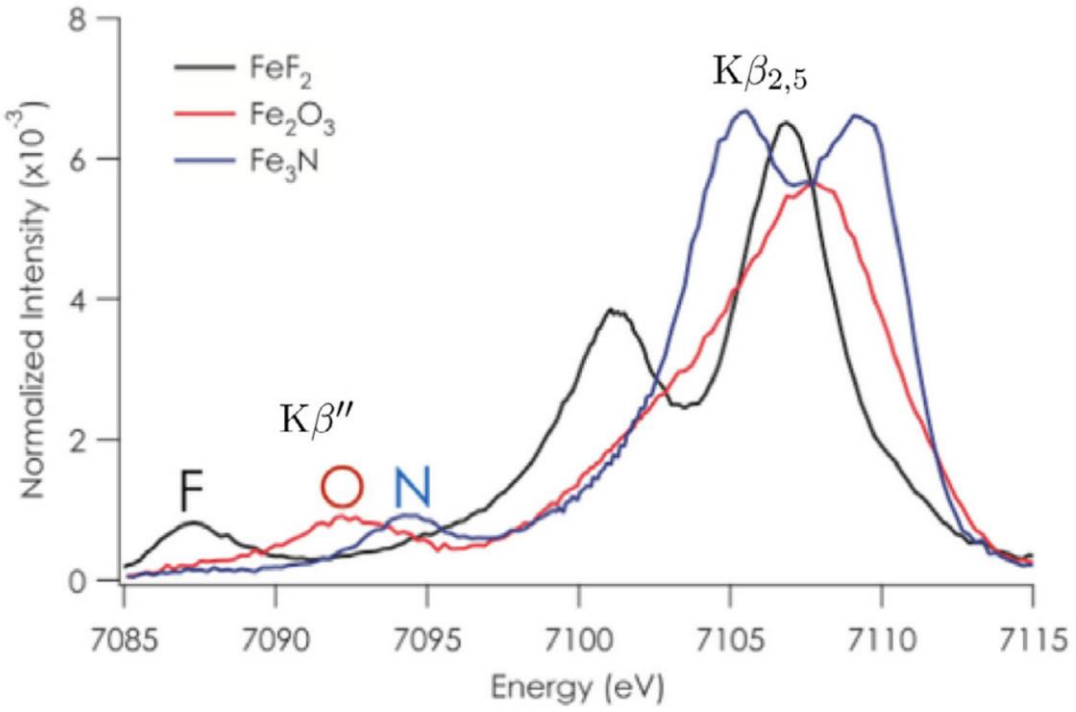


Inorg. Chem.2020, 59, 12518−12535

High energy resolution techniques

X-ray emission spectroscopy: valence-to-core





Coordination Chemistry Reviews, 423(2020)213466

Data analysis

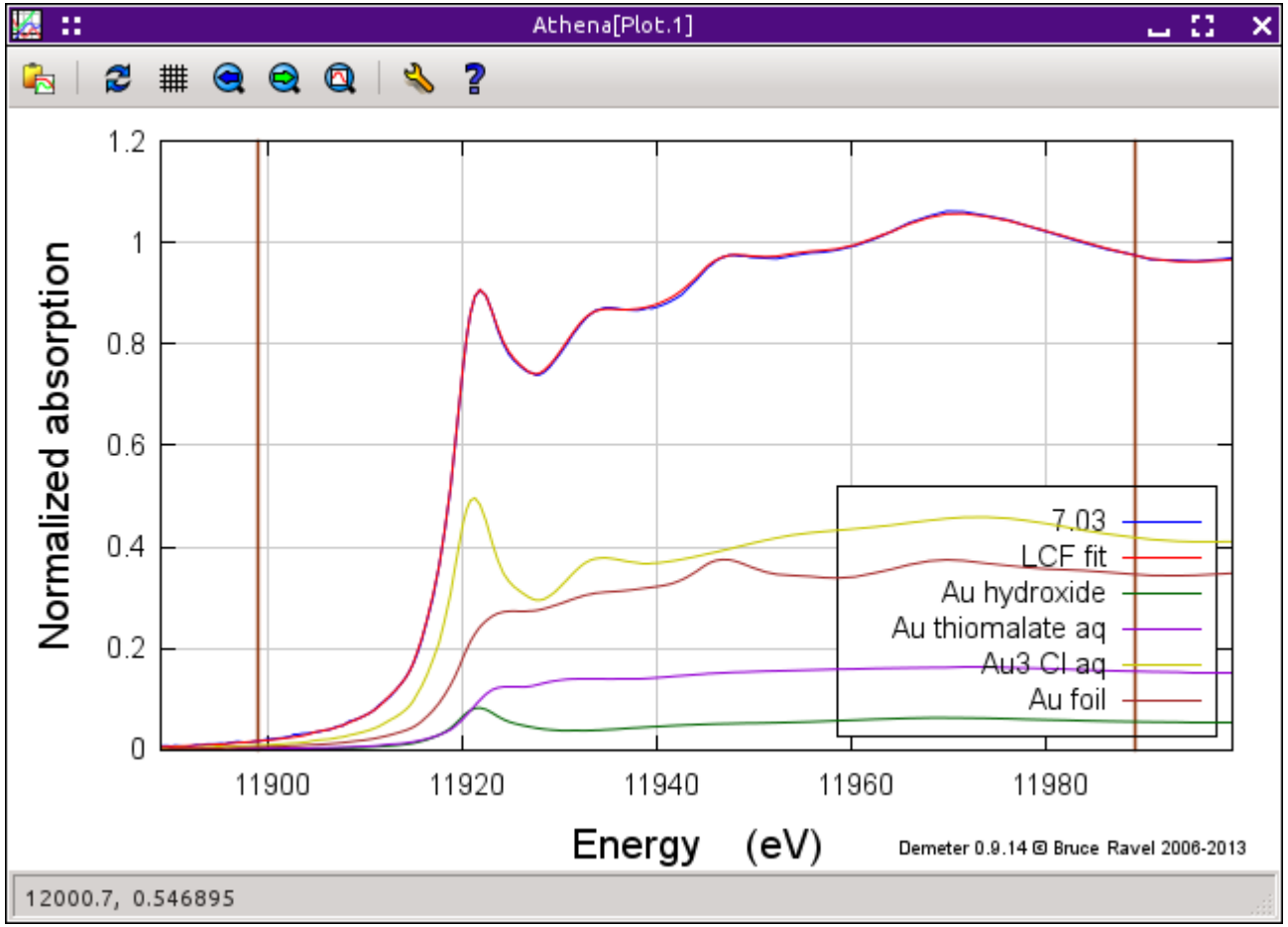
Data analysis

- Pre-edge and raising edge sensitive to:
  - Oxidation state
  - Spin
  - Multiplet structure
  - Symmetry
  - Bond length
  - Covalency
- Software for data analysis:
  - Demeter – Athena
  - Larch – Larix
- Software for XANES calculations:
  - FEFF
  - Ocean
  - MXAN
  - DFT

Data analysis

Analysis of mixtures – Linear Combination Fitting

- Real systems often contain more than one specie
- Composition of mixtures can be analyzed by using reference spectra
- As total contributions are the sum of individual ones, LCF can be used to quantify the extent of each contribution
- If many components are present in the sample, you might need to run many different combinations to figure out which one fits the best

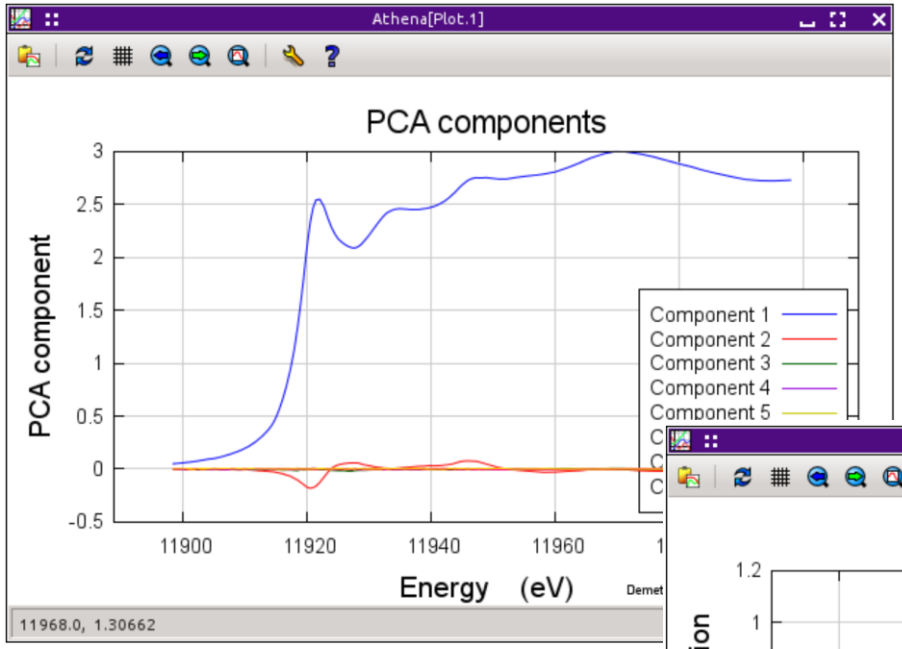


Bruce Ravel, Athena documentation

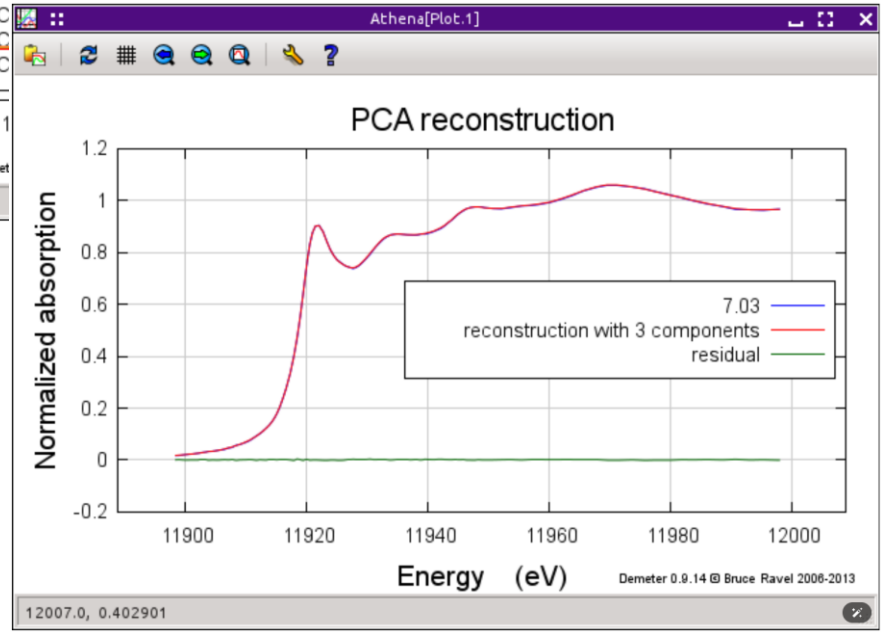
Data analysis

Analysis of mixtures – Principal Components Analysis

- Decompose a series of spectra into an orthogonal set of eigenvectors
- Number of eigenvalues equals the number of physical components of the system
- Target transform can be used to test potential physical components against the eigenvectors
- If dataset is not properly aligned and normalized, additional eigenvectors non-eligible eigenvectors may show up



