



2020  
High Energy X-ray  
Techniques Workshop

# High Energy X-ray Spectroscopy

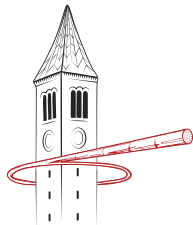
X-ray spectroscopy and materials research

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# Schedule

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## 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?

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## **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

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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





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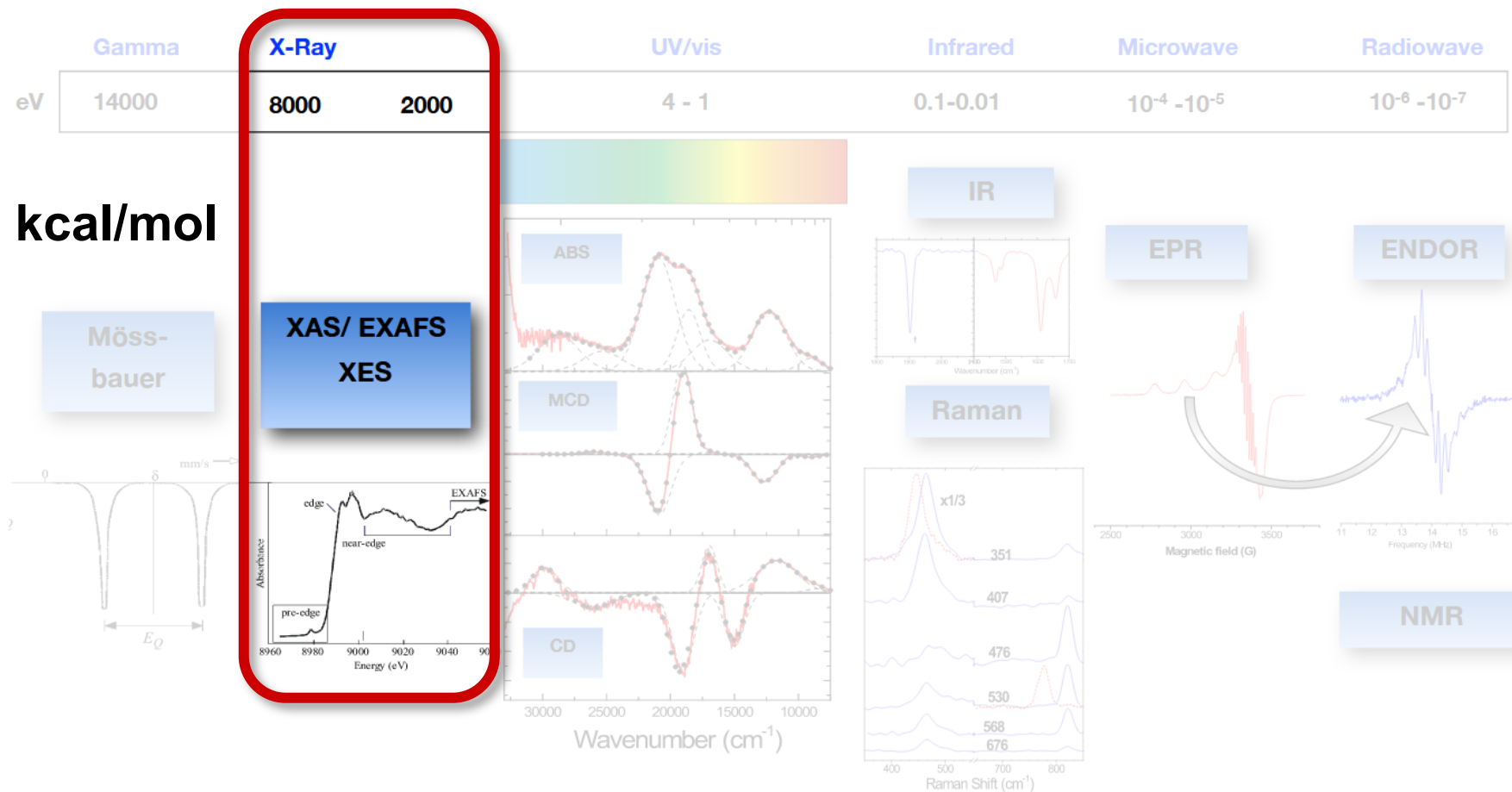
# Part I: Overview



# 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

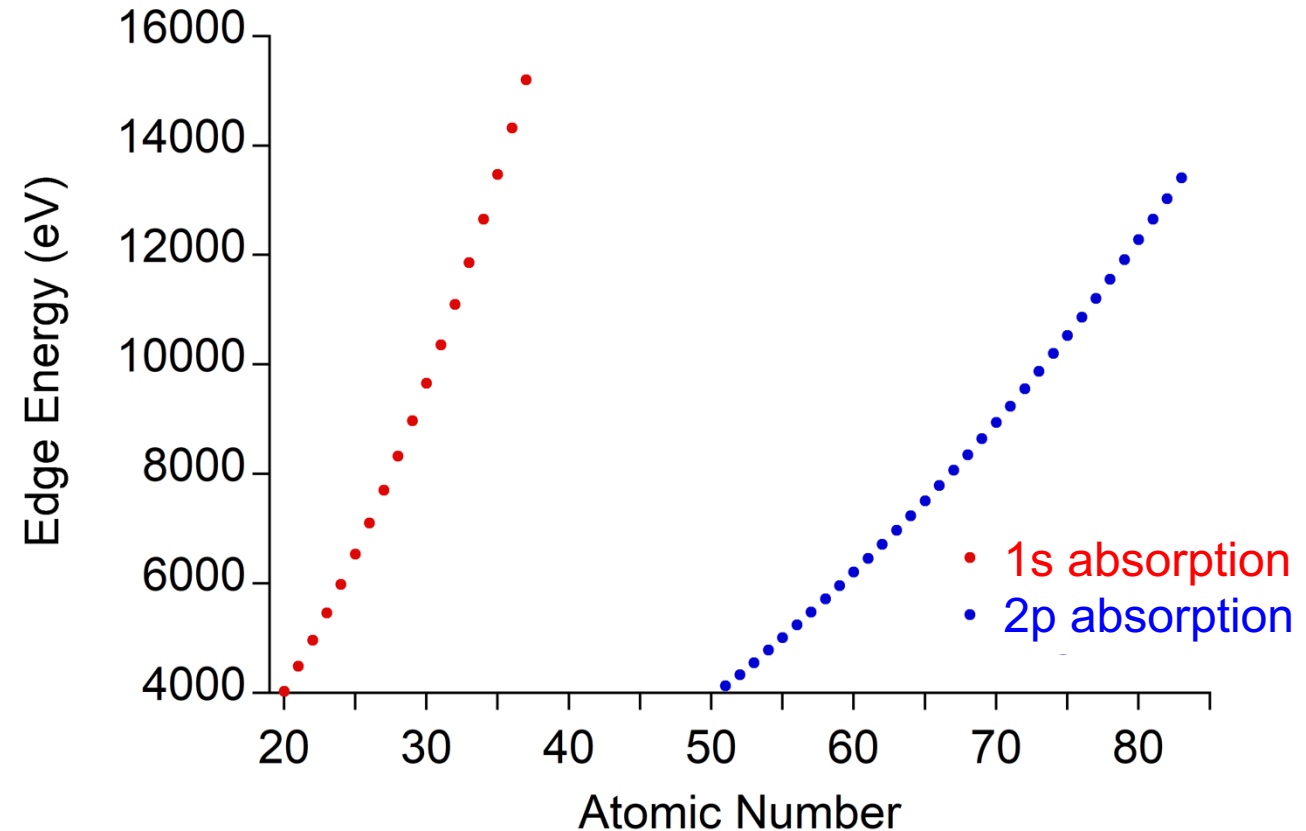
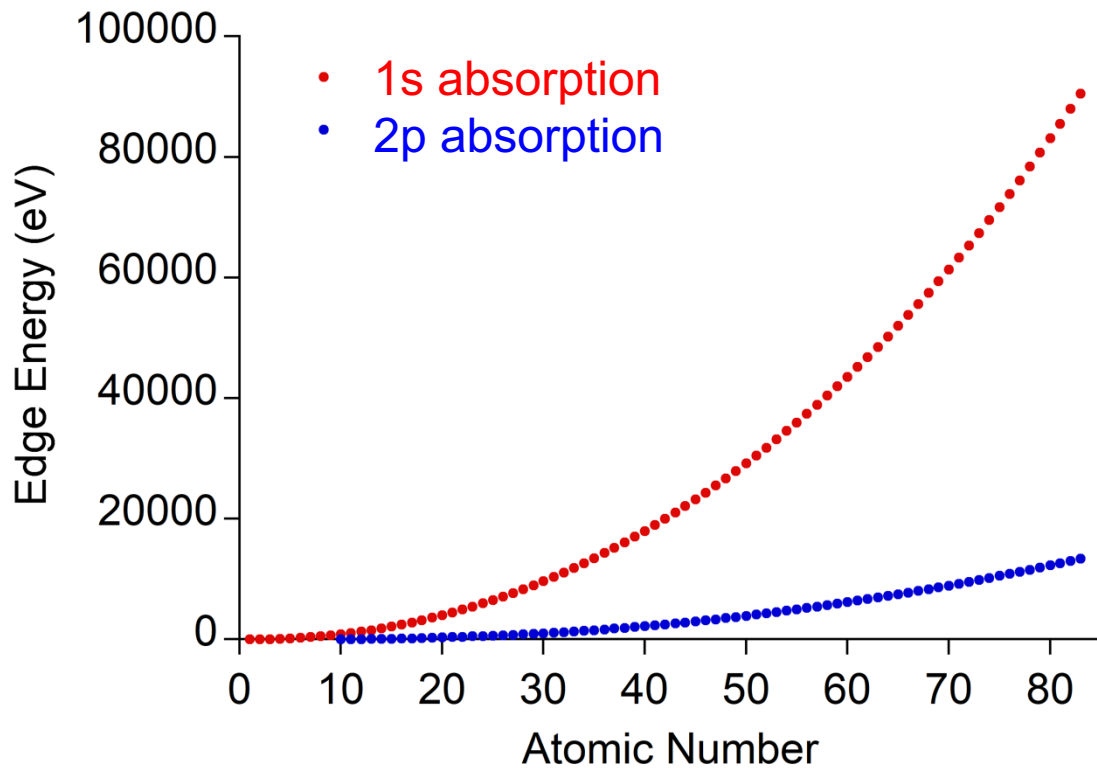
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Most x-ray spectroscopy is performed at a synchrotron, since these facilities provide an intense, energy-tunable source of x-rays



# Element Selectivity

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





# Periodic Table of the Edges

## 4 – 16 keV

1s absorption

2p absorption

1 IA <b>H</b> Hydrogen 1.008																	18 VIIIA <b>He</b> Helium 4.002602
3 <b>Li</b> Lithium 6.94	4 IIA <b>Be</b> Beryllium 9.0121831											5 IIIA <b>B</b> Boron 10.81	6 IVA <b>C</b> Carbon 12.011	7 VA <b>N</b> Nitrogen 14.007	8 VIA <b>O</b> Oxygen 15.999	9 VIIA <b>F</b> Fluorine 18.998403163	10 Neon 20.1797
11 <b>Na</b> Sodium 22.98976928	12 IIA <b>Mg</b> Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA <b>Al</b> Aluminium 26.9815385	14 IVA <b>Si</b> Silicon 28.085	15 VA <b>P</b> Phosphorus 30.973761998	16 VIA <b>S</b> Sulfur 32.06	17 VIIA <b>Cl</b> Chlorine 35.45	18 Argon 39.948
19 <b>K</b> Potassium 39.0983	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.955912	22 <b>Ti</b> Titanium 47.88	23 <b>V</b> Vanadium 50.9415	24 <b>Cr</b> Chromium 51.9961	25 <b>Mn</b> Manganese 54.938044	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933194	28 <b>Ni</b> Nickel 58.6934	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.63	33 <b>As</b> Arsenic 74.921595	34 <b>Se</b> Selenium 78.97	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798
37 <b>Rb</b> Rubidium 85.4678	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.90584	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.90637	42 <b>Mo</b> Molybdenum 95.95	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.90550	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.8682	48 <b>Cd</b> Cadmium 112.414	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.710	51 <b>Sb</b> Antimony 121.757	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90447	54 <b>Xe</b> Xenon 131.29
55 <b>Cs</b> Cesium 132.90545196	56 <b>Ba</b> Barium 137.327	57 - 71 Lanthanoids	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.94788	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.222	78 <b>Pt</b> Platinum 195.084	79 <b>Au</b> Gold 196.966569	80 <b>Hg</b> Mercury 200.592	81 <b>Tl</b> Thallium 204.38	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98040	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)
87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89 - 103 Actinoids	104 <b>Rf</b> Rutherfordium (261)	105 <b>Db</b> Dubnium (268)	106 <b>Sg</b> Seaborgium (269)	107 <b>Bh</b> Bohrium (270)	108 <b>Hs</b> Hassium (285)	109 <b>Mt</b> Meitnerium (276)	110 <b>Ds</b> Darmstadtium (281)	111 <b>Rg</b> Roentgenium (282)	112 <b>Cn</b> Copernicium (285)	113 <b>Nh</b> Nihonium (286)	114 <b>Fl</b> Flerovium (289)	115 <b>Mc</b> Moscovium (289)	116 <b>Lv</b> Livermorium (293)	117 <b>Ts</b> Tennessine (294)	118 <b>Og</b> Oganesson (294)

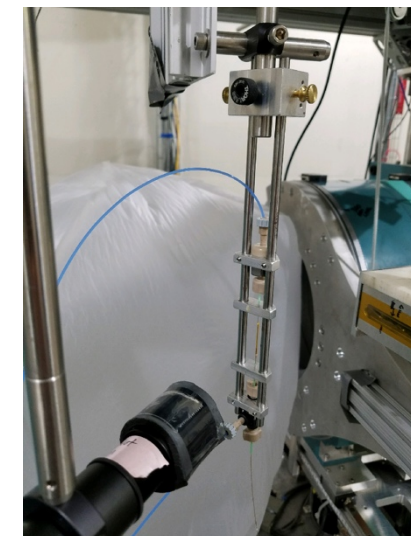
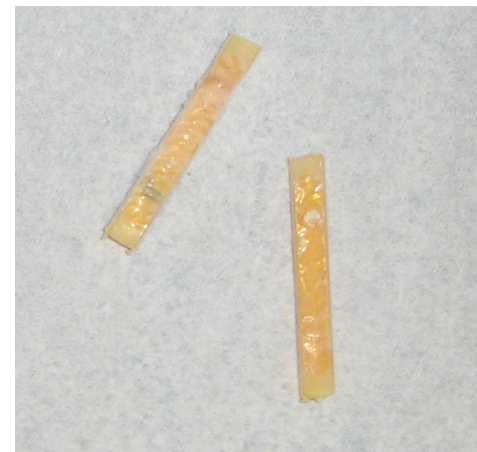
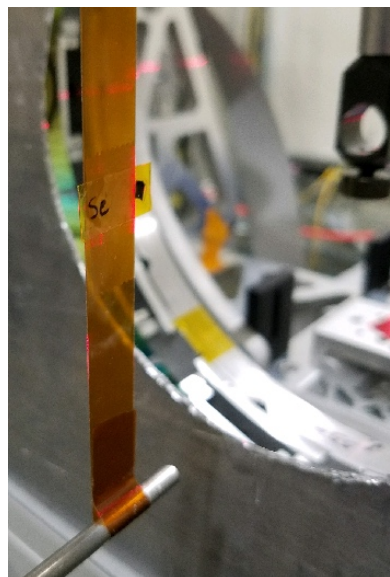
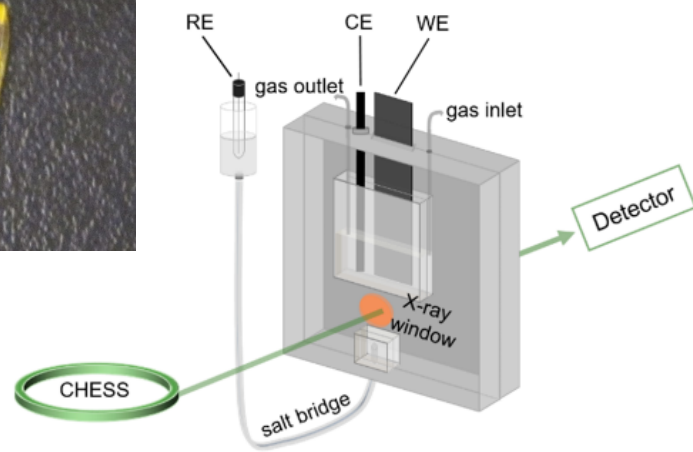
57 <b>La</b> Lanthanum 138.90487	58 <b>Ce</b> Cerium 140.12	59 <b>Pr</b> Praseodymium 140.90766	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92532	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93032	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93402	70 <b>Yb</b> Ytterbium 173.054	71 <b>Lu</b> Lutetium 174.967
89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.0377	91 <b>Pa</b> Protactinium 231.03688	92 <b>U</b> Uranium 238.02891	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (260)



# 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



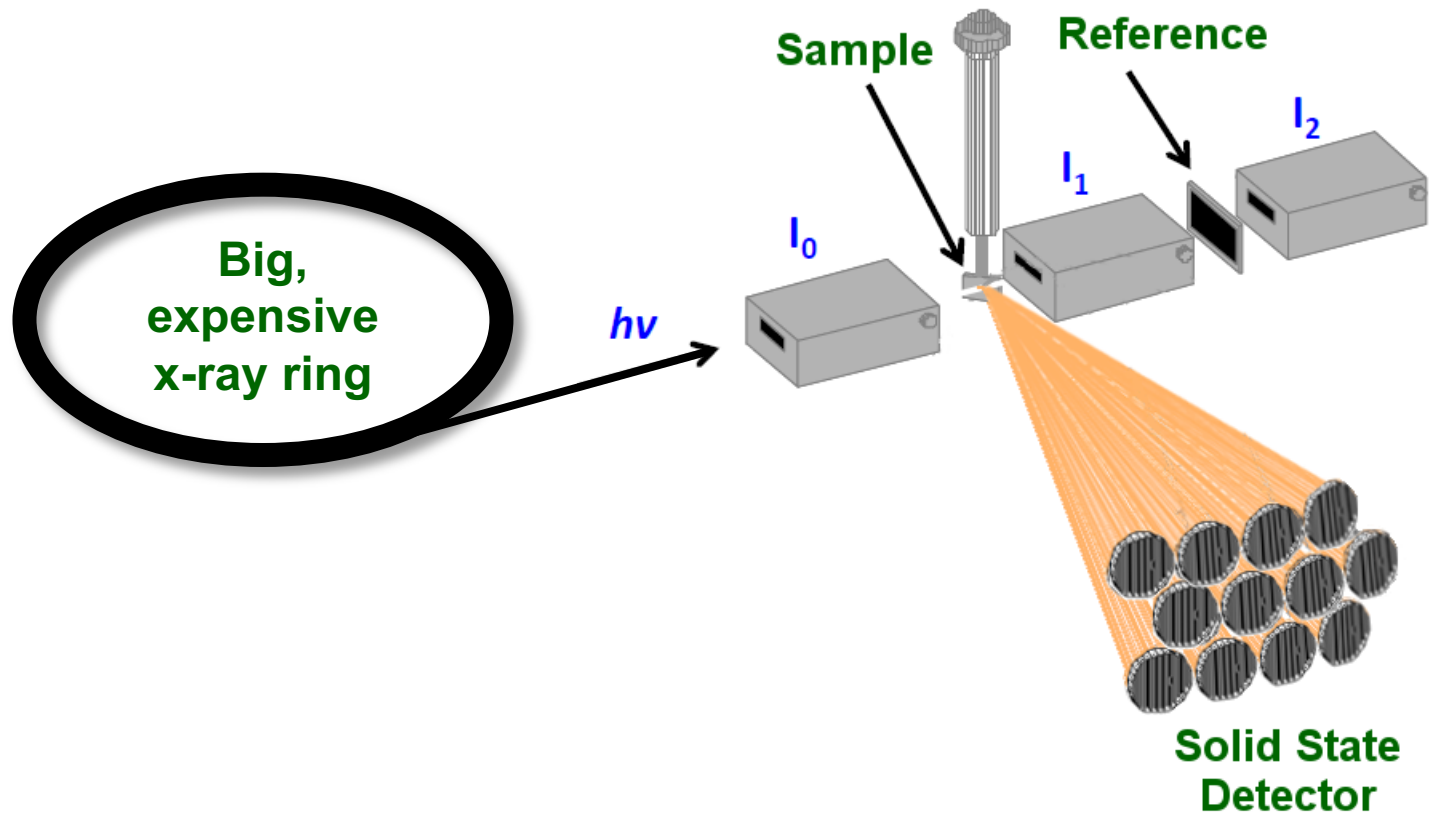
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# Part II:

# XAS / EXAFS



# XAS Experimental Setup



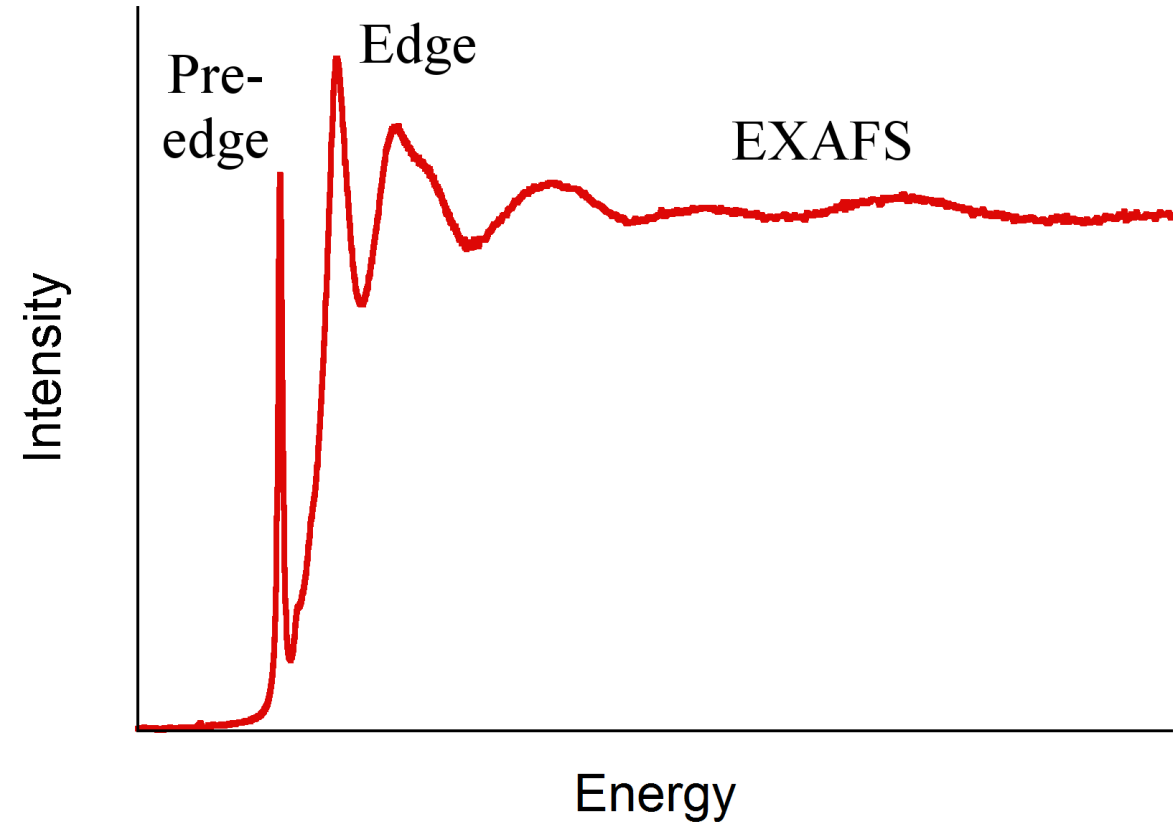
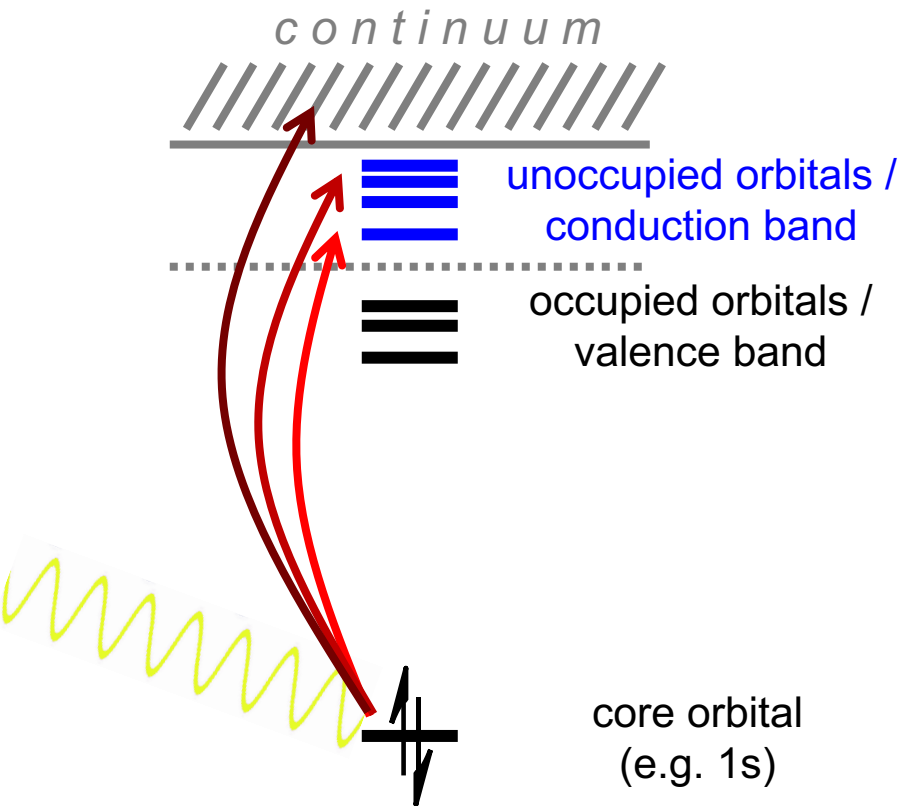
XAS measures the absorption of x-rays of a material as the incident energy is changed

Spectra can either be measured in transmission mode or fluorescence mode

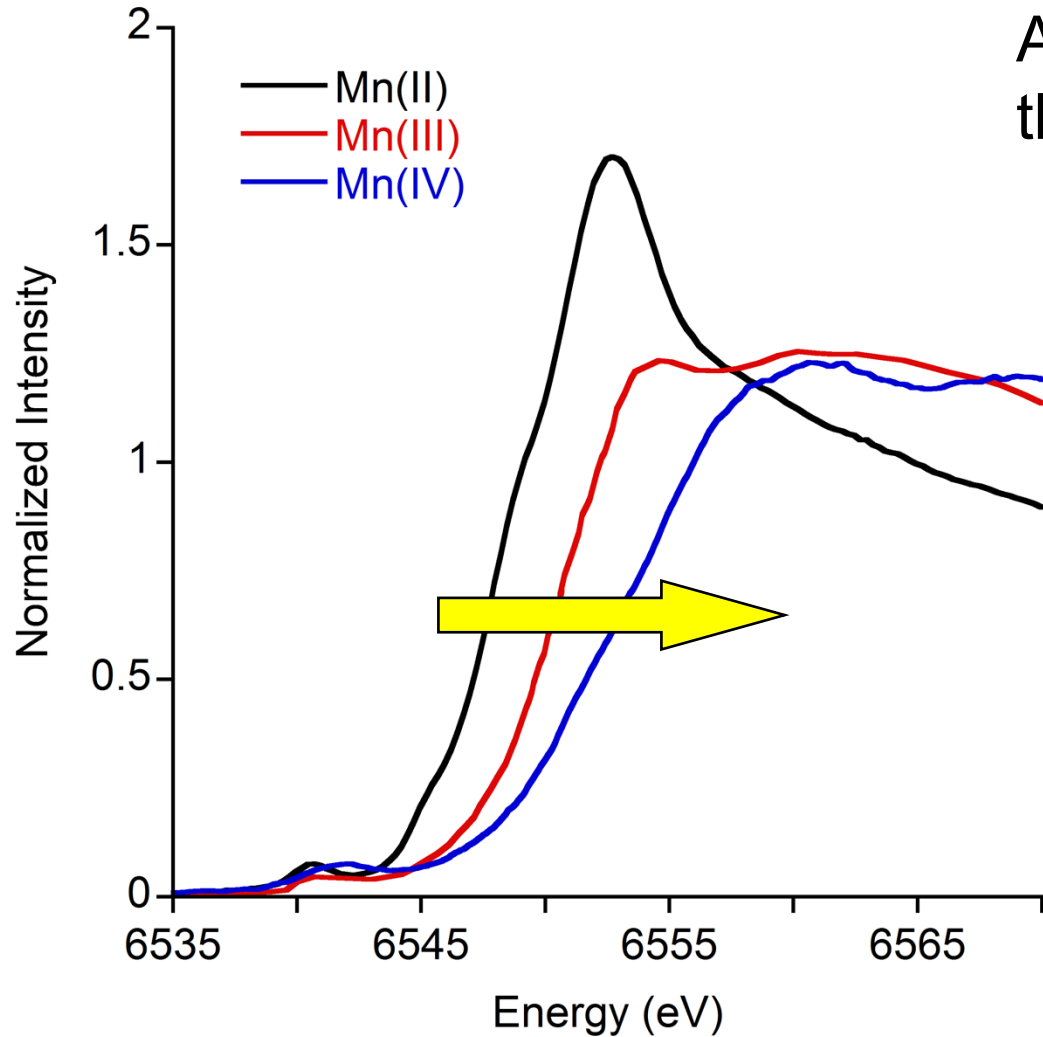
X-rays can penetrate 10s to many 100s of microns into a sample, making this a bulk sensitive technique



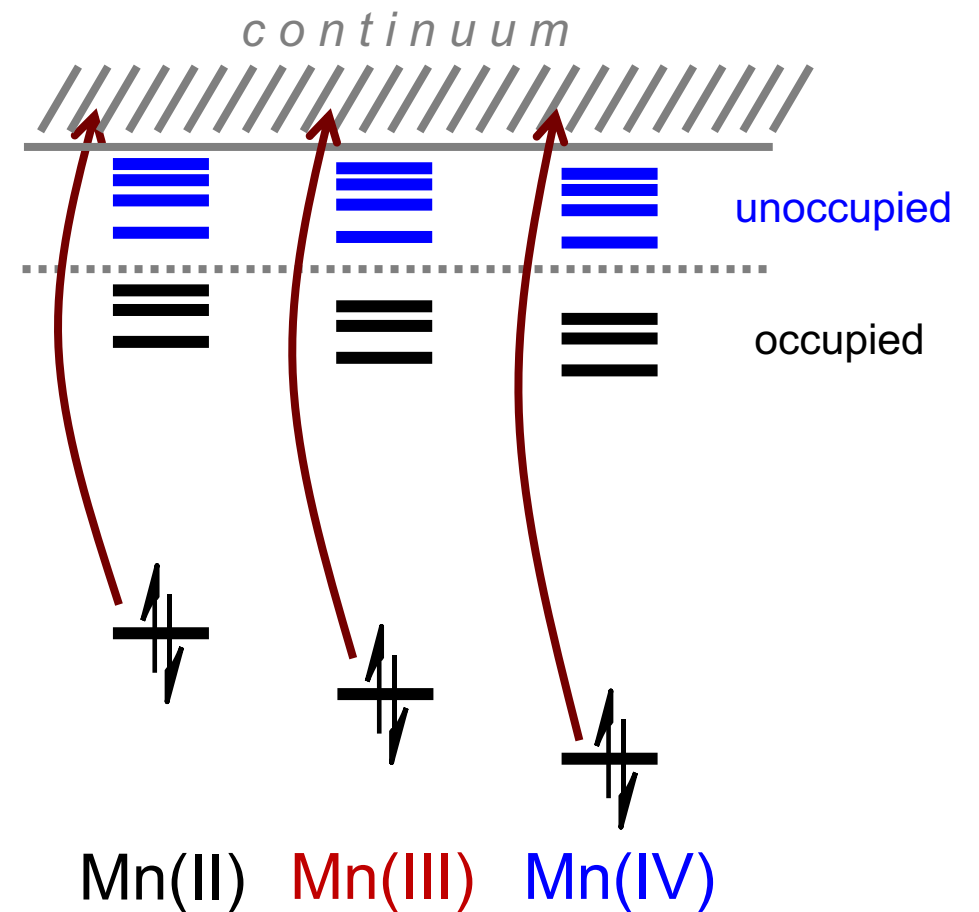
# K-edge X-ray Absorption Spectroscopy (XAS)



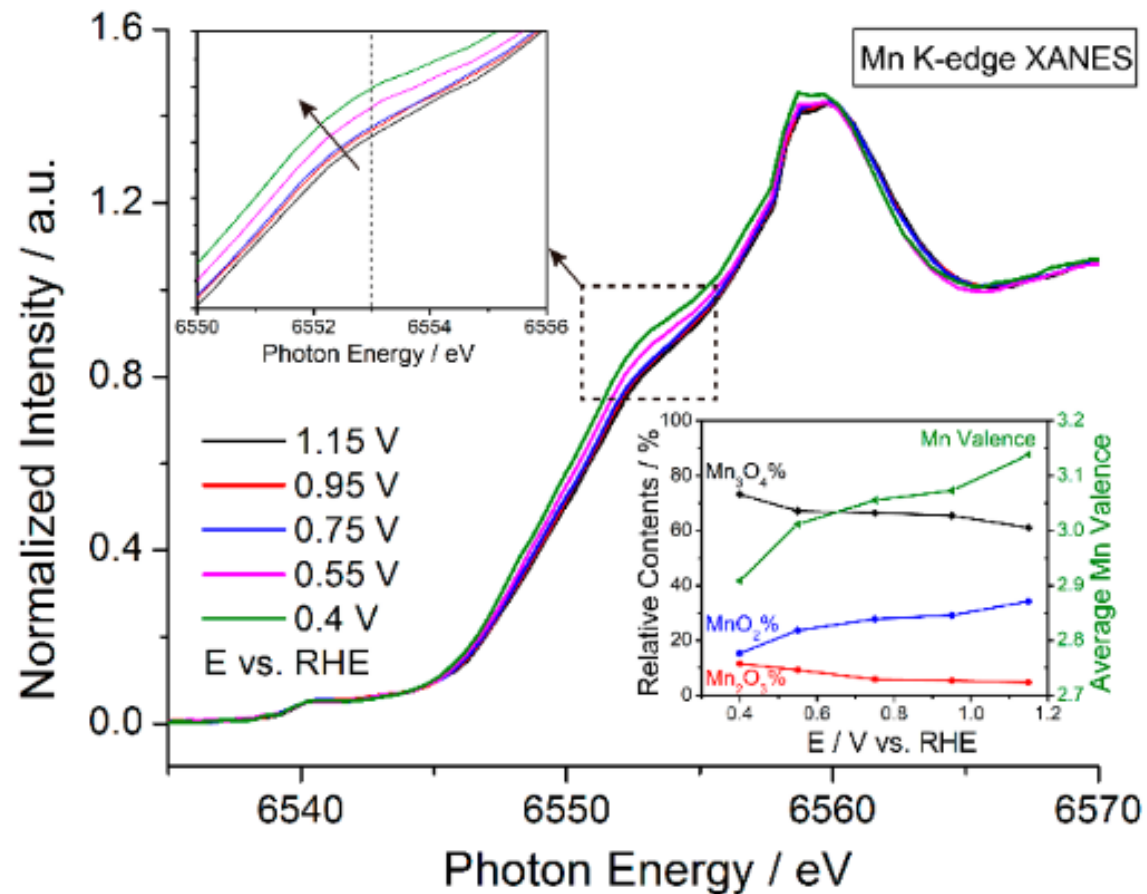
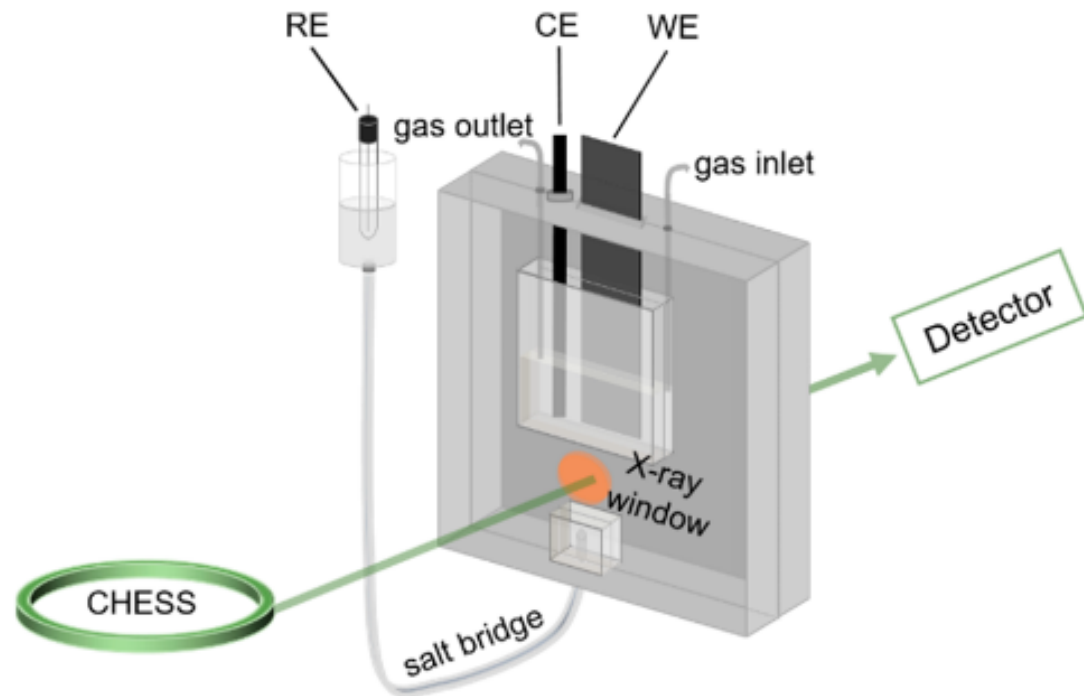
# Sensitivity to Oxidation State



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



# Sensitivity to Oxidation State



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

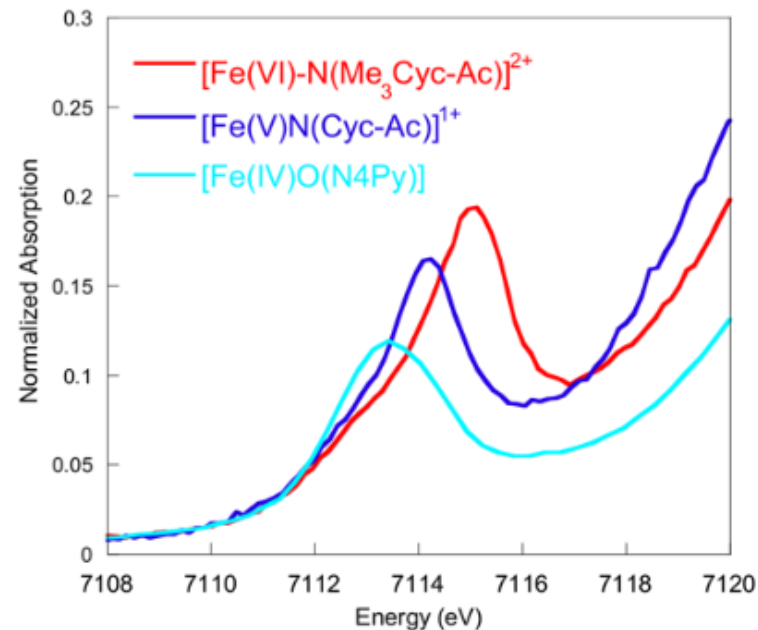
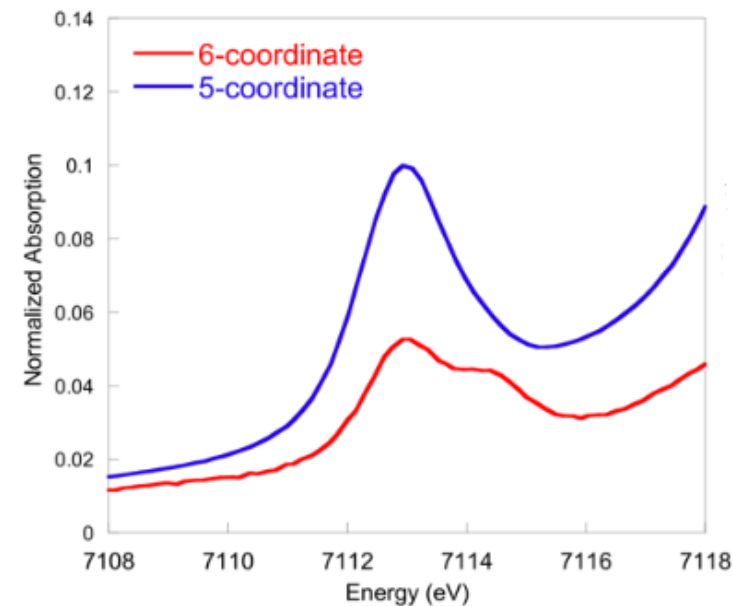
# Sensitivity to Geometry

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

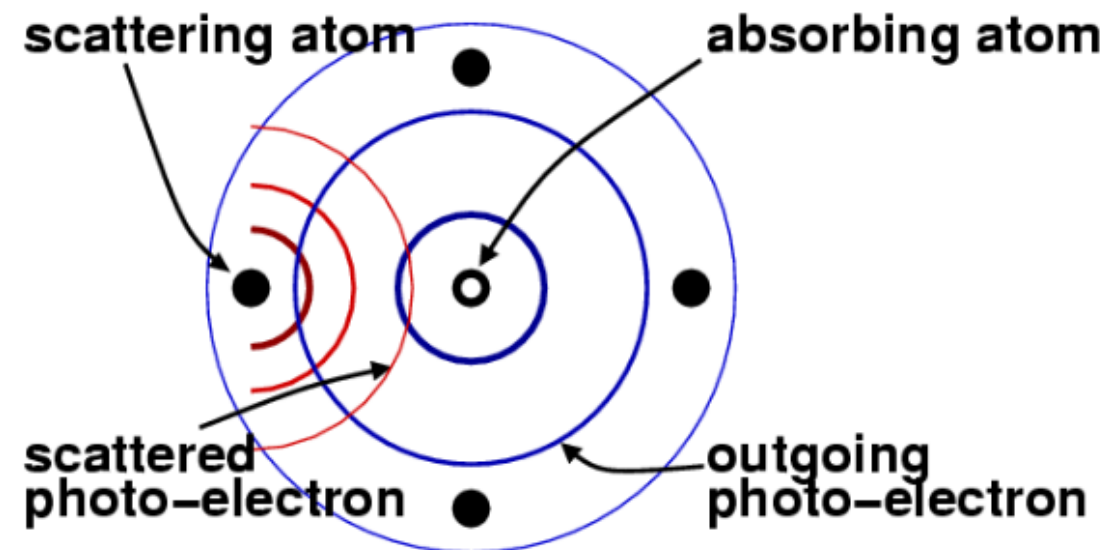
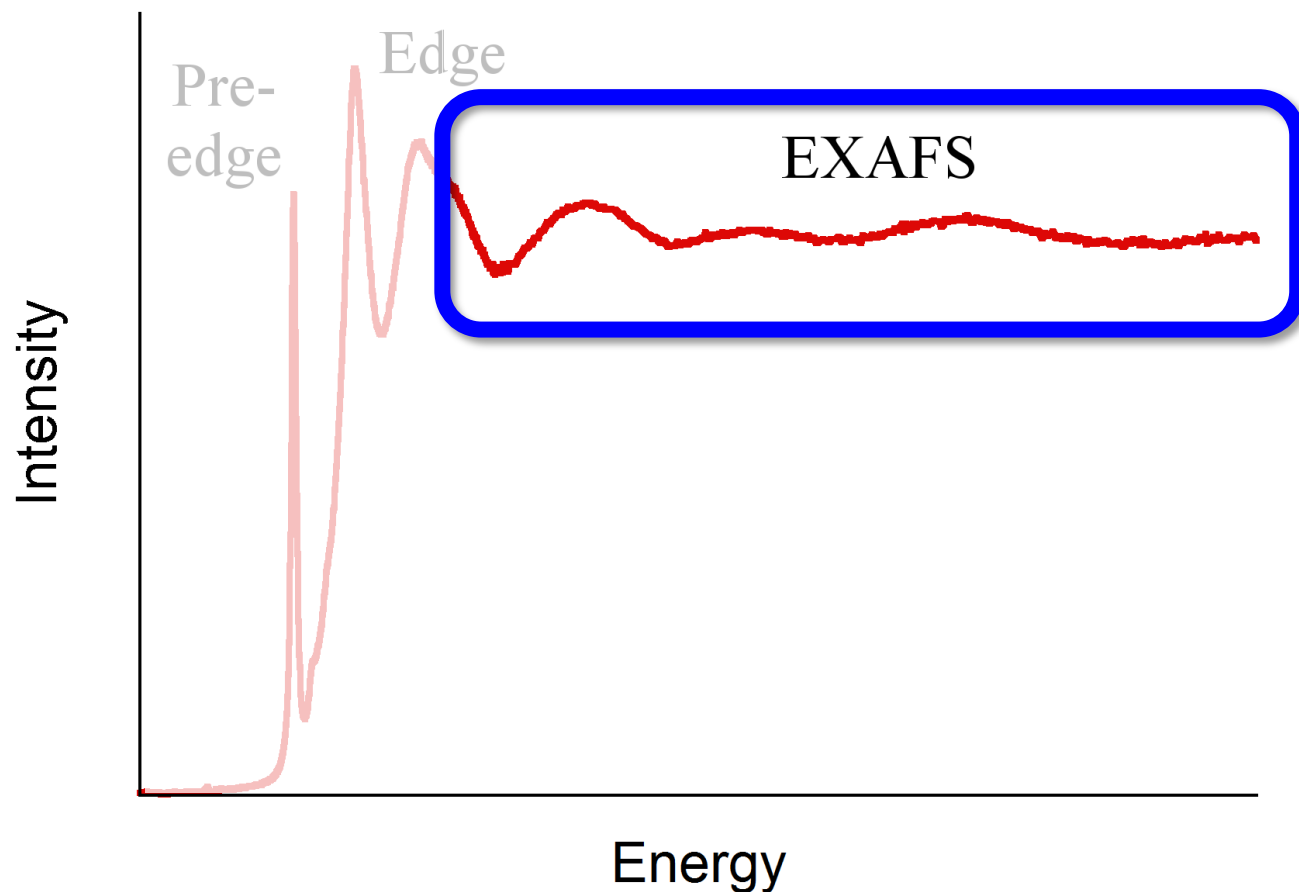
XAS pre-edge are formally forbidden  $s \rightarrow d$  orbital transitions, so their intensity is weak

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

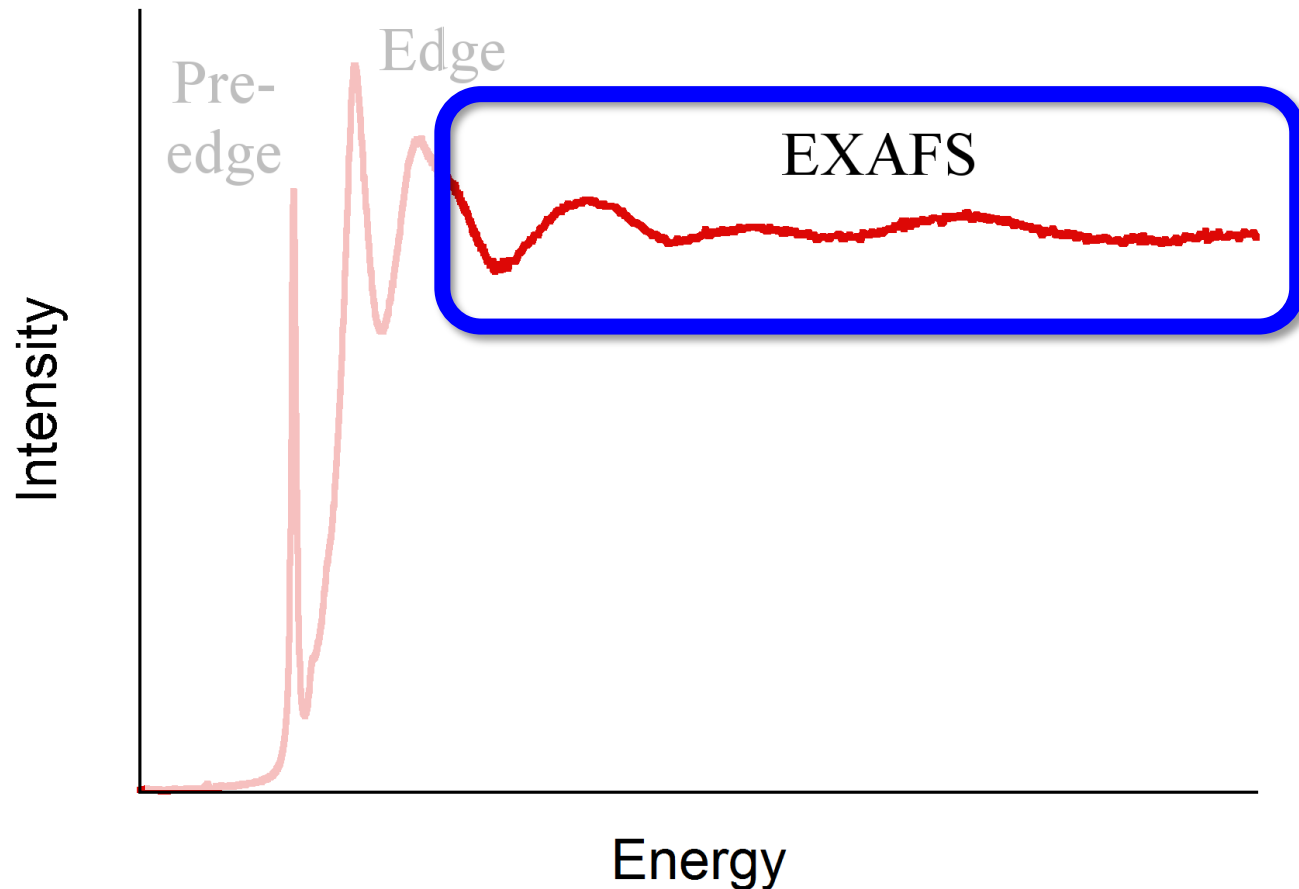


# Extended X-ray Absorption Fine Structure (EXAFS)



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

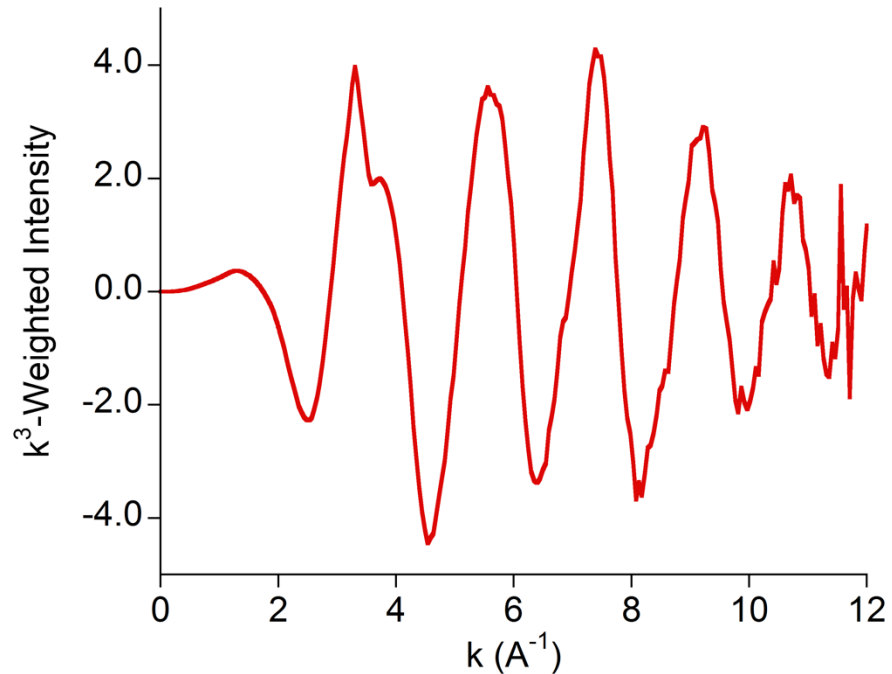
# Extended X-ray Absorption Fine Structure (EXAFS)



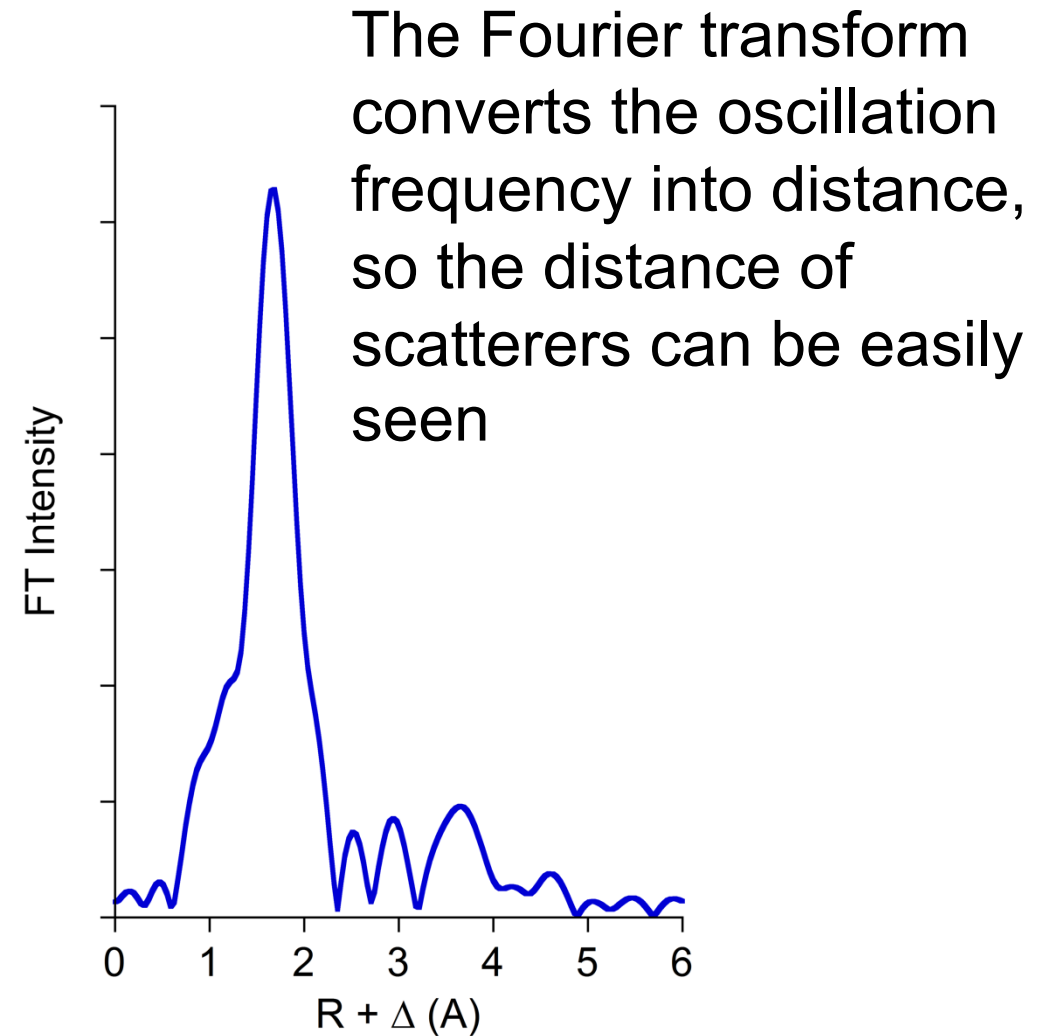
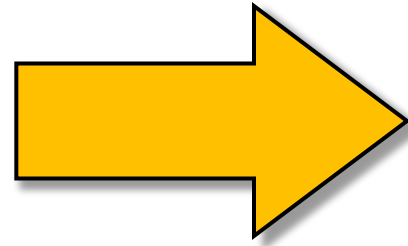
From EXAFS we can learn:

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

# Fourier Transformed EXAFS



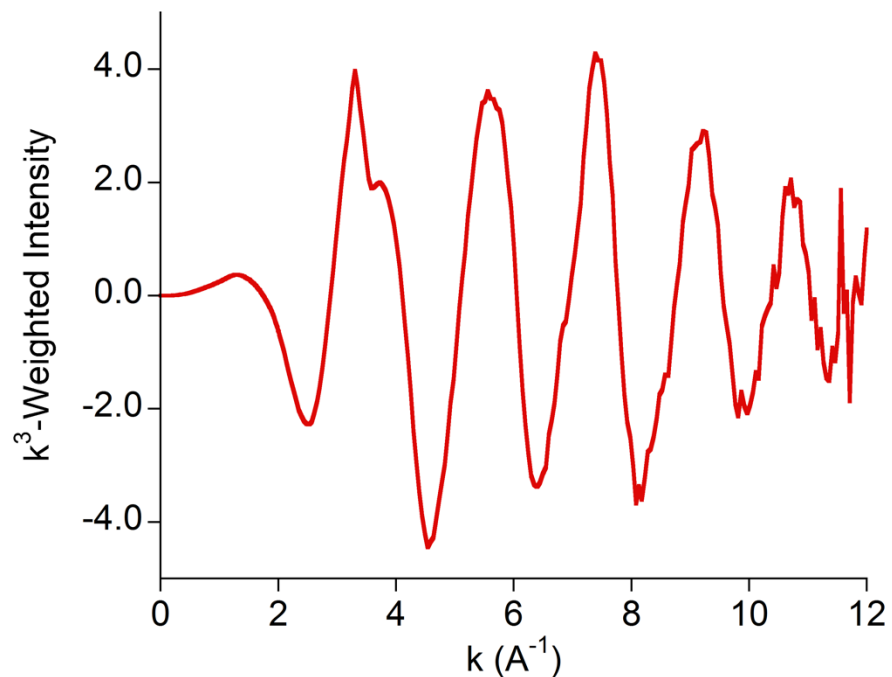
Fourier Transform



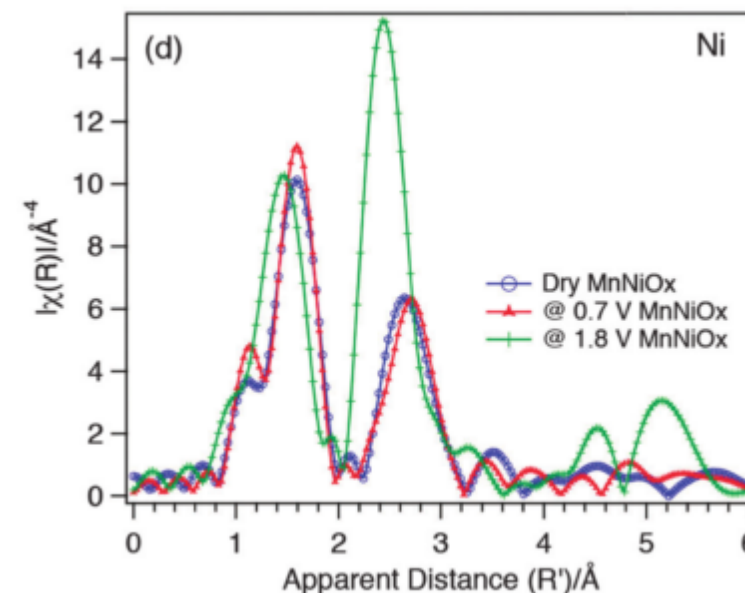
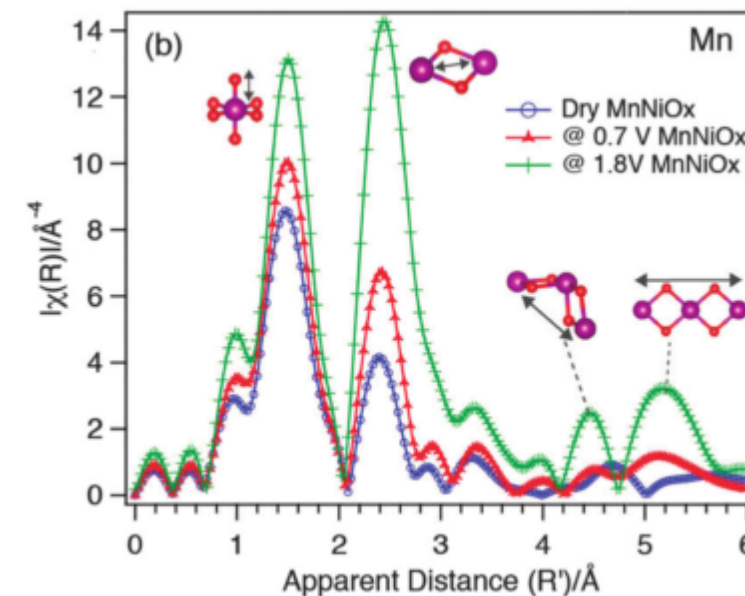
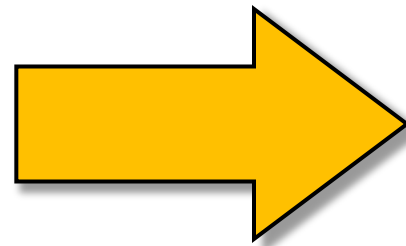
After some math, the EXAFS oscillations can be extracted

Hard to intuitively interpret

# Fourier Transformed EXAFS



Fourier Transform



After some math, the EXAFS oscillations can be extracted

Hard to intuitively interpret

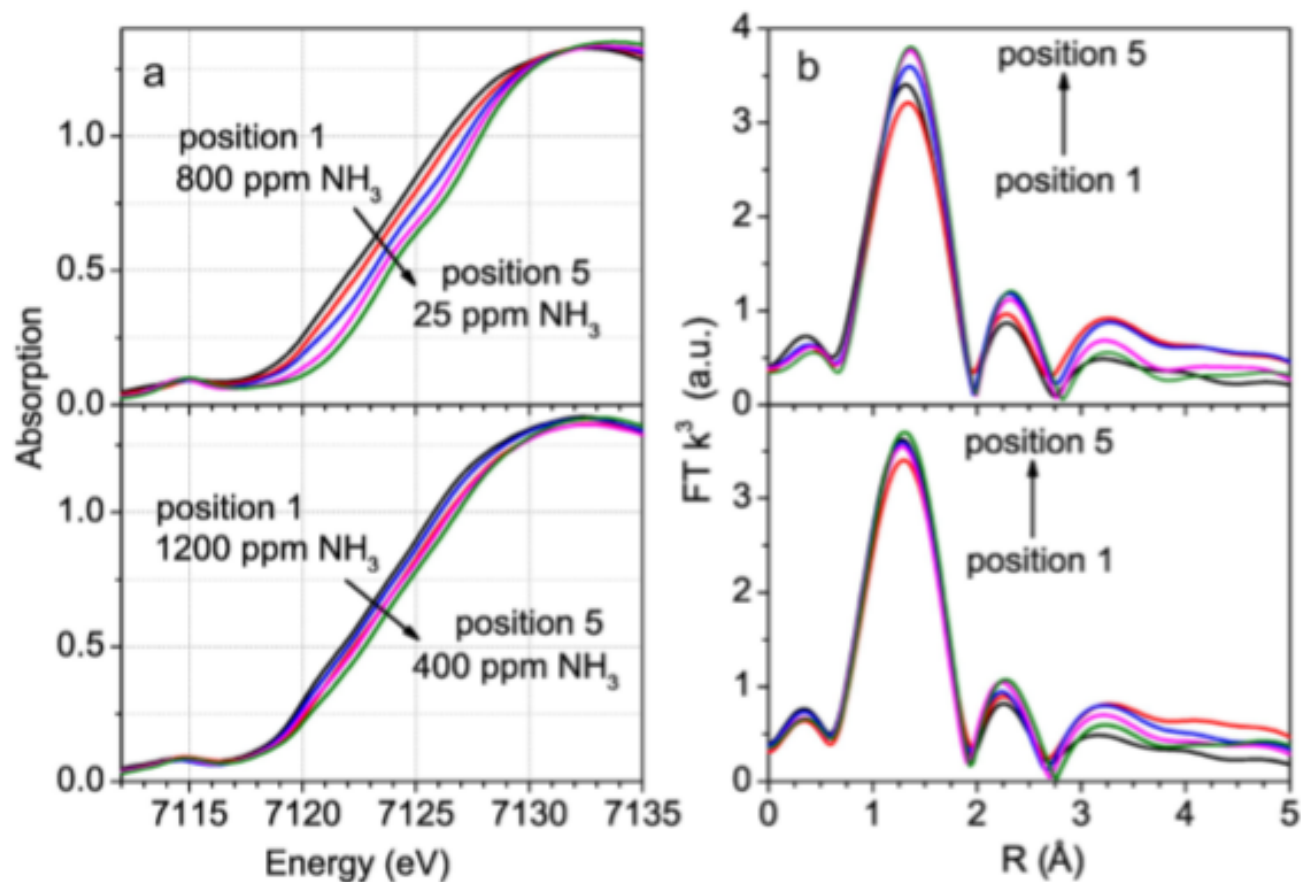
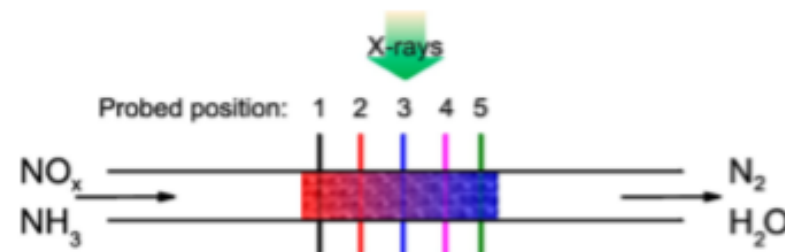


# Example EXAