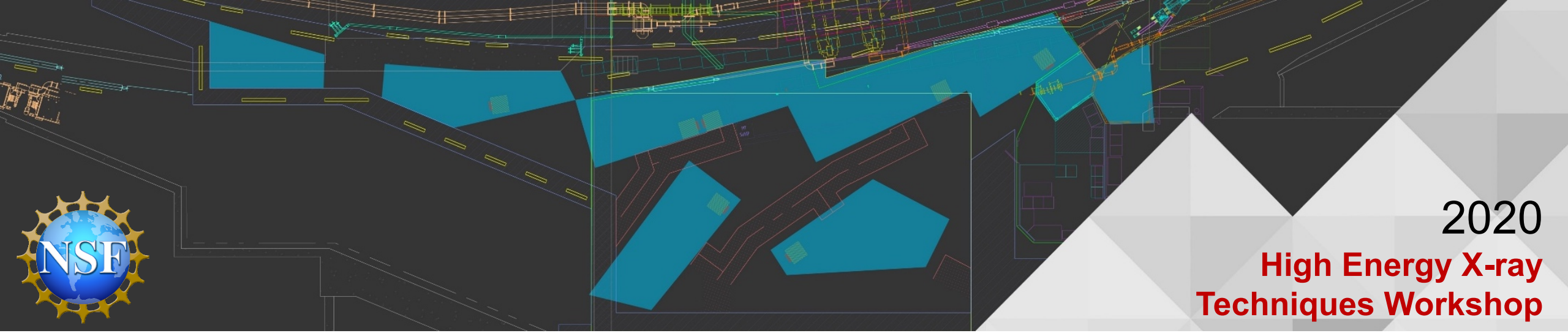


2020

High Energy X-ray Techniques Workshop

High Energy X-ray Spectroscopy

X-ray spectroscopy and materials research

Chris Pollock, Staff Scientist

Cornell High Energy Synchrotron Source (CHESS)

cjp227@cornell.edu

CHESS
CORNELL HIGH ENERGY SYNCHROTRON SOURCE

Schedule

Wednesday, June 10, 2020

09:00	Methods II: Spectroscopy – Chris Pollock
09:45	Spectroscopy Q/A
10:00	Break
10:15	Spectroscopy “Hands-on” Section
12:00	End

What is X-ray Spectroscopy and How Can it Help Me?

Hard x-ray spectroscopies are inherently element-selective

- A single element can be measured even within a complicated matrix

These techniques are bulk-sensitive and applicable to a wide variety of sample cells / environments

- Operating electrochemical cells, flowing solutions, and solid state reactors are all accessible

Quick data collection can enable time-resolved experiments

- Time resolution down to milliseconds (and faster!) can be achieved

These methods allow access to unique chemical information!

Common Techniques We'll Talk About

Introduction and Experimental Overview

X-ray Absorption Spectroscopy (XAS) + Extended X-ray Absorption Fine Structure (EXAFS)

X-ray Emission Spectroscopy (XES)

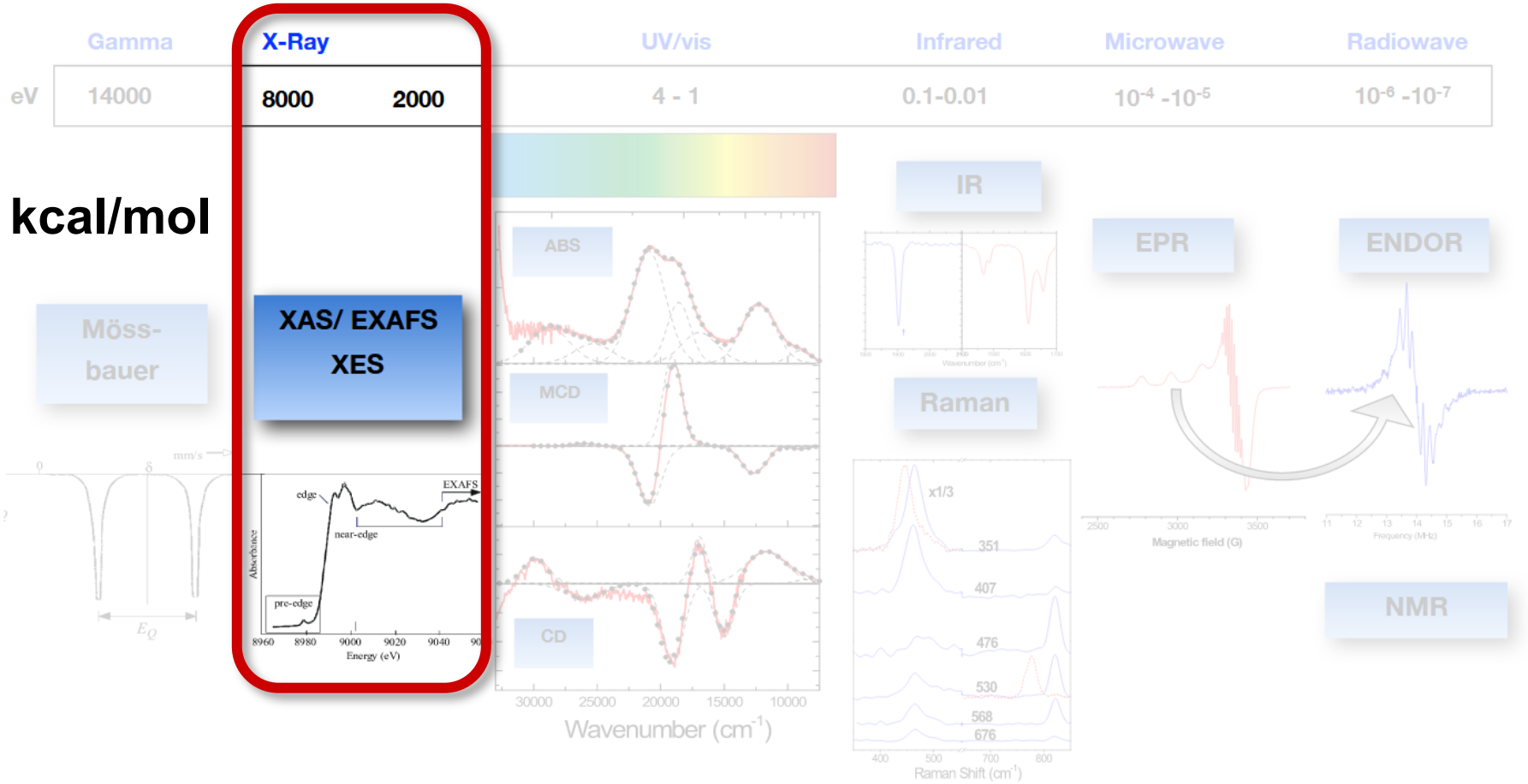
High Energy Resolution Fluorescence Detected (HERFD) XAS

Part I: Overview

What is X-ray Spectroscopy and How Can it Help Me?

X-ray spectroscopy involves using x-rays to monitor transitions of core electrons in a molecule or material

1 eV = 23.06 kcal/mol

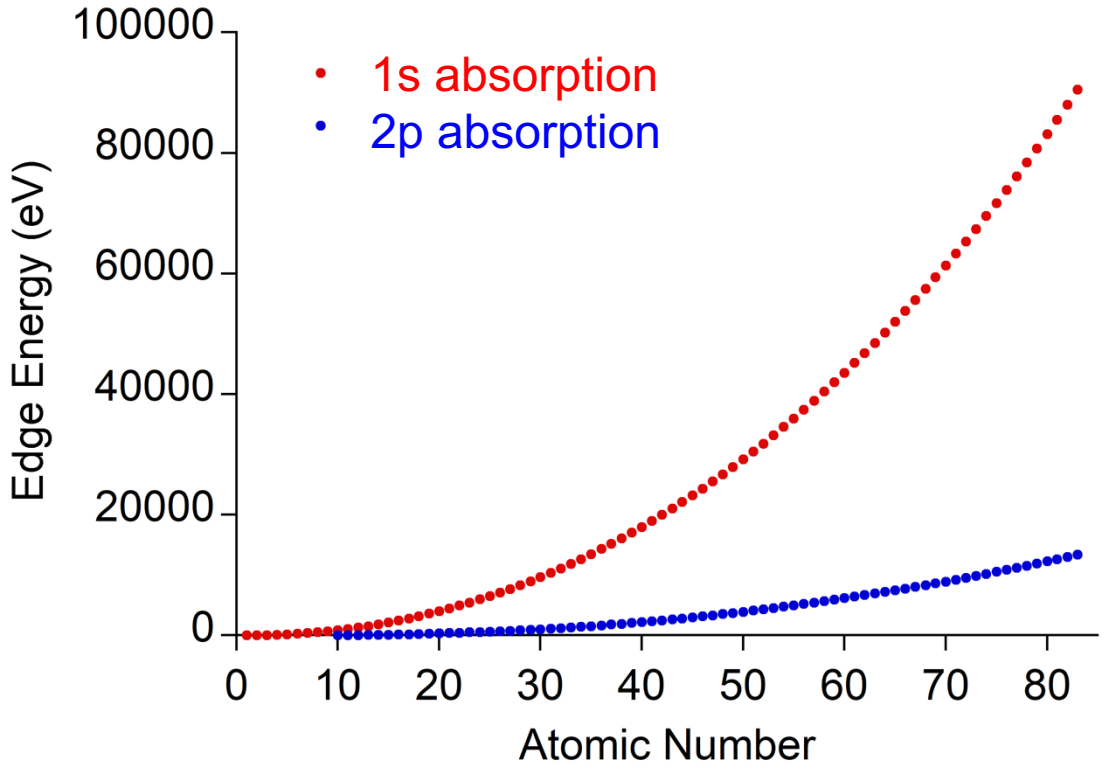


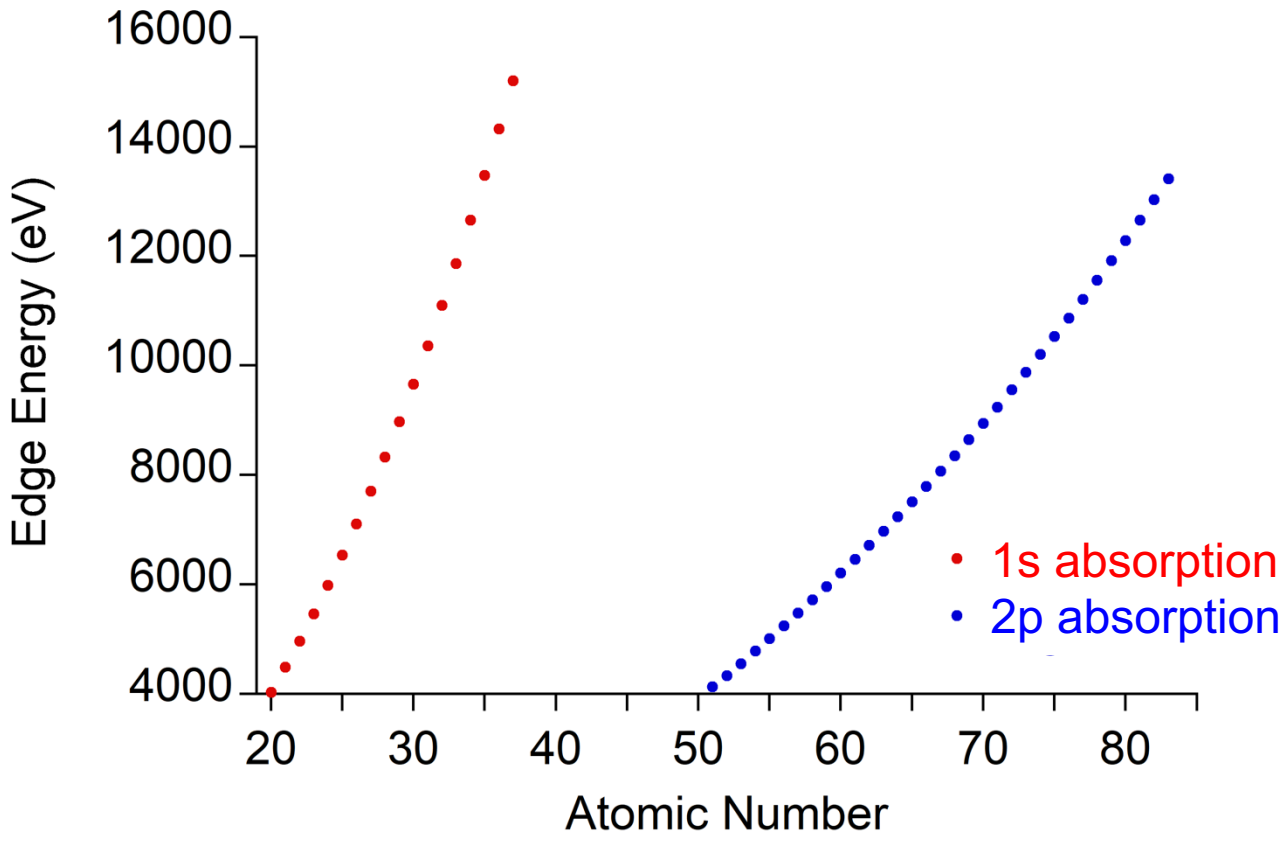
Experiment Overview

Most x-ray spectroscopy is performed at a synchrotron, since these facilities provide an intense, energy-tunable source of x-rays

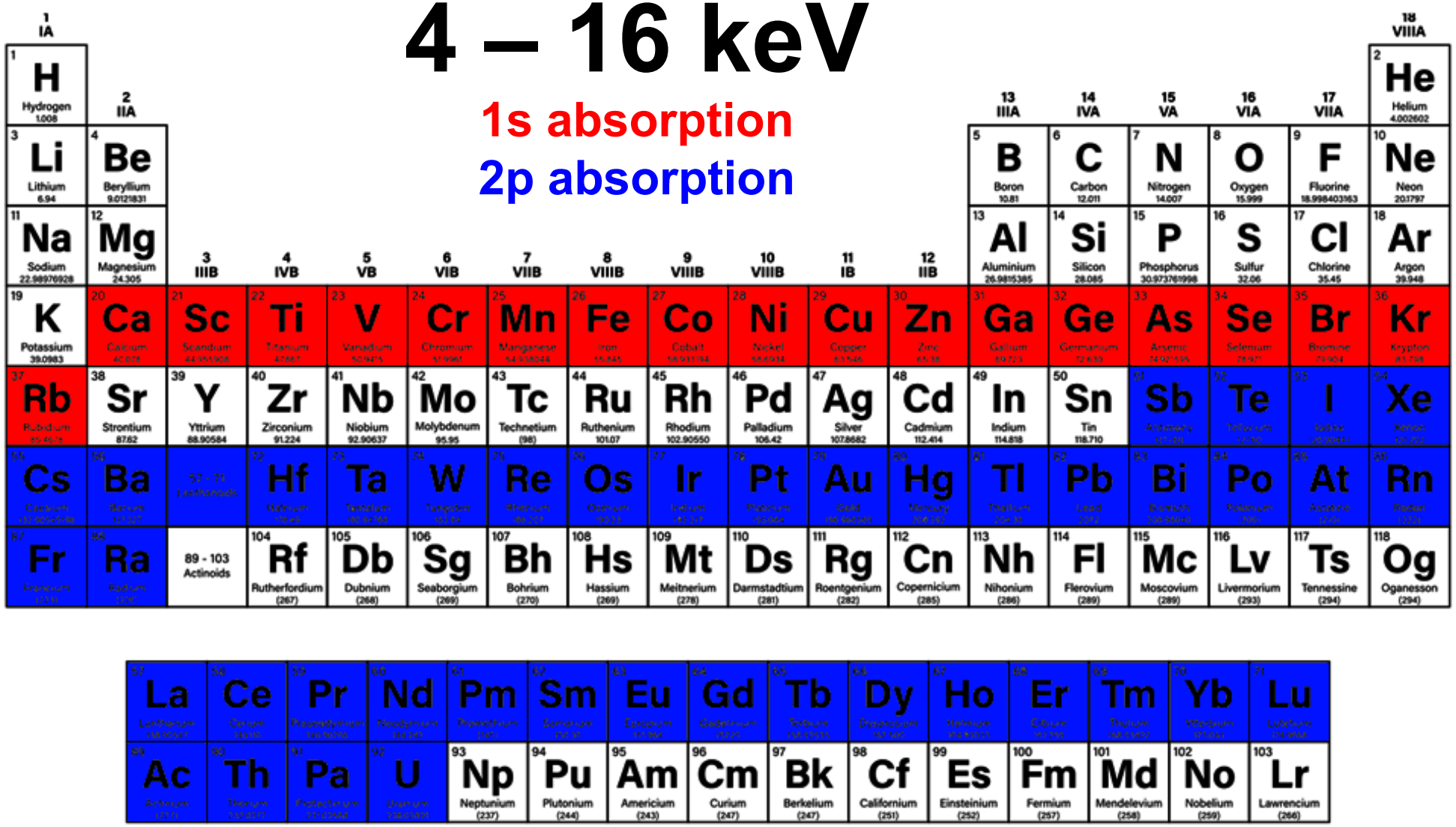
Element Selectivity

Every element absorbs x-rays at unique energies that can be selectively probed by x-ray spectroscopy





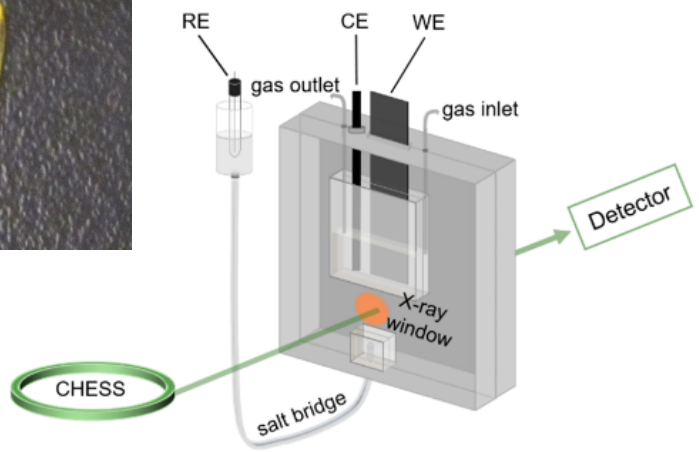
Periodic Table of the Edges

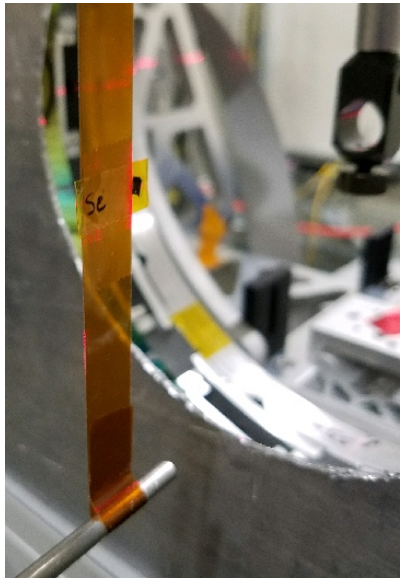


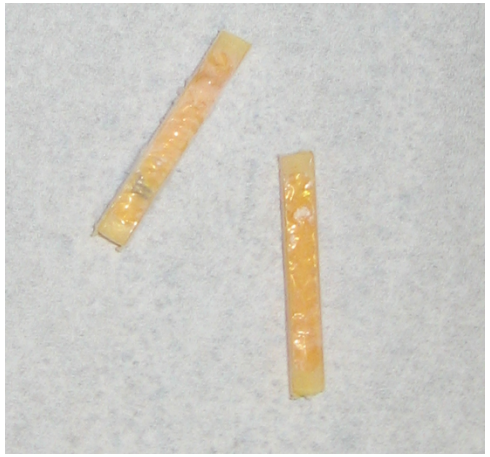
Samples: What Can We Measure?

One of the benefits of x-ray spectroscopies is the wide variety of sample environments they can accommodate

Solids, static or flowing solutions, supported species, high / low temperatures, electrochemical cells, high pressures, etc

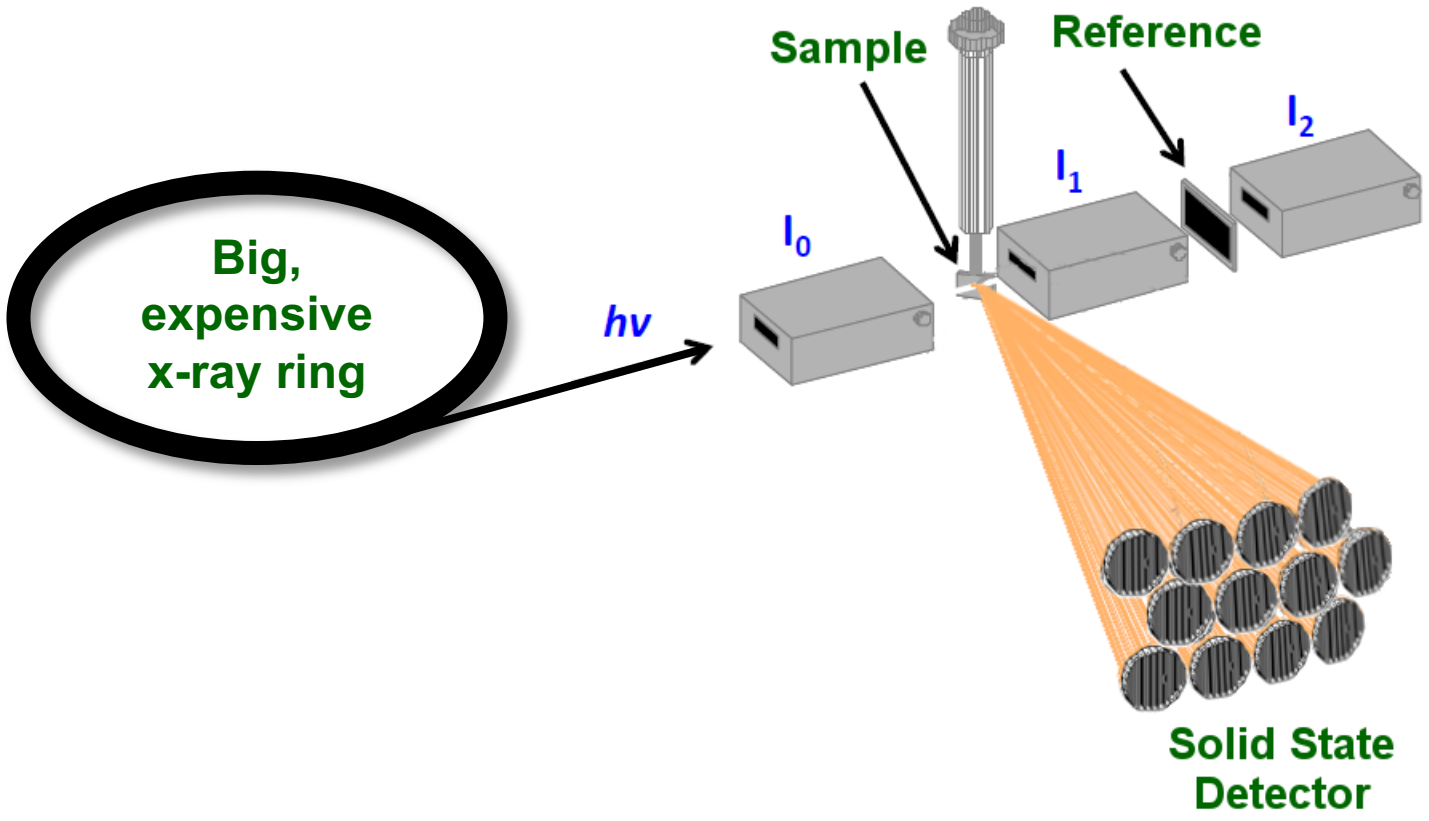






Part II:
XAS / EXAFS

XAS Experimental Setup

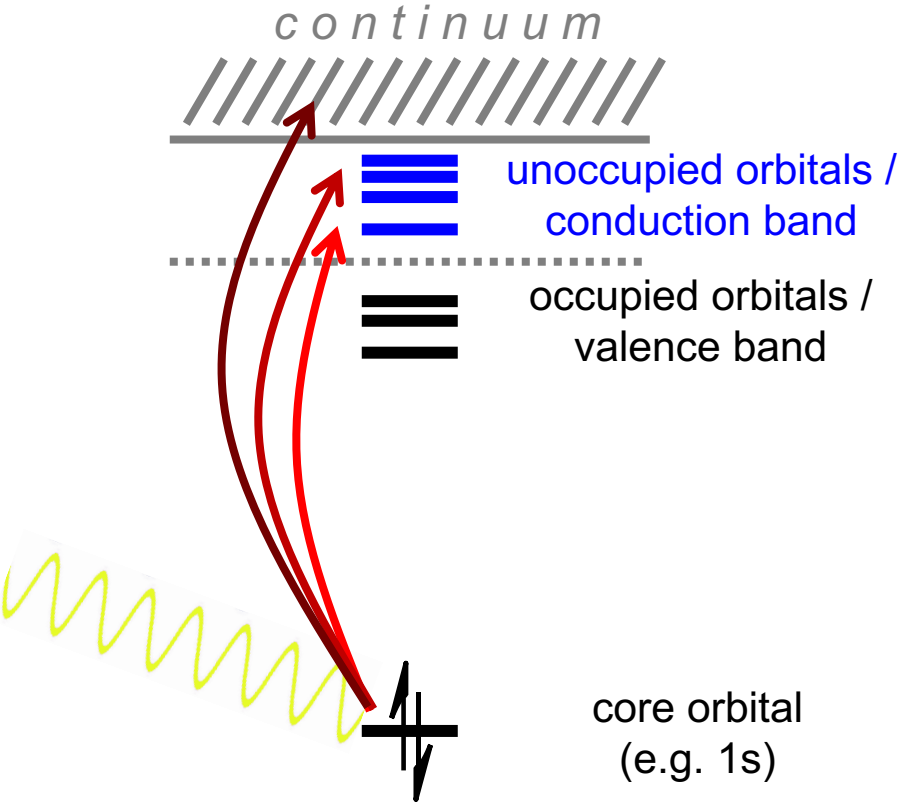


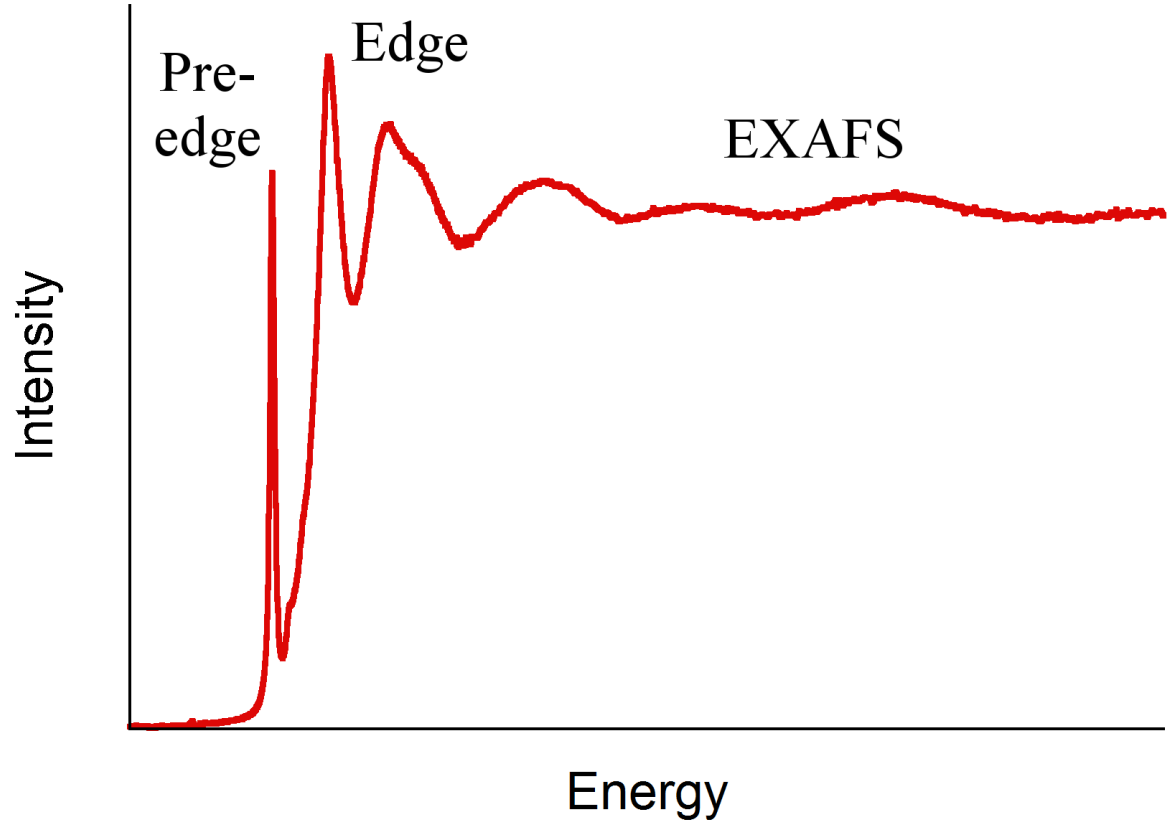
XAS measures the absorption of x-rays of a material as the incident energy is changed

Spectra can either be measured in transmission mode or fluorescence mode

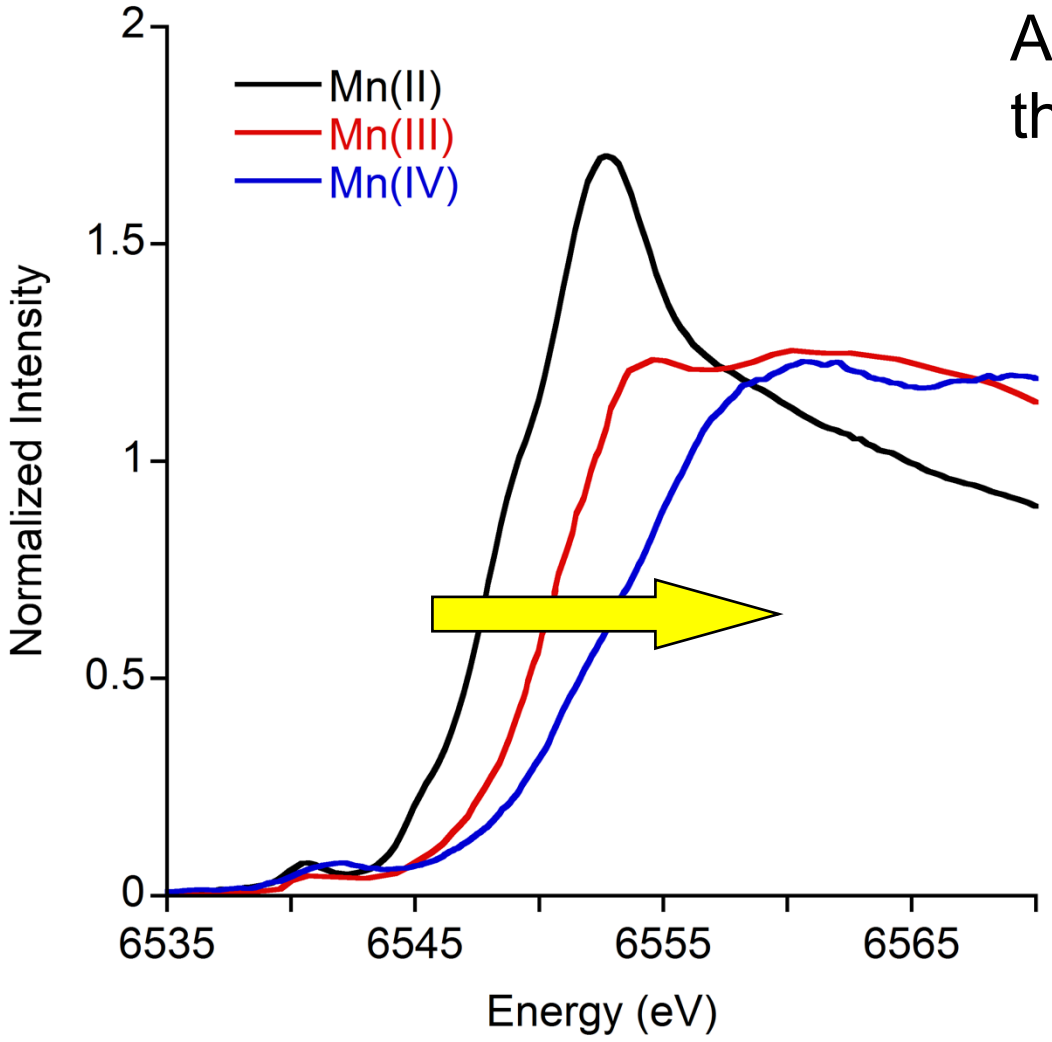
X-rays can penetrate 10s to many 100s of microns into a sample, making this a bulk sensitive technique

K-edge X-ray Absorption Spectroscopy (XAS)

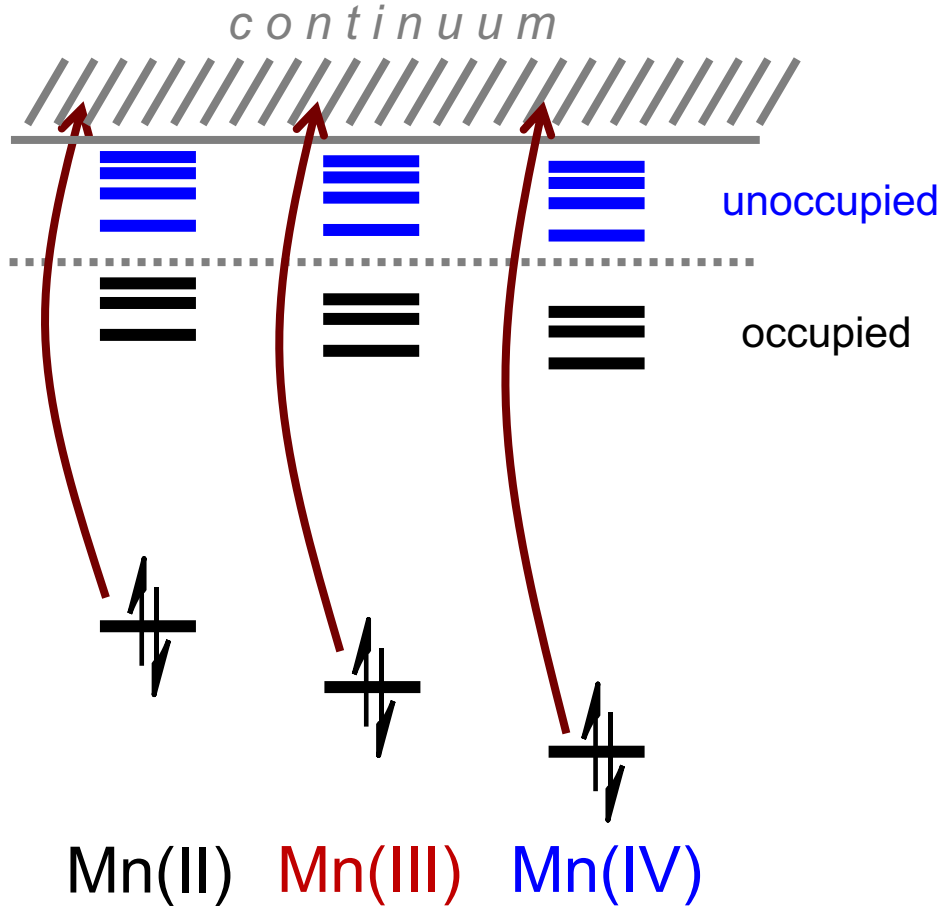




Sensitivity to Oxidation State

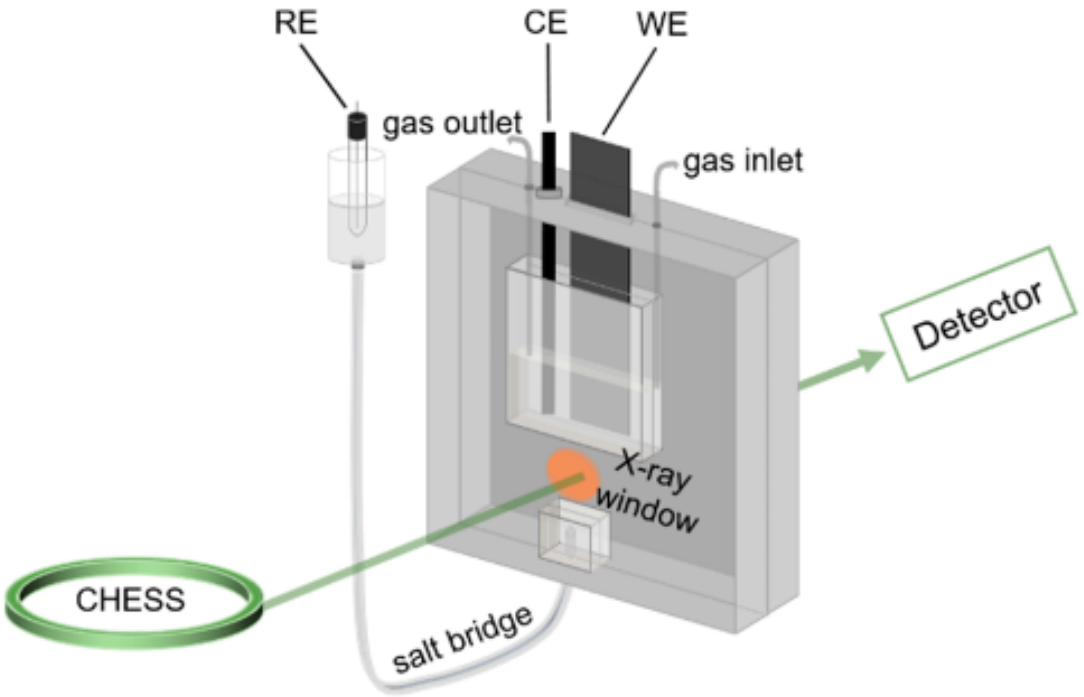


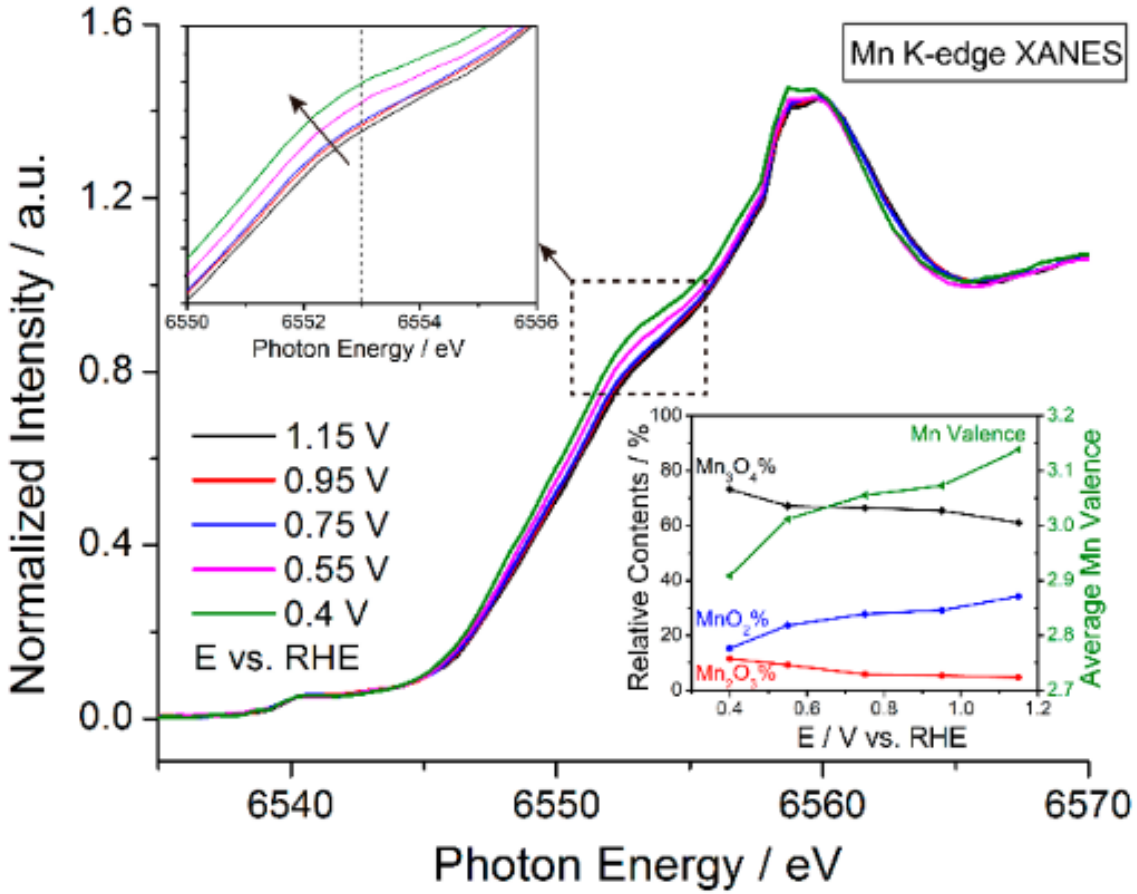
As the oxidation state of an element increases, the edge energy also tends to increase



Sensitivity to Oxidation State

Abruña, *J. Am. Chem. Soc.*, **2019**, *141*, 1463-1466





Abruña group used XAS edges to quantify oxidation changes in a Co-Mn oxygen reduction catalyst

Sensitivity to Geometry

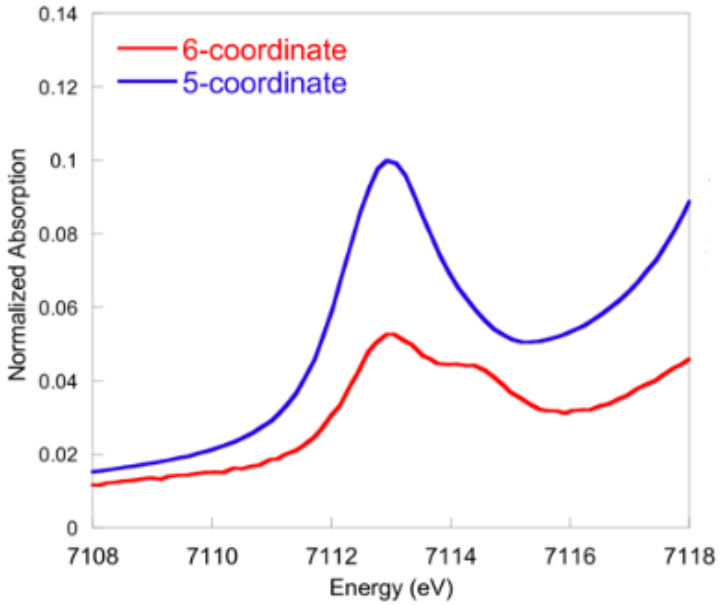
Westre, *J. Am. Chem. Soc.*, **1997**, *119*, 6207.; Lim, *PNAS*, **2003**, *100*, 3665.
Aliaga-Alcalde, *ACIE*, **2005**, *44*, 2908.; Barry, *Science*, **2006**, *312*, 1937.

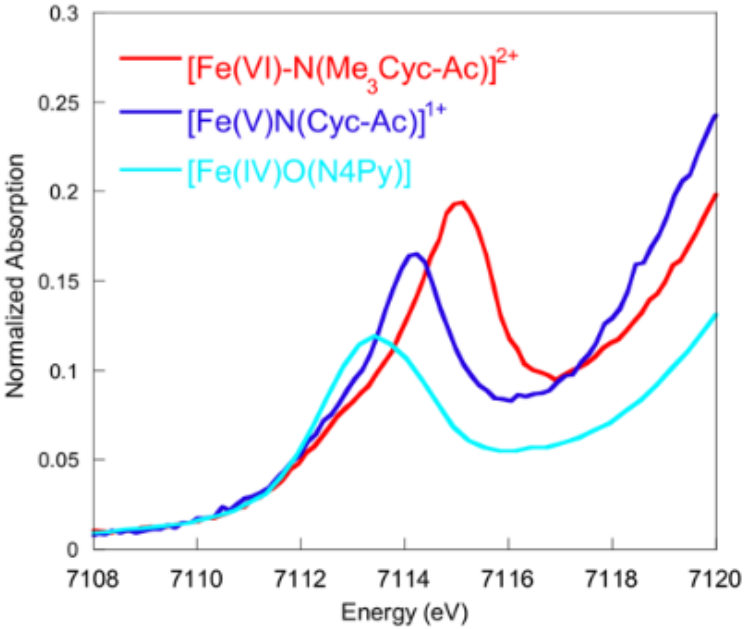
XAS pre-edge are formally forbidden s -> d orbital transitions, so their intensity is weak

In certain symmetries, the p and d orbitals can mix, making pre-edges more intense

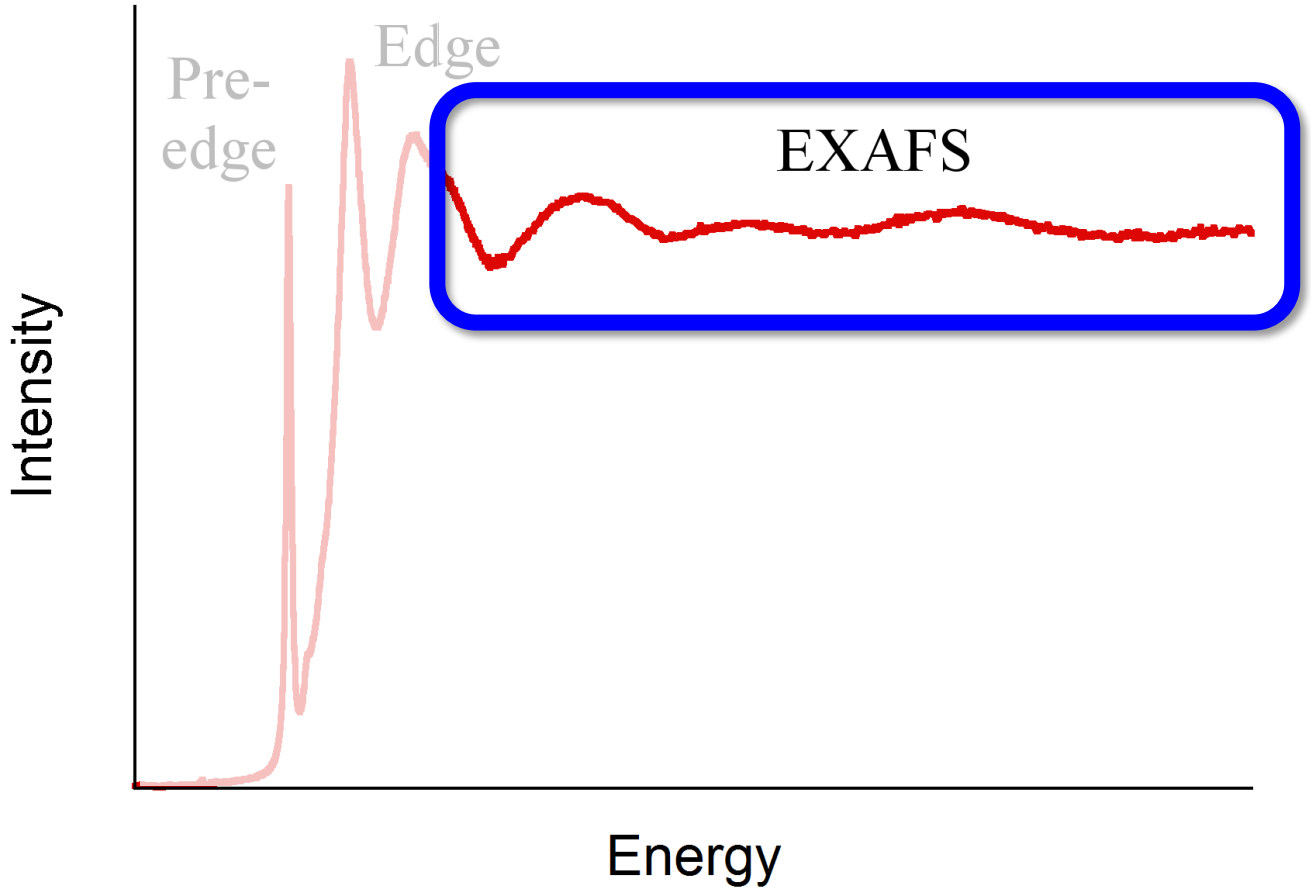
- Geometries where the metal isn't centrosymmetric

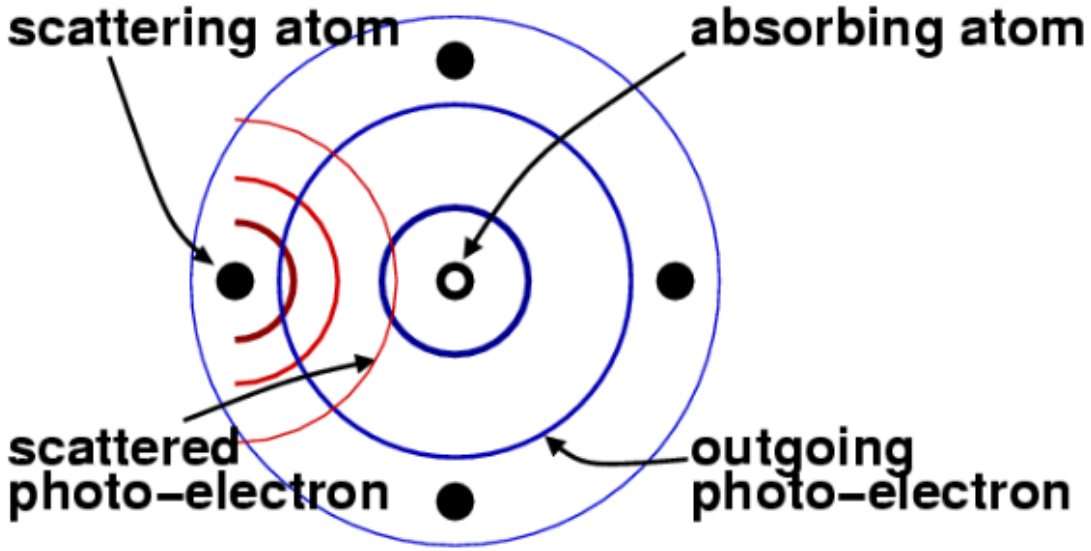
Shorter metal-ligand bonds also promote p/d mixing





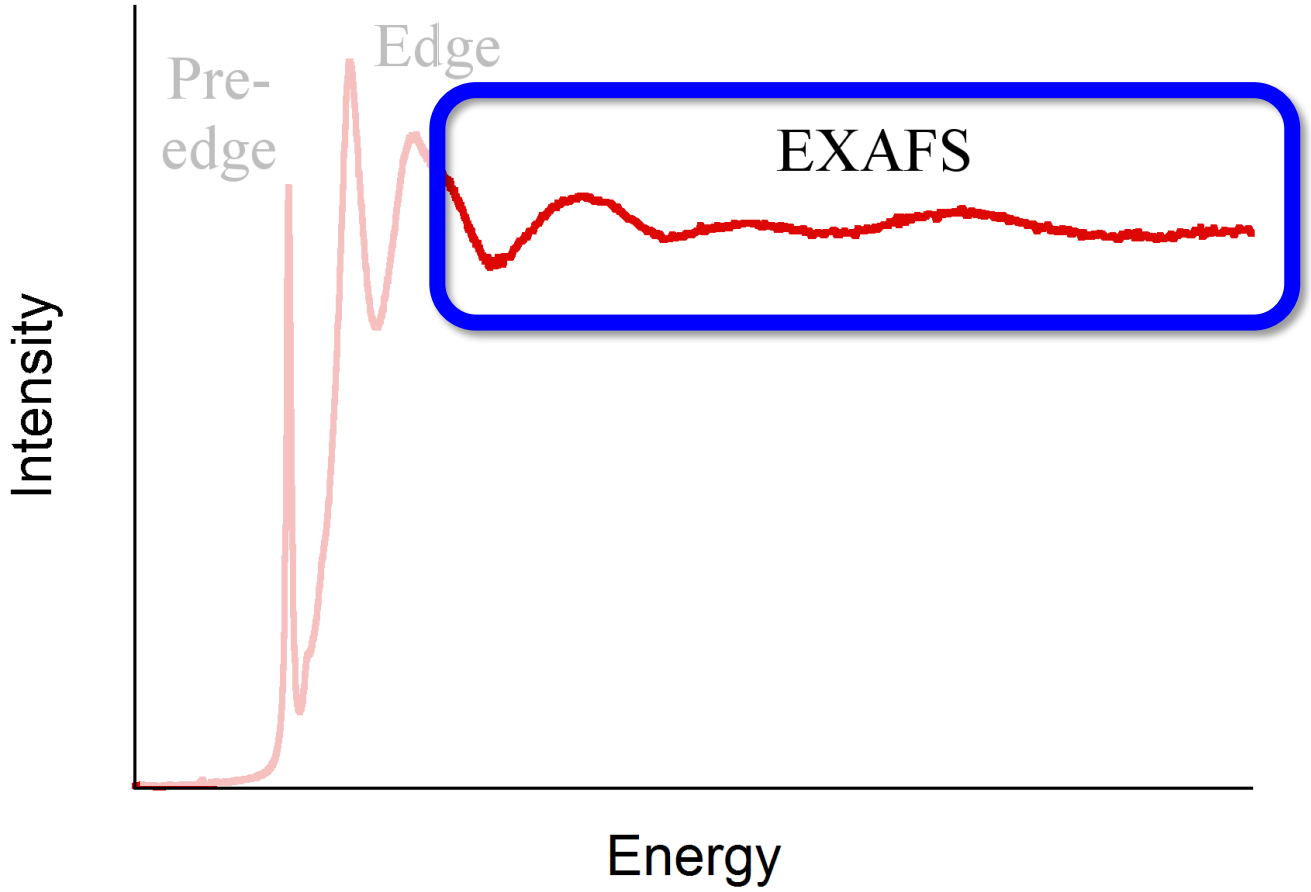
Extended X-ray Absorption Fine Structure (EXAFS)





Once an electron is ionized from an atom, it can scatter of the electron clouds of adjacent atoms, giving rise to oscillations in the absorption signal (EXAFS)

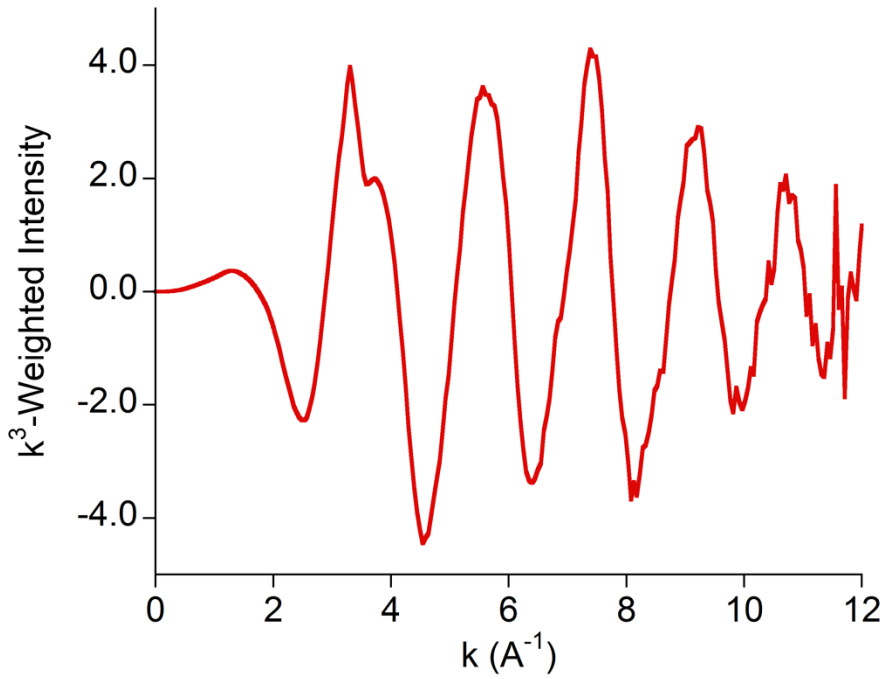
Extended X-ray Absorption Fine Structure (EXAFS)



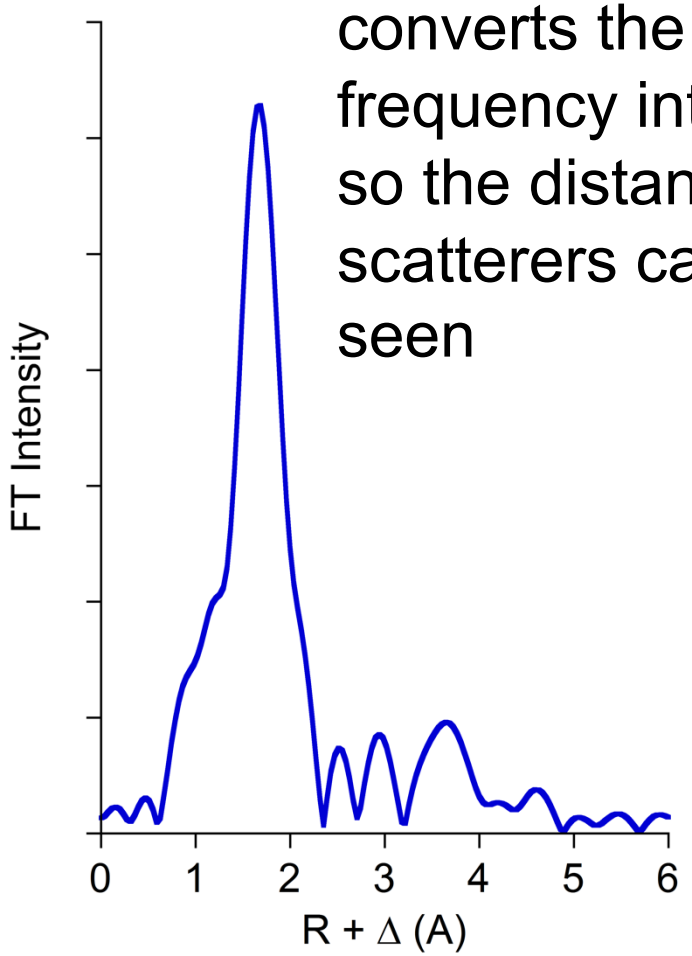
From EXAFS we can learn:

- **Distance** of scattering atoms from the absorber
- **Number** of scattering atoms
- **Identities** of scattering atoms

Fourier Transformed EXAFS



Fourier Transform



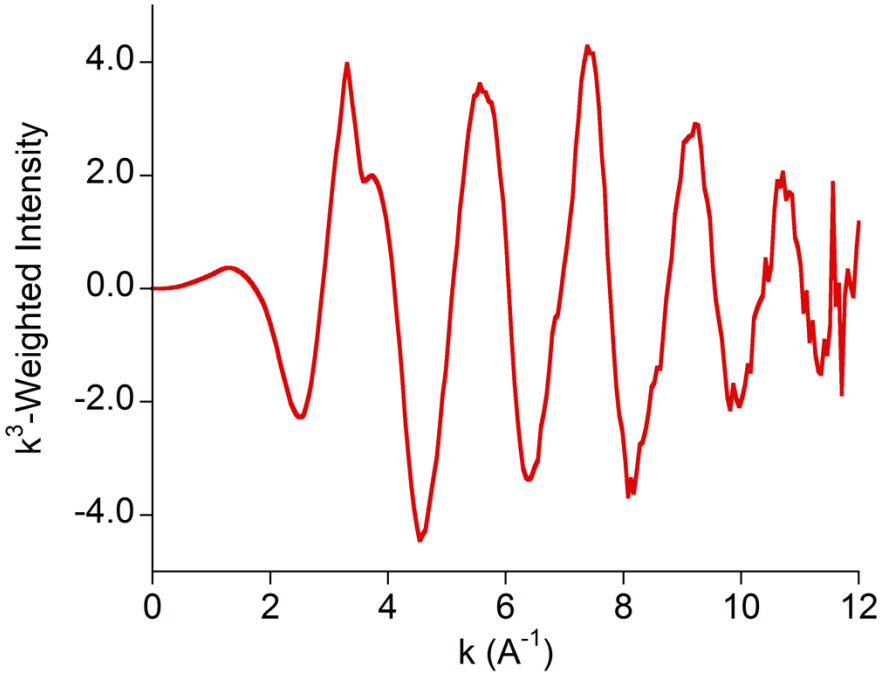
The Fourier transform converts the oscillation frequency into distance, so the distance of scatterers can be easily seen

After some math, the EXAFS oscillations can be extracted

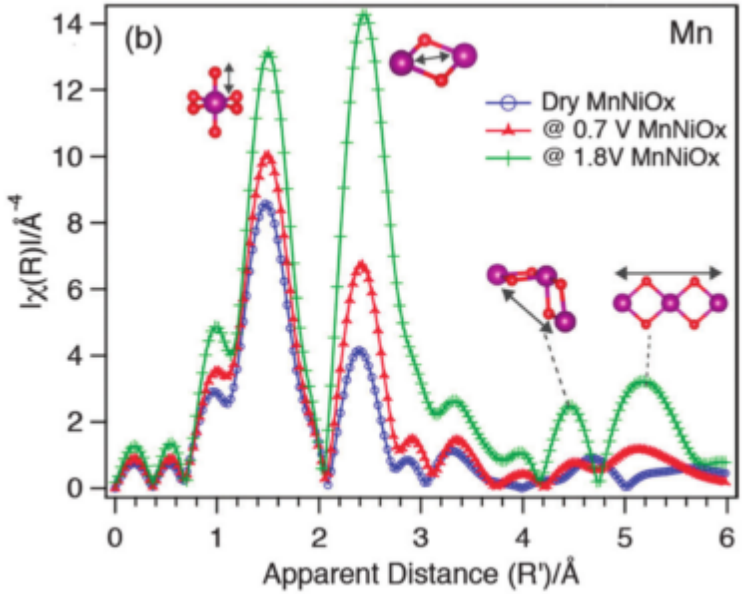
Hard to intuitively interpret

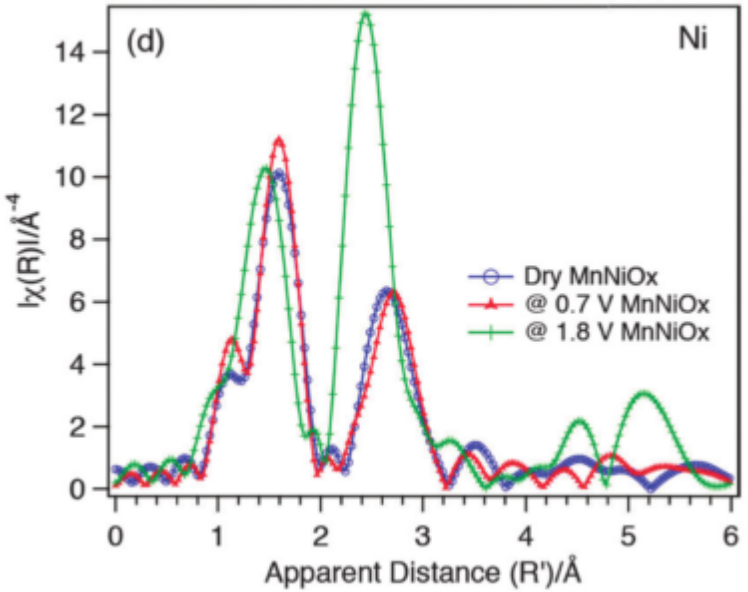
Fourier Transformed EXAFS

Gul, *PCCP*, **2015**, *17*, 8901



Fourier Transform





After some math, the EXAFS oscillations can be extracted

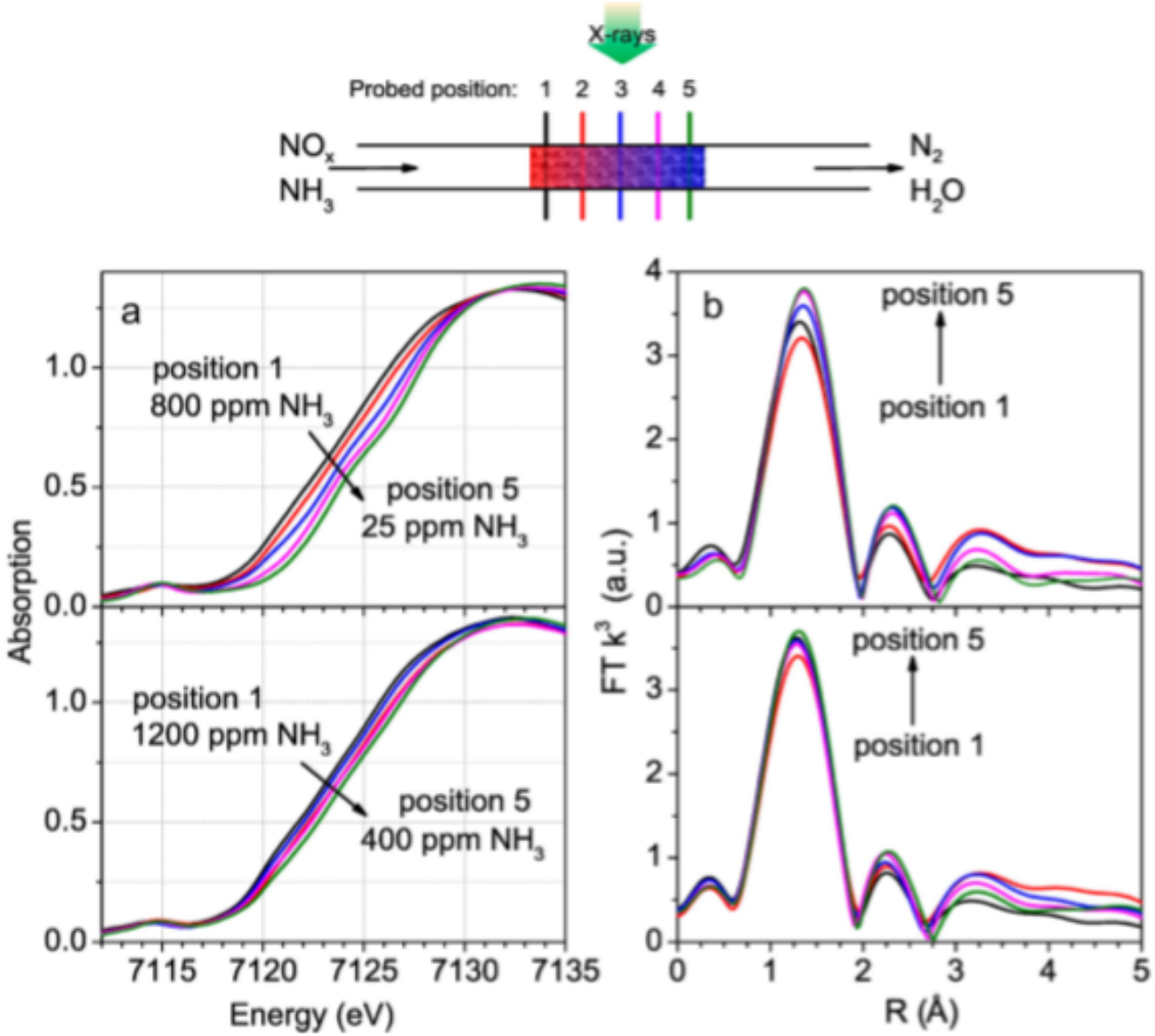
Hard to intuitively interpret

Example EXAFS – Catalysis

Doronkin, *J. Phys. Chem. C.*, **2014**, 10204.

Here, EXAFS, together with XANES, was used to monitor a solid state catalyst as it performed the NO_x reduction reaction

By flowing the gasses along the catalyst, they could monitor different positions and correlate those positions to different reaction times



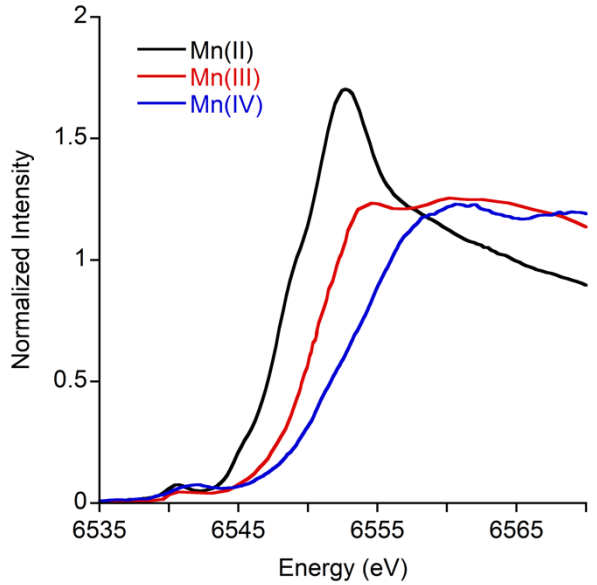
XAS / EXAFS Cheat Sheet

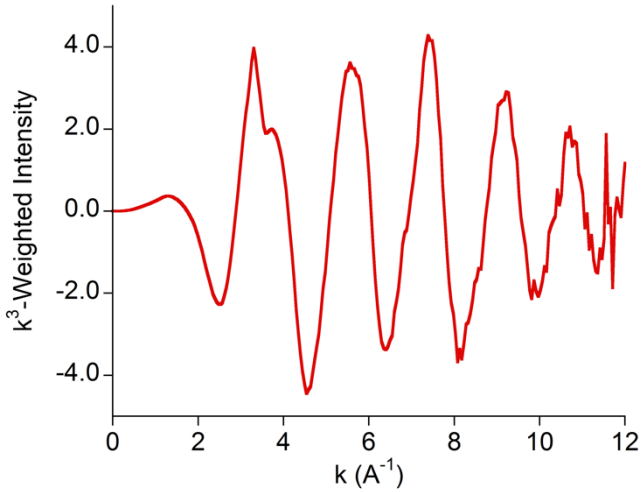
XAS is **element selective** and can be applied to **nearly any element** in a wide **variety of sample environments**

Edges contain information about absorbing atom **oxidation state**

Pre-edges indicate site **symmetry / geometry**

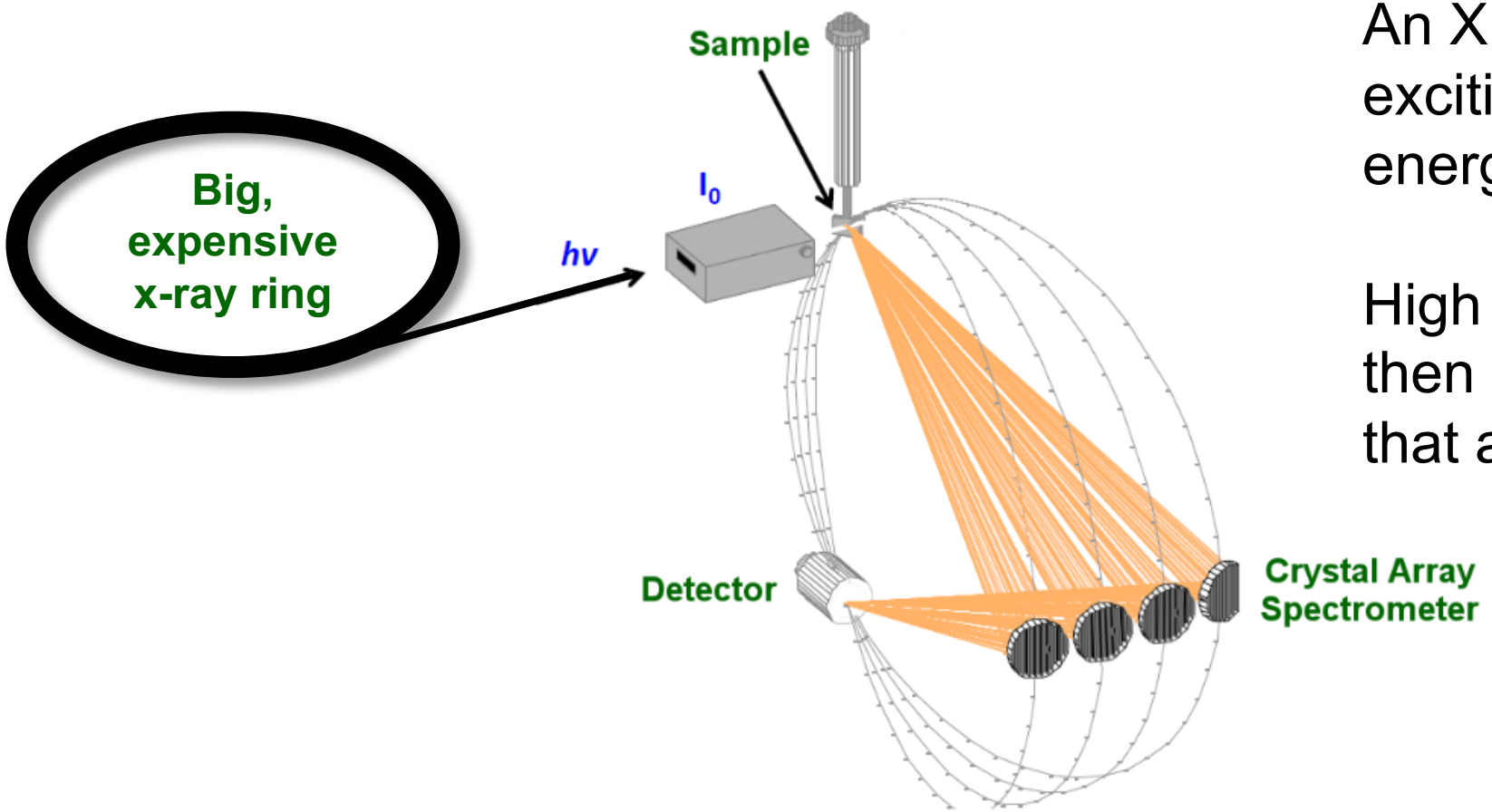
EXAFS allow **metal-ligand bond metrics** to be precisely determined





Part III:
XES

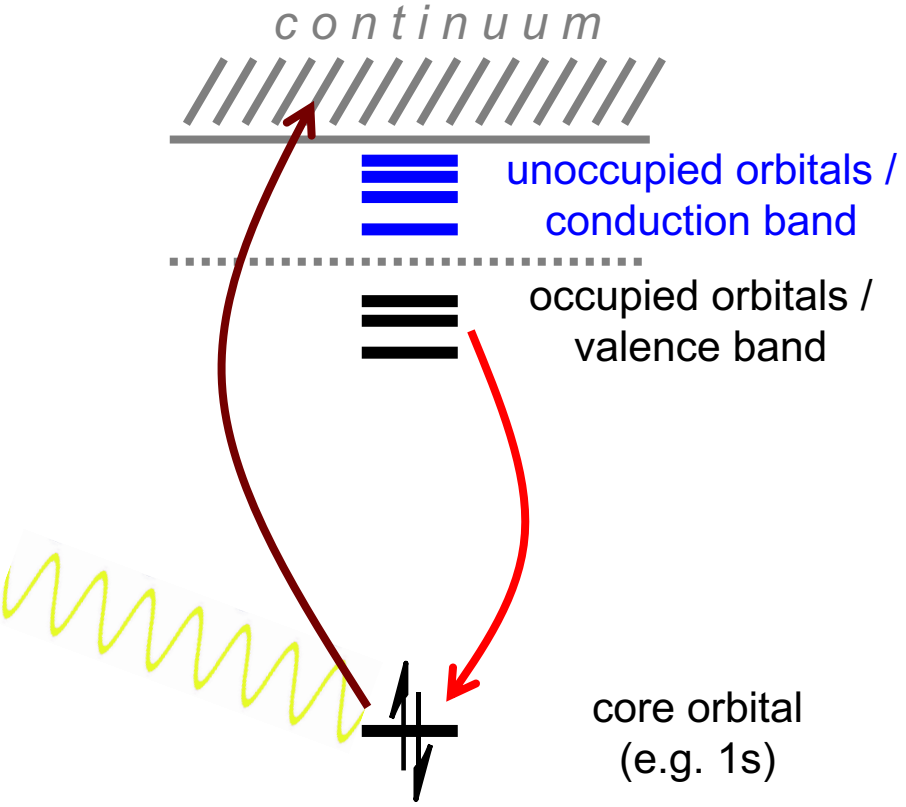
XES Experimental Setup

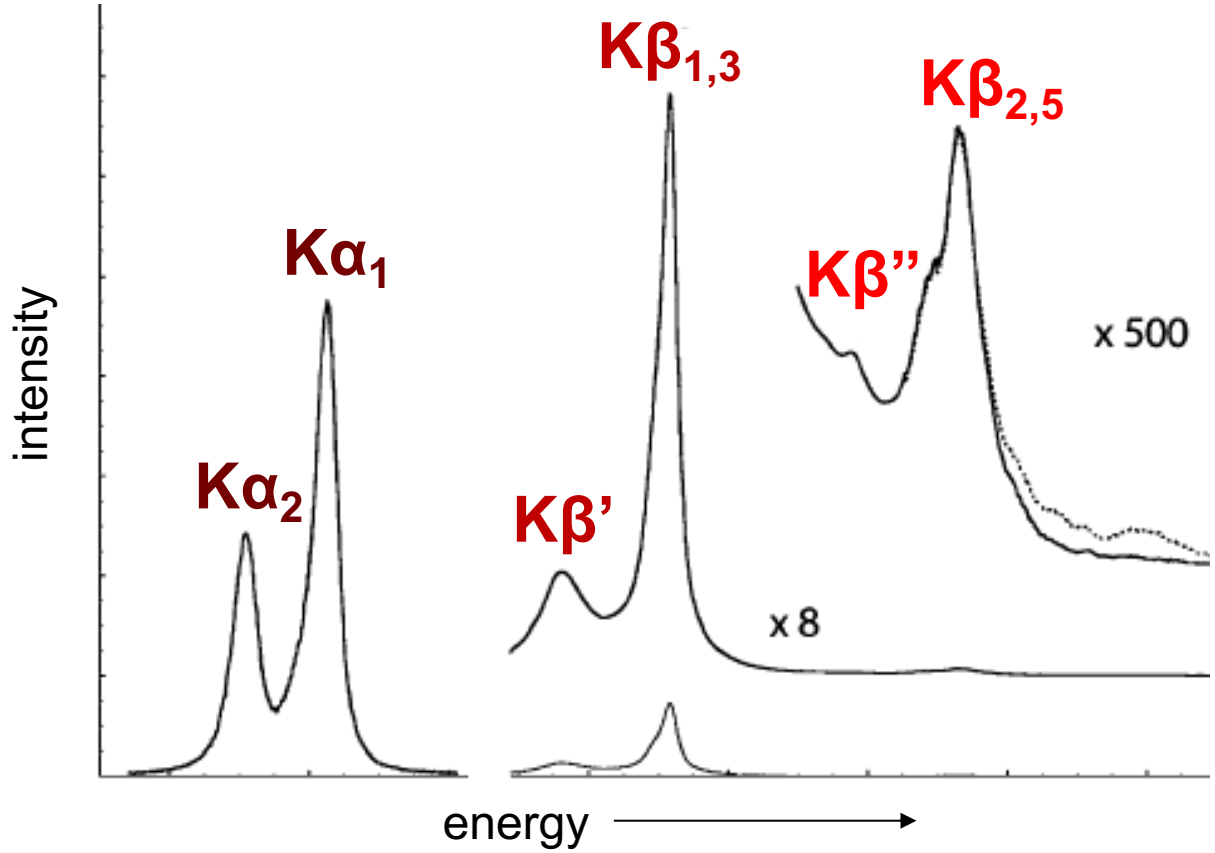


An XES experiment begins by exciting a sample with a high energy x-ray (>> absorption edge)

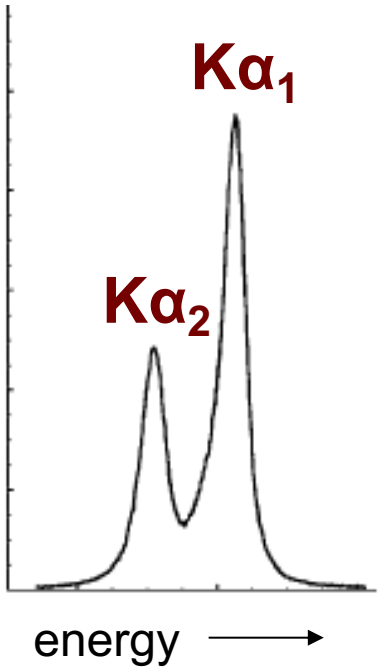
High resolution crystal analyzers then collect the fluorescent x-rays that are produced from the sample

X-ray Emission Spectroscopy (XES)

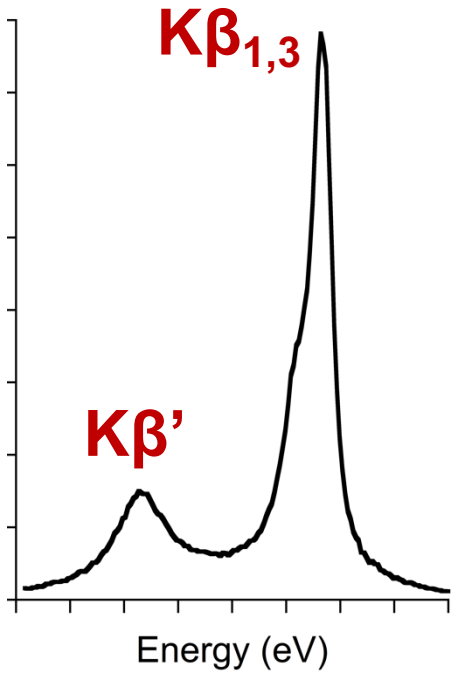




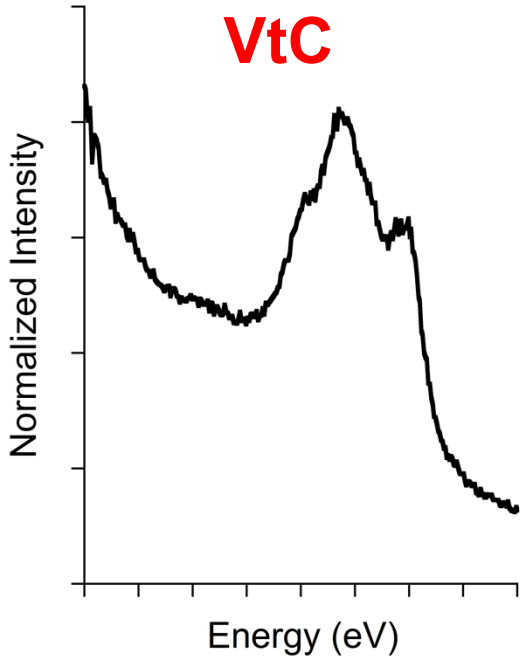
X-ray Emission Transitions



Kα XES are 2p -> 1s transitions; they are intense but have limited chemical information



Kβ XES are 3p -> 1s transitions; they contain information about spin state and metal-ligand covalency

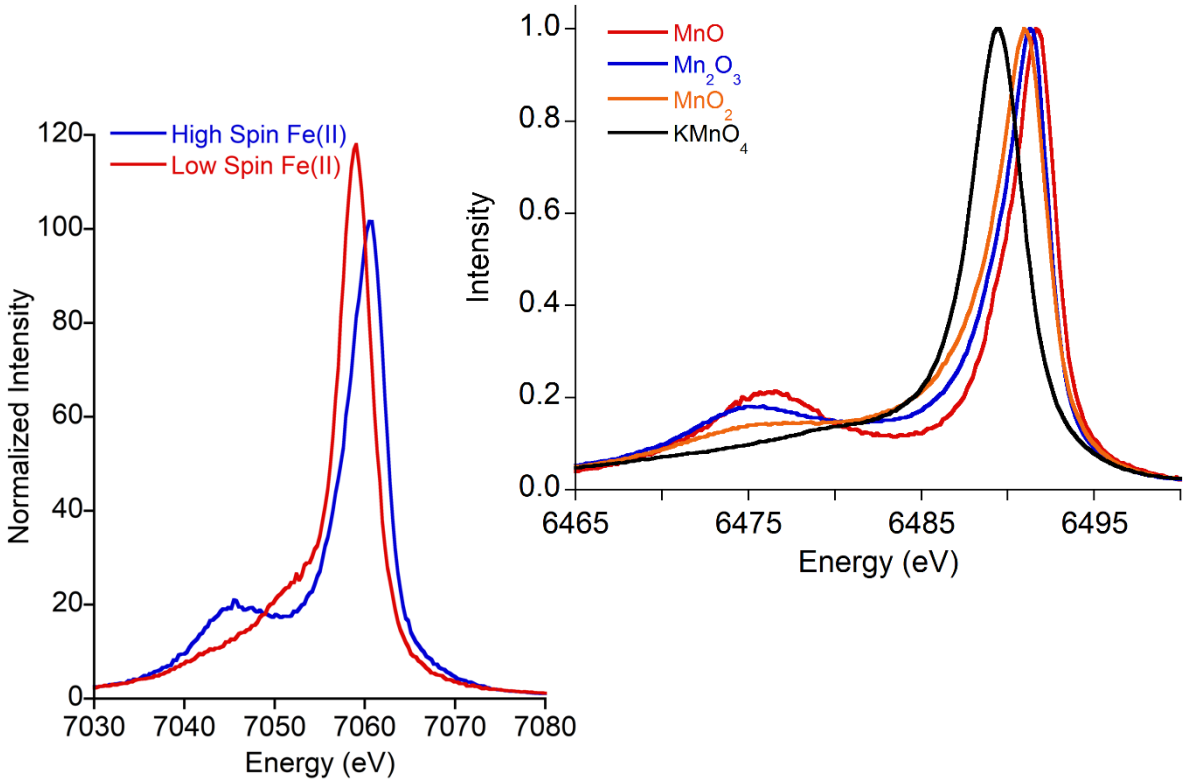


VtC XES are weak valence -> 1s transitions that directly probe the ligand electronic structure

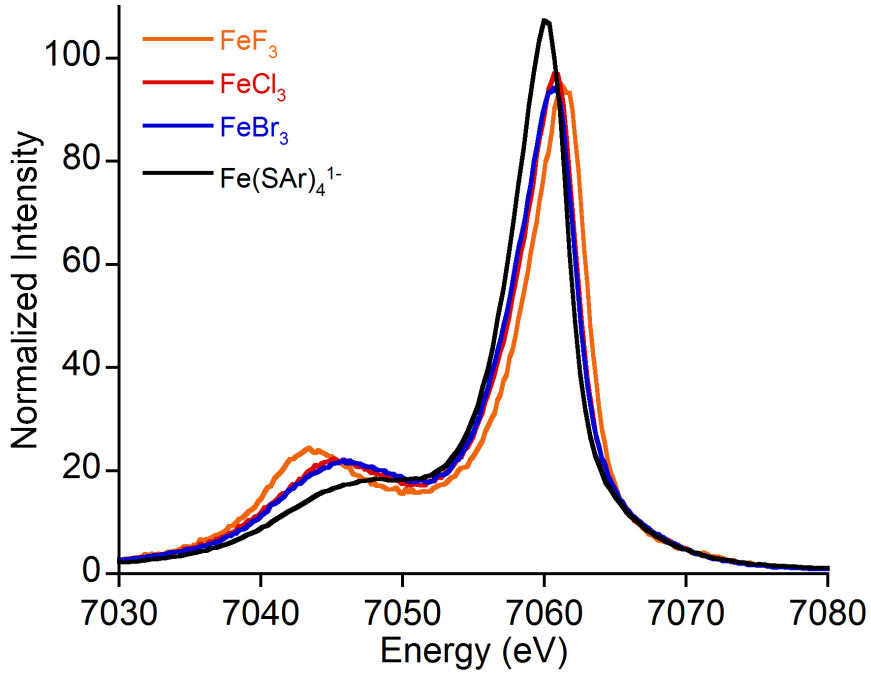
Kβ Mainline XES

Pollock, *JACS.*, **2014**, *136*, 9453

Kβ mainlines are primarily sensitive to the spin state of the emitting atom



Additionally, these spectra are also affected by the covalency of the bonds between the emitting atom and its ligands

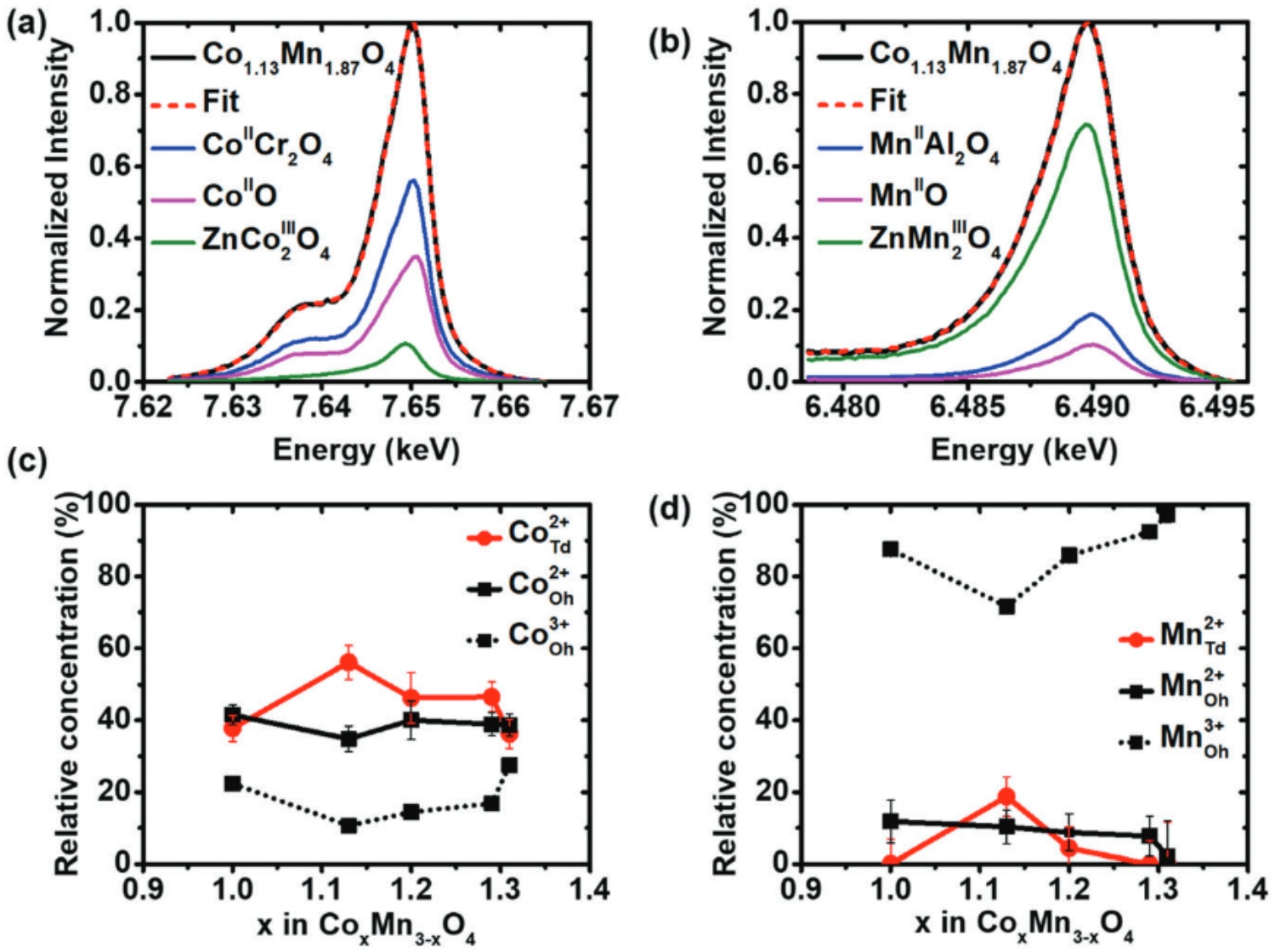


Kβ Mainline XES – Oxidation State Sensitivity

Bhargava, *PCCP.*, **2018**, *20*, 28990

The sensitivity of Kβ mainlines to metal oxidation state can be exploited to quantify mixtiures with varying oxidation state

In this study, the compositions of Co/Mn oxide nanoparticles were determined using Kβ mainlines

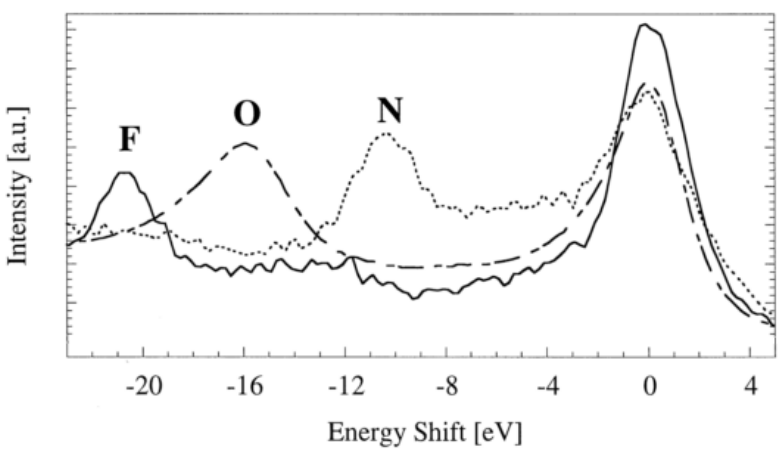


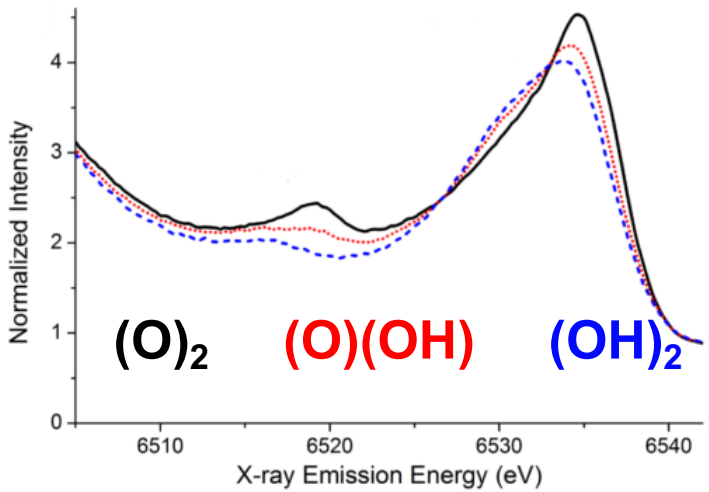
Valence-to-Core (VtC) XES

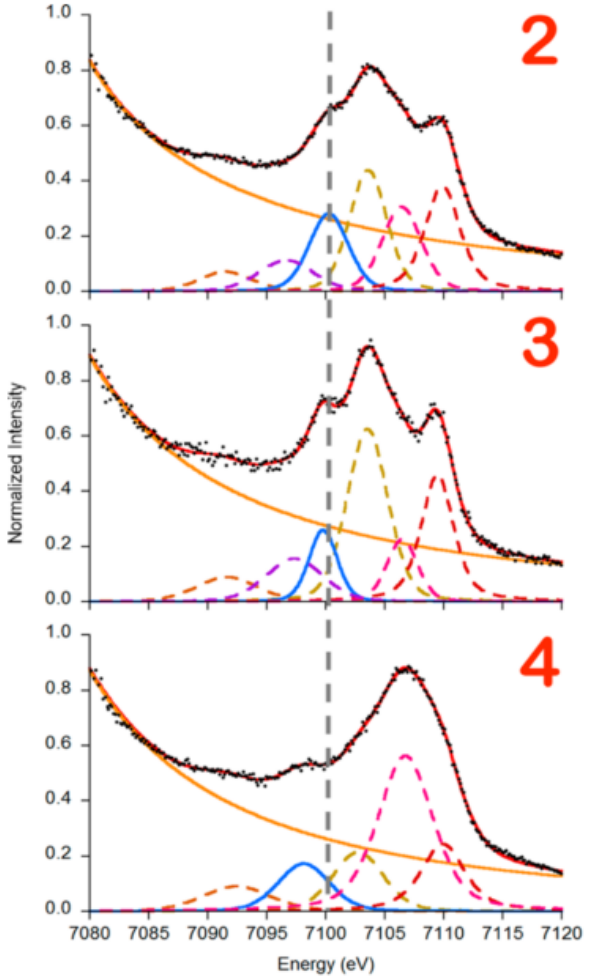
Bergmann, et al, *Chem Phys Lett*, **1999**, *302*, 119.
Pollock, et al, *JACS*, **2013**, *135*, 11803.
Lassalle-Kaiser, et al, *Inorg Chem*, **2013**, *52*, 12915.

VtC transitions result when ligand-localized valence electrons fill the 1s hole

Depending on the system being studied, information such as the **number** and **atomic identity** of ligands, ligand **protonation state**, **intra-ligand bond activation** can all be obtained





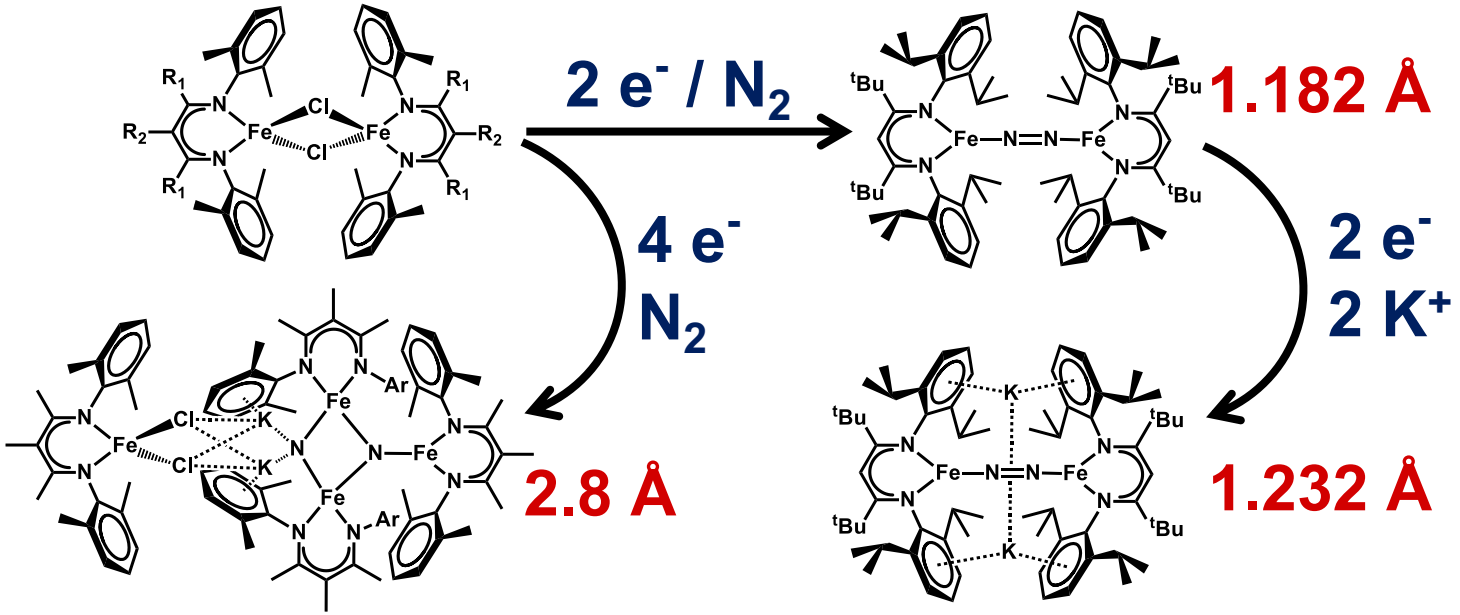


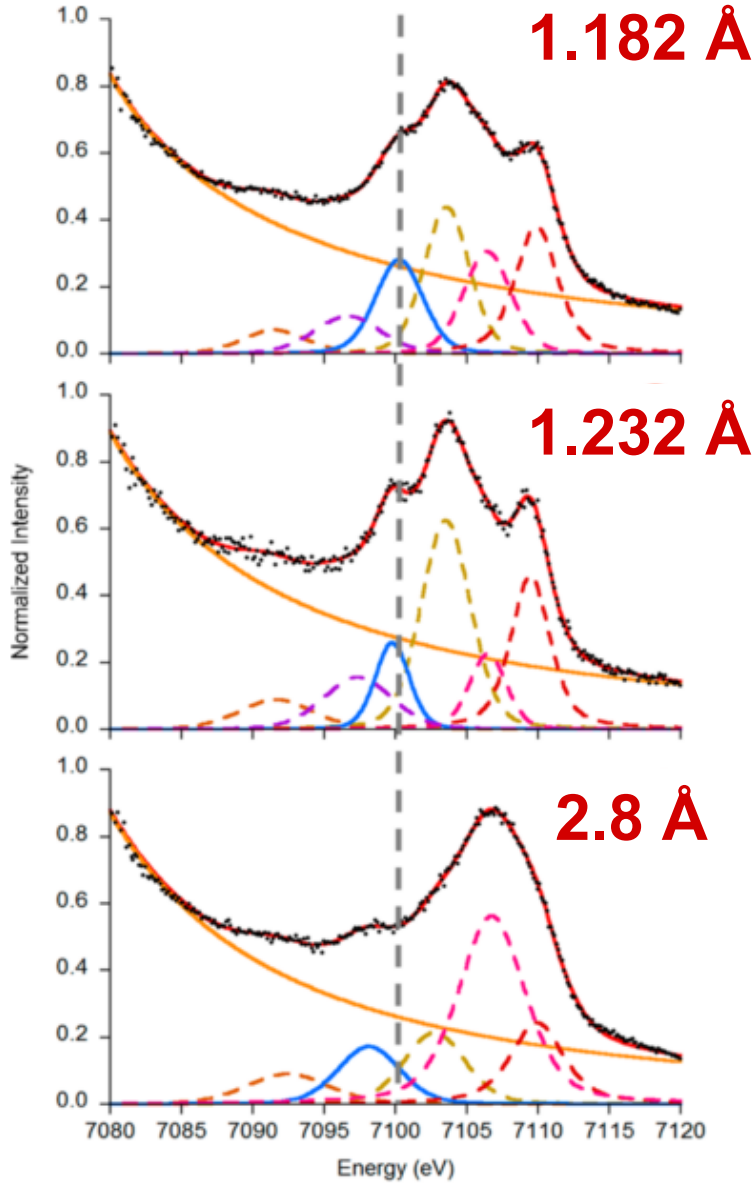
N-N Bond Activation

Pollock, et al, *JACS*, **2013**, *135*, 11803.

Because VtC XES is sensitive to the ligand electronic structure, geometric changes happening to the ligands can (potentially) be probed using VtC spectra

One catalytically interesting example is bond activation





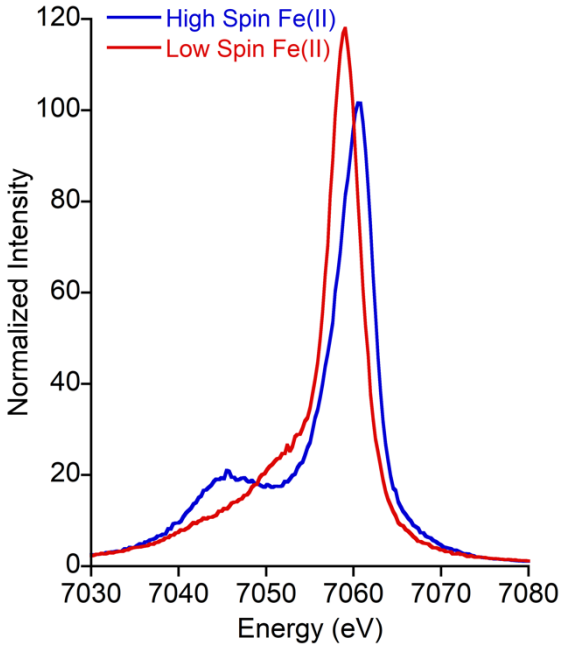
XES Cheat Sheet

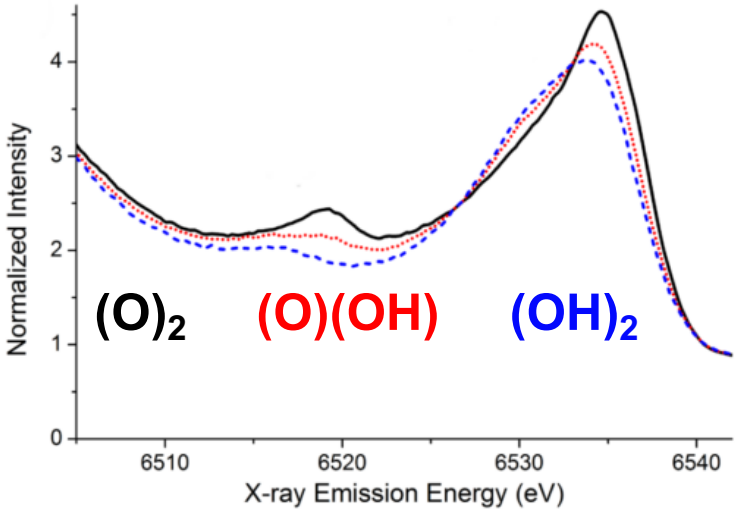
XES is **element selective** and can be applied to **nearly any element** in a wide **variety of sample environments**

Kα lines are intense but have **limited chemical information**

Kβ mainlines contain information about metal **spin state**

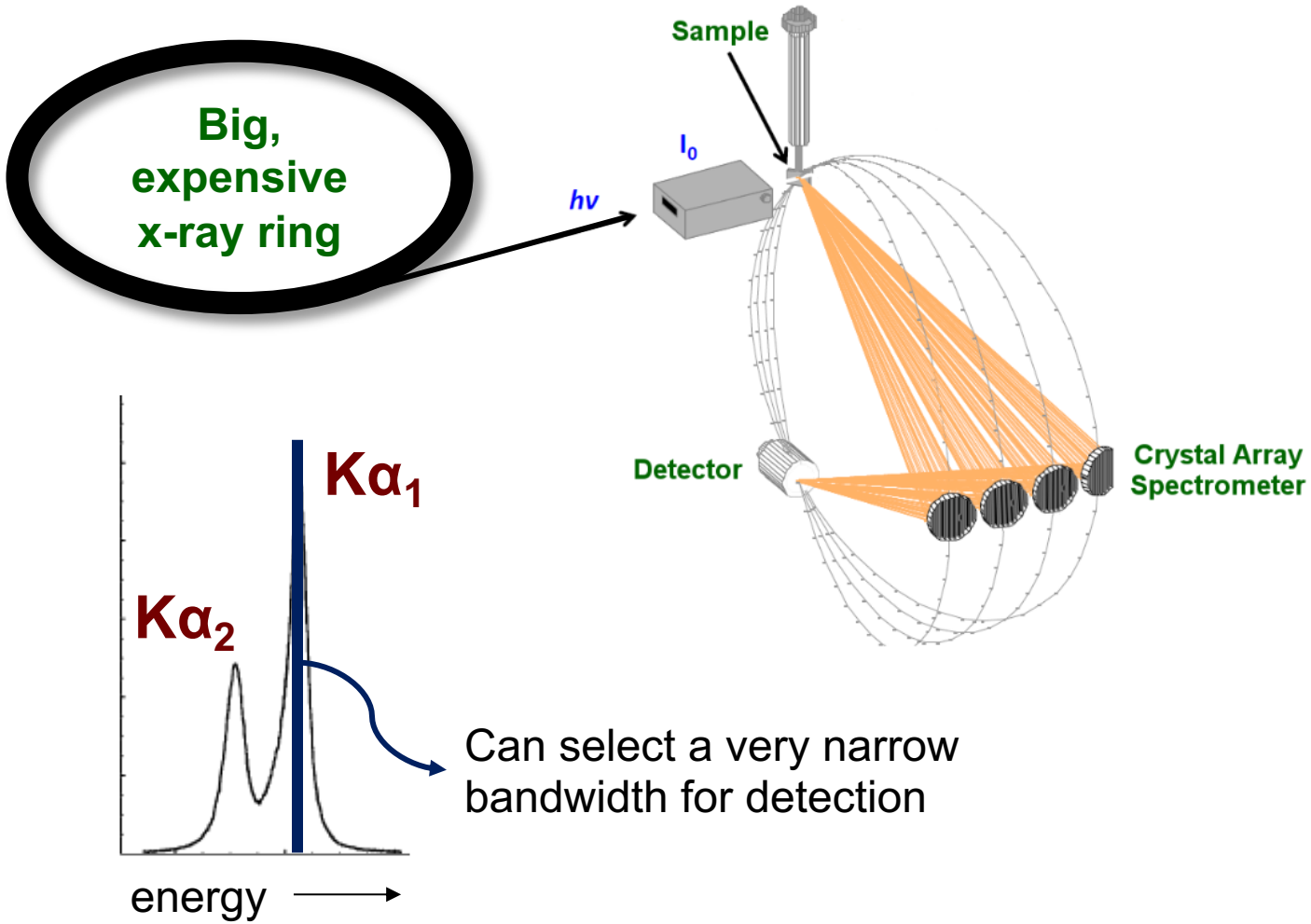
Valence-to-core transitions probe ligand electronic structure, including **number of ligands**, **ligand identity**, and **intra-ligand bond activation**





Part IV: HERFD

High Energy Resolution Fluorescence Detected (HERFD) XAS

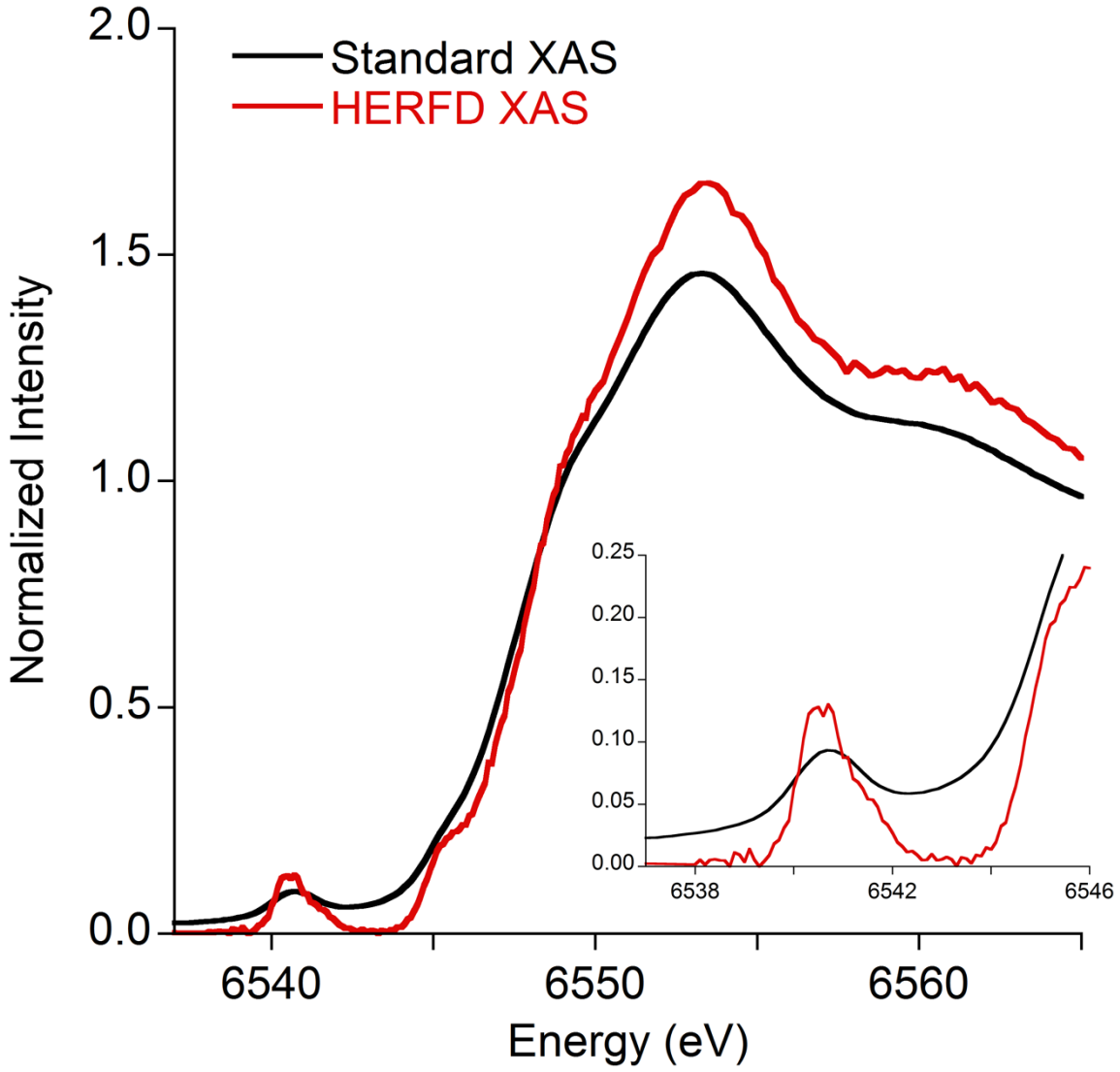


HERFD XAS is fluorescence-detected XAS with a twist—instead of using a solid state detector, a high resolution crystal spectrometer is used

Unlike an XES measurement, in HERFD XAS, the spectrometer stays at a constant energy while the incident energy is scanned

In this way, HERFD XAS is like a combination of XAS and XES

HERFD XAS Spectra



HERFD XAS spectra are much higher resolution than transmission / fluorescence detected XAS

Lower background than conventional XAS

- Also lower signal!

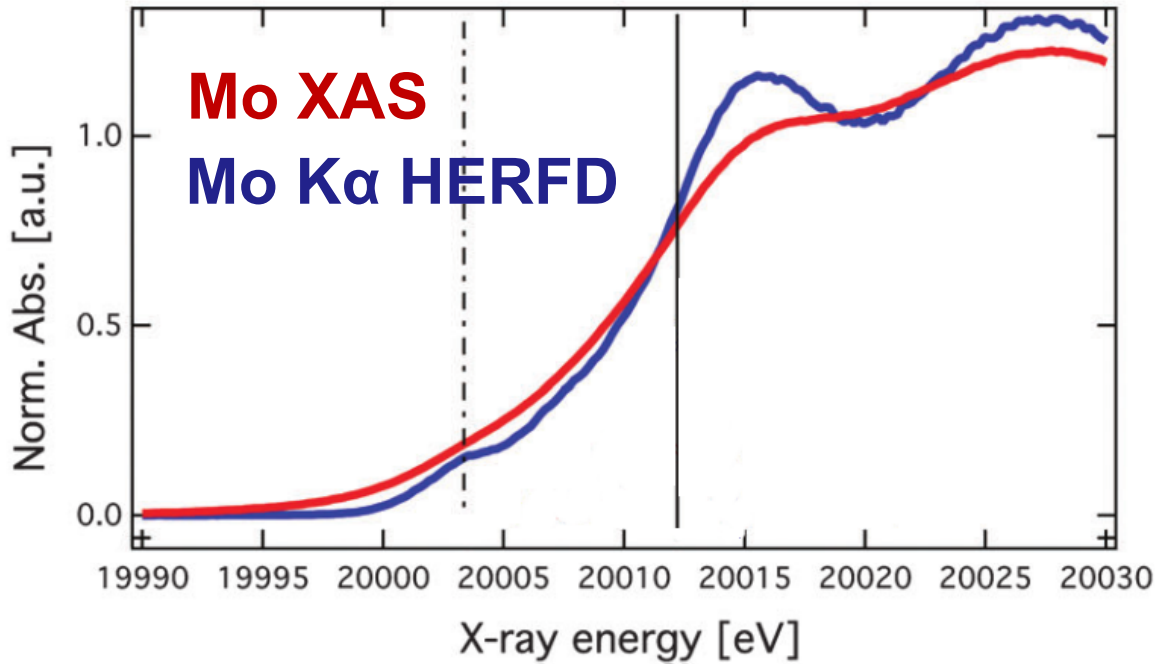
The precise sensitivity of the spectra can be tuned depending on the XES transition being monitored

Improved Resolution for Heavy Atoms

Lima, et al, *PCCP*, **2013**, *15*, 20911.

The resolution in XAS measurements generally gets worse as the incident energy gets higher

This is a big problem for 2nd and 3rd row transition metals as important features become too broad to see in conventional XAS

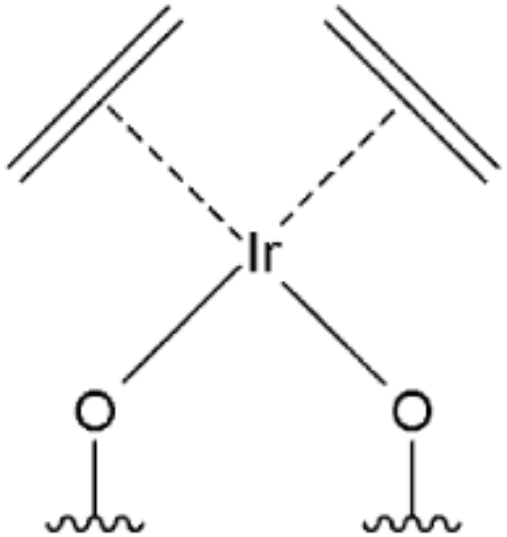


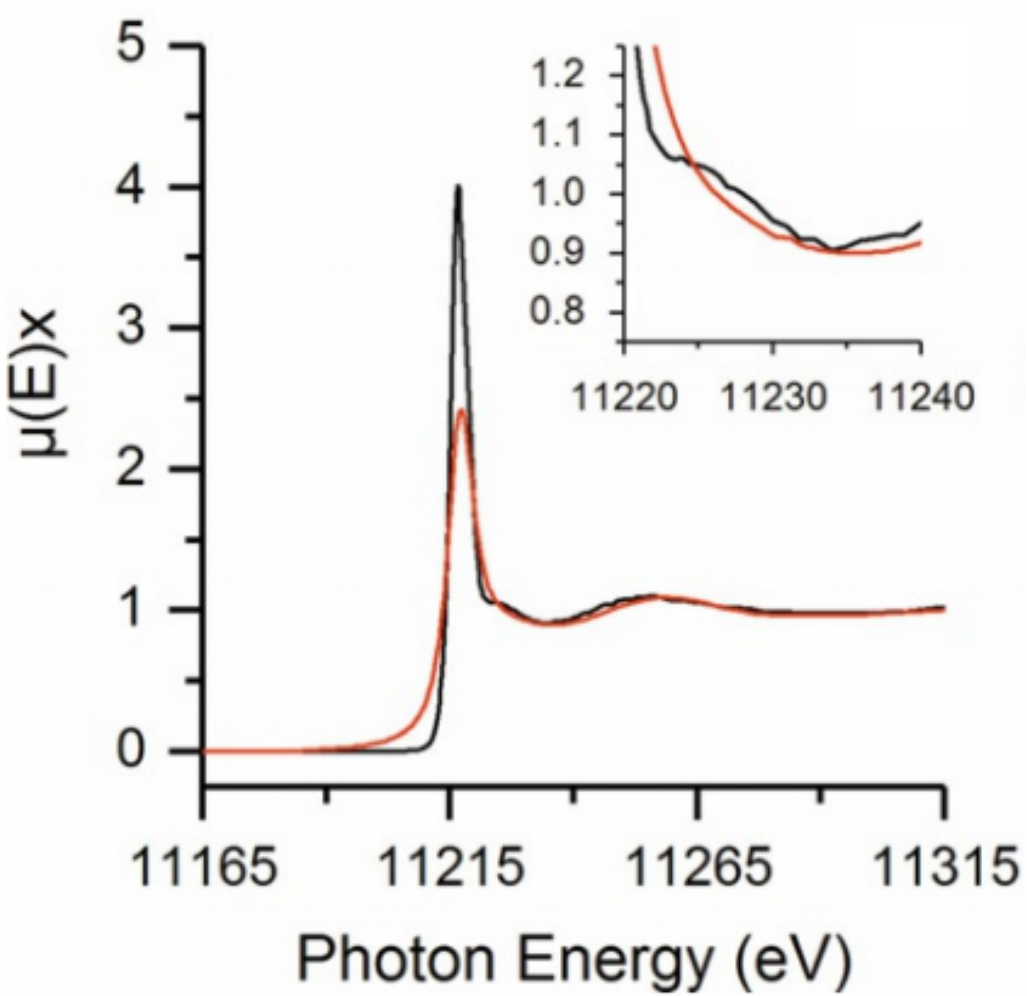
Increased resolution of the HERFD measurements allows additional information to be extracted from the XAS spectra

Improved Resolution for Heavy Atoms

Hoffman, *Chem. Eur. J.*, **2017**, *23*, 14760.

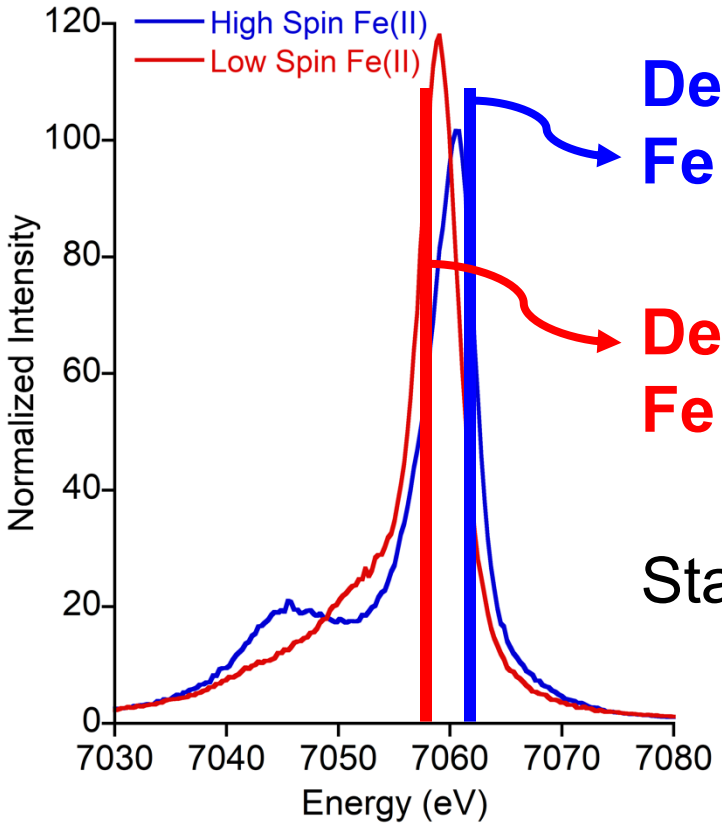
Similarly, for an Ir catalyst, features appear in the HERFD XAS spectra that are invisible in the conventional XAS experiment





Increased Selectivity Using HERFD

Because HERFD XAS detects the spectra using an XES transition, we can exploit the chemical sensitivity of XES – e.g. chemically-selective XAS!



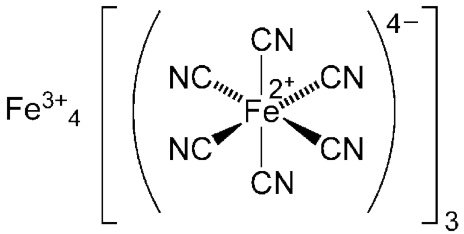
Detection here would be selective for a high spin Fe species

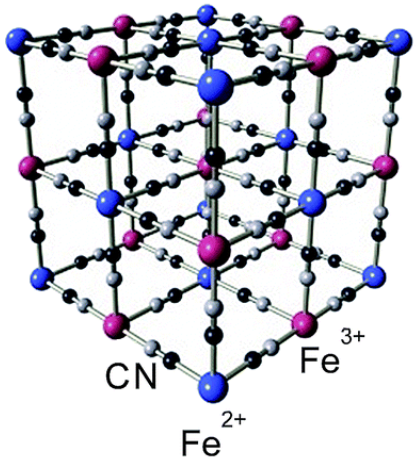
Detection here would be selective for a low spin Fe species

Standard XAS would only see an average of both species!

Site-Selective EXAFS Using HERFD

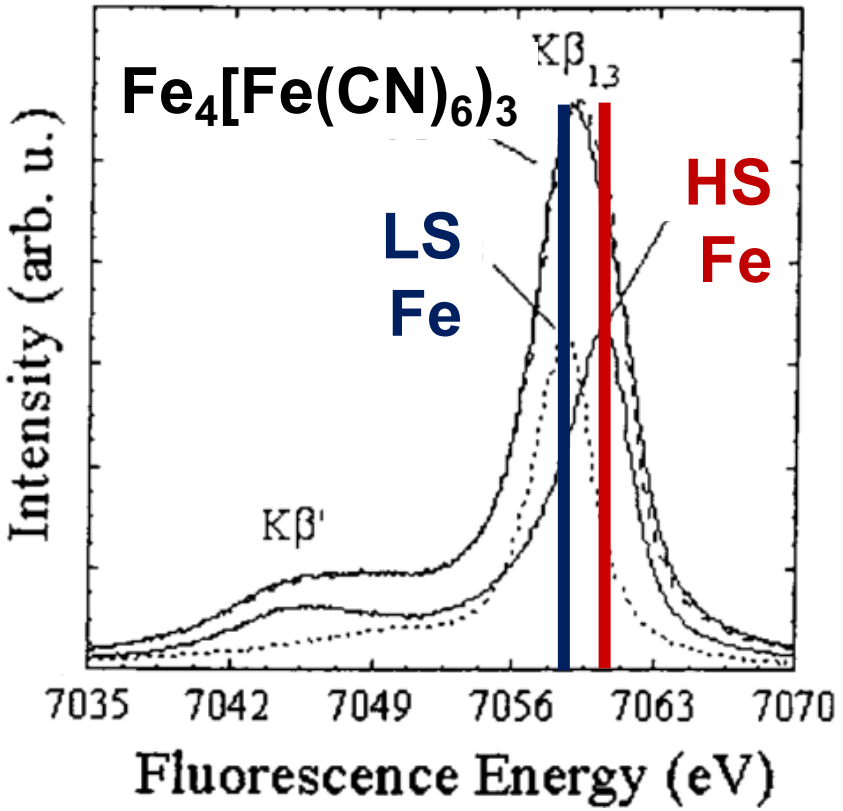
Glatzel, et al, *Inorg Chem*, **2002**, *41*, 3121.

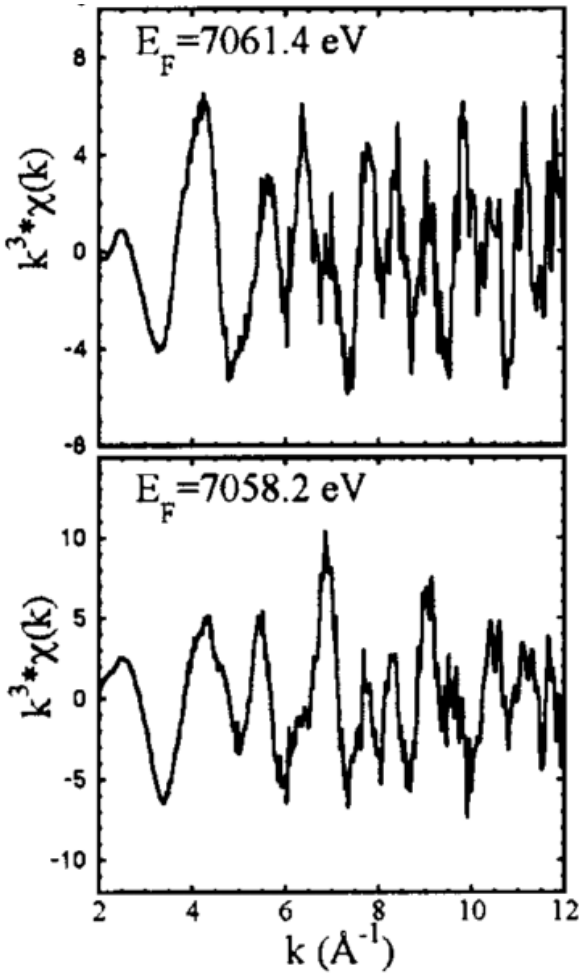




Prussian blue is a compound containing two unique iron ions

- one high spin Fe(III)
- one low spin Fe(II)



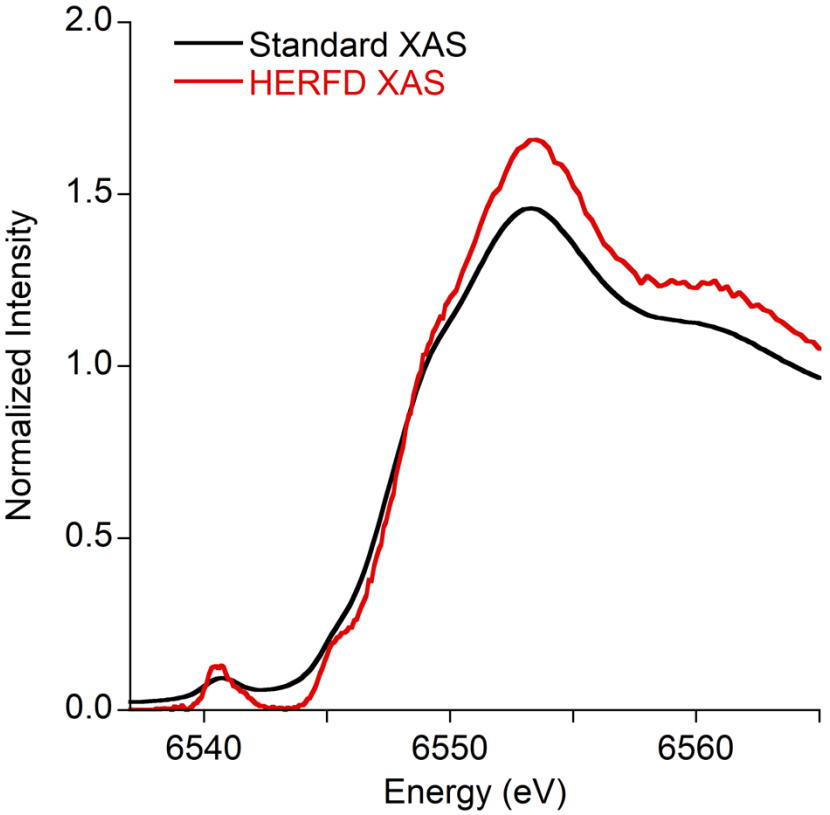


HERFD XAS Cheat Sheet

HERFD XAS is **element selective** and can be applied to **nearly any element** in a wide **variety of sample environments**

HERFD spectra have **higher resolution** than standard XAS measurements

Depending on emission line chosen for detection, HERFD spectra can have **enhanced selectivity** over standard XAS



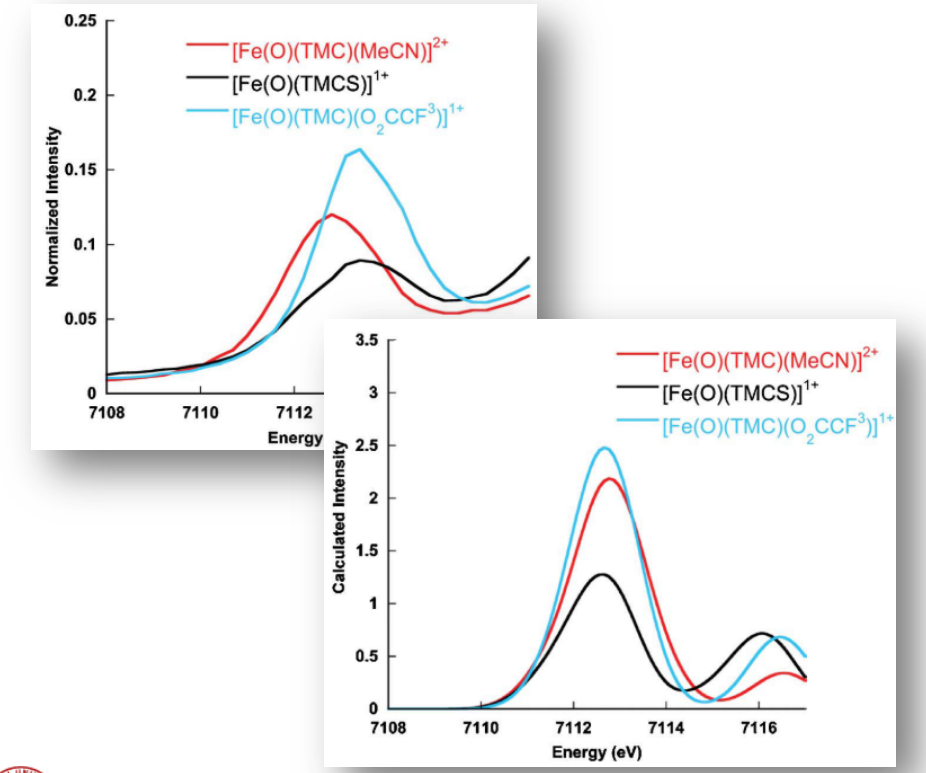
Part V: Calculations

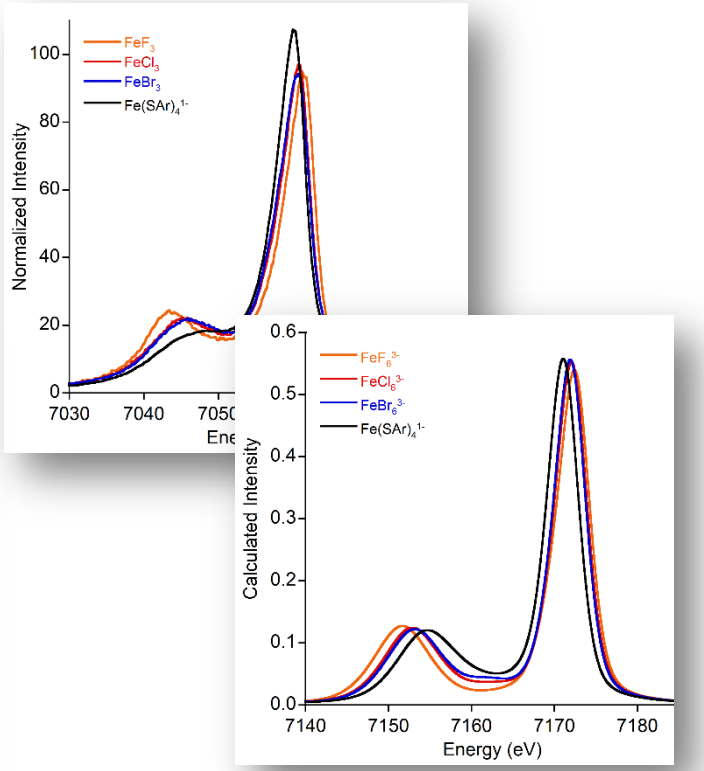
Help from DFT

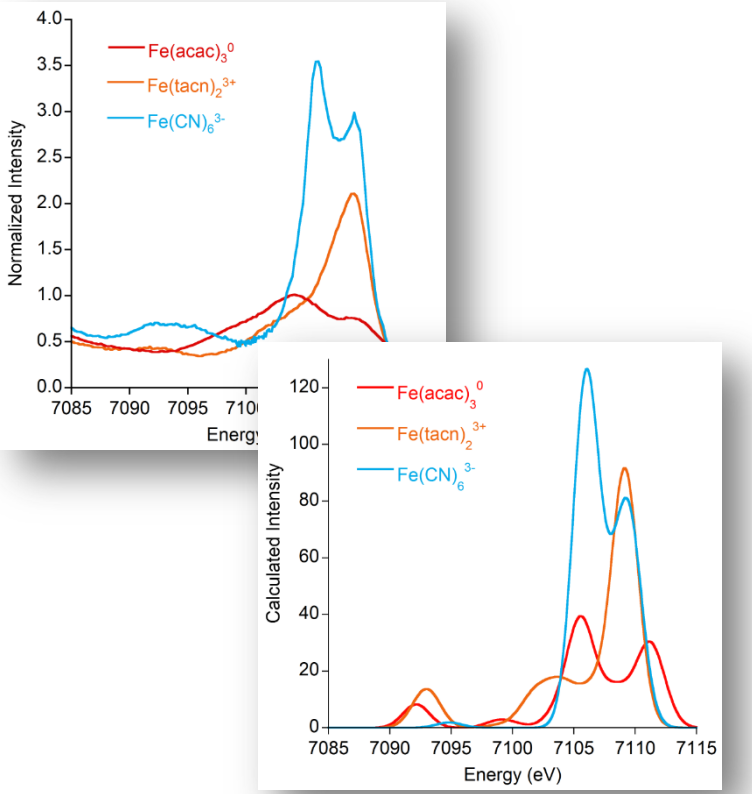
Stieber, *Dalton*, **2011**, *40*, 11070
Pollock, *JACS*, **2014**, *136*, 9453
Lee, *JACS*, **2010**, *132*, 9715

Most types of x-ray spectra—including XAS and HERFD XAS pre-edges, as well as Kα, Kβ, and VtC XES—can be calculated using DFT / *ab initio* methods

Calculations can help with analysis and interpretation of x-ray spectra





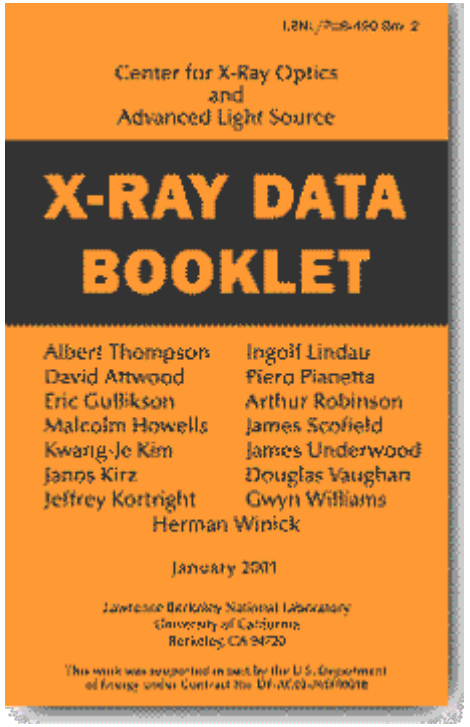


Resources for Planning Experiments

Some useful resources for planning experiments are:

- Center for X-ray Optics (http://www.cxro.lbl.gov/)
- X-ray Data Booklet (https://xdb.lbl.gov/)
- Lightsources.org (https://lightsources.org/)
- CHESS (https://www.chess.cornell.edu/)
- SSRL Glitch Library (https://www-ssrl.slac.stanford.edu/smbin/dataextractnew.pl)
- Your friendly neighborhood beamline scientist

lightsources.org



Questions?

If you have any questions later or today or after you leave, don't hesitate to contact a CHESS scientist! We like talking to (potential) users about experiments!

Ken Finkelstein
kdf1@cornell.edu

Chris Pollock
cjp227@cornell.edu

Louise Debefve
lmd252@cornell.edu