- Sequential reduction of gold chloride to metal

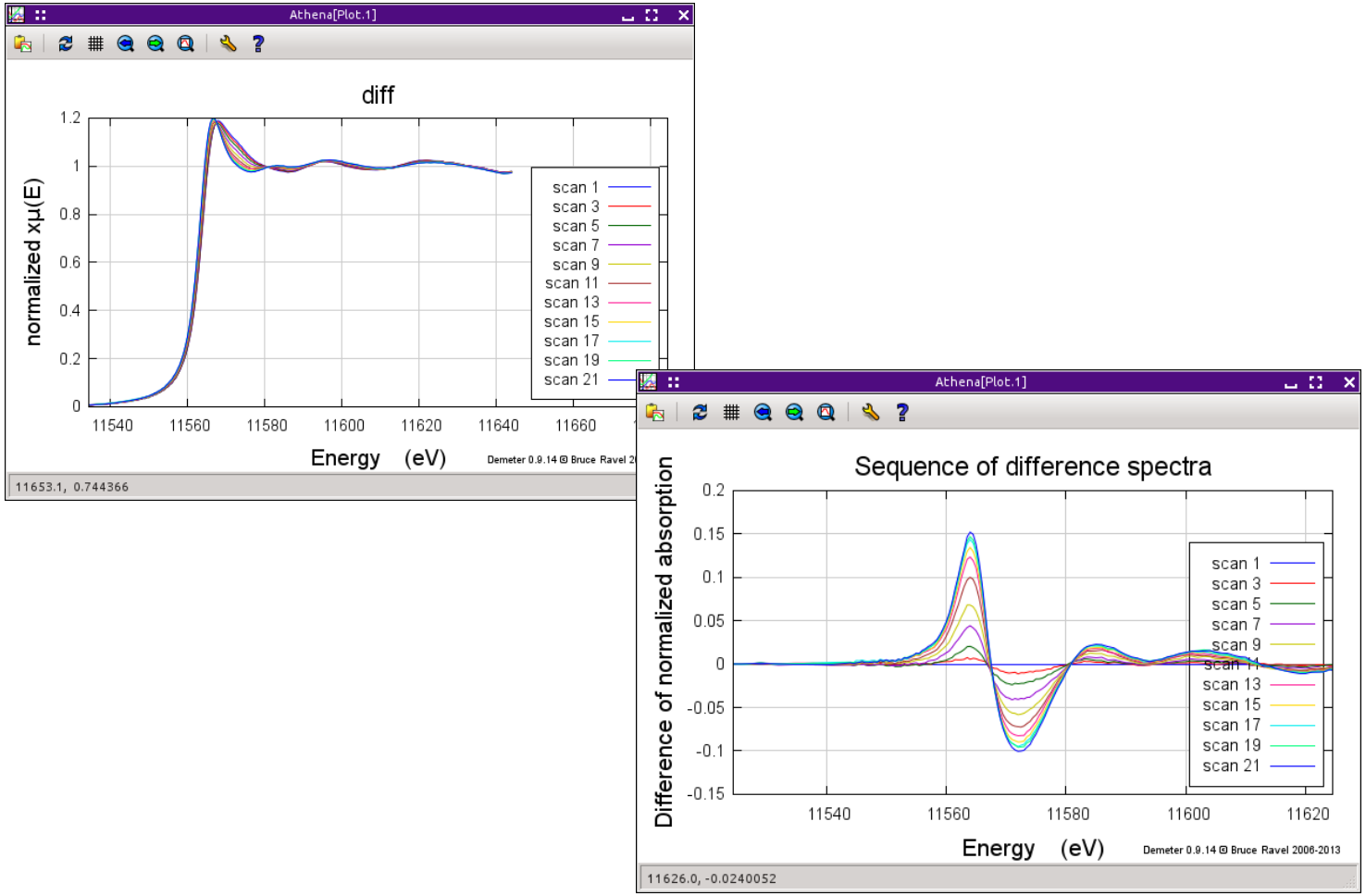


Bruce Ravel, Athena documentation

Data analysis

Analysis of mixtures – Difference Spectra

- Subtraction of a series of spectra by initial (reference) spectrum
- Commonly used to highlight subtle changes in a data sequence
- Provided example for Pt sequential coverage by hydrogen

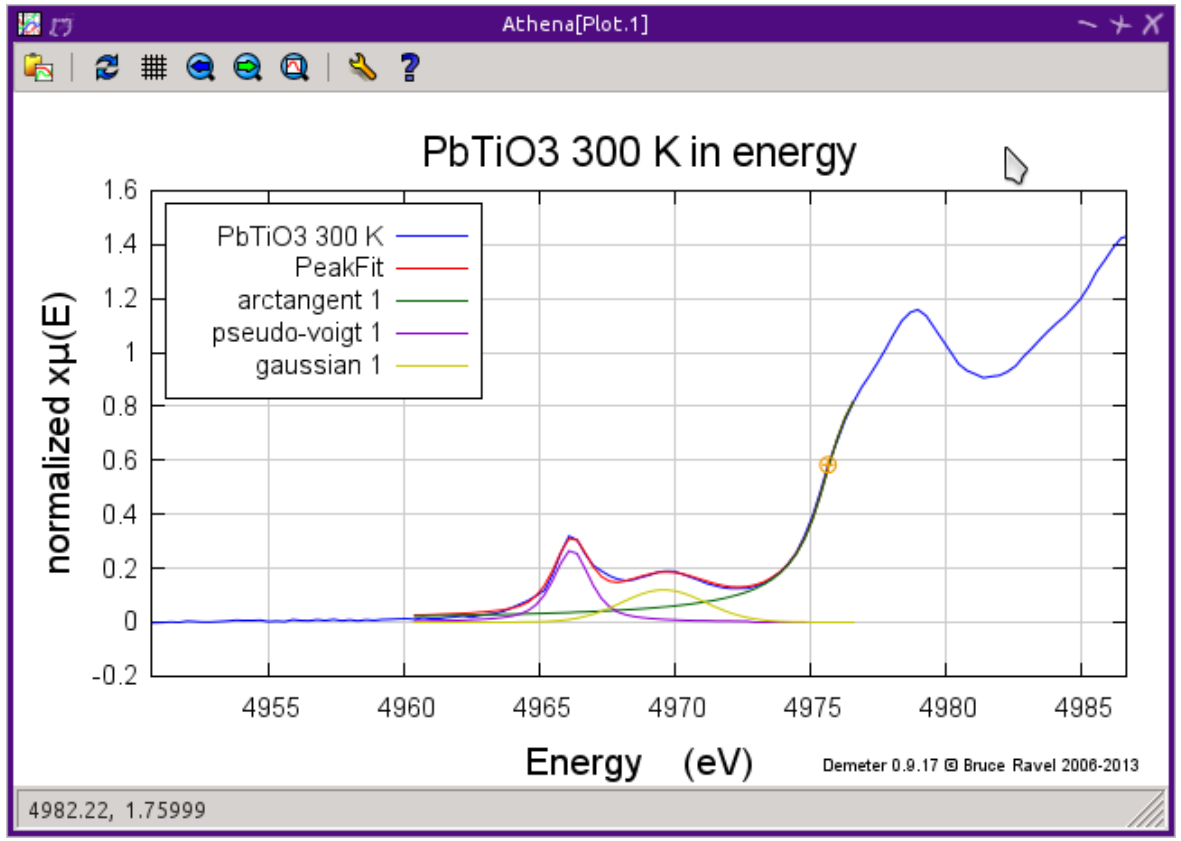


Bruce Ravel, Athena documentation

Data analysis

Analysis of mixtures – Peak fitting

- Spectrum deconstruction into a set of step-like and peak functions
- More meaningful when performed across related data
- Main drawback: physical significance of the line-shapes is not well understood



Bruce Ravel, Athena documentation

Final remarks

XANES – what can we get?

- Oxidation state
- Spin
- Multiplet structure
- Symmetry
- Covalency
- Bond lengths

Compared to

EXAFS

- Larger signal – can be collected at lower concentration
- Easier to crudely interpret – fingerprinting
- Harder to fully interpret – big efford needed for modeling/fitting spectra features

On high energy resolution techniques

- Techniques as HERFD-XAS, XES, and RIXS result complimentary on providing insights into electronic structure of materials
- HERFD-XAS: cleaner data, enhanced sensitivity
- XES: spin, ligand speciation
- RIXS: covalency, bonding
- Special care on avoiding sample damage

More questions?

Thanks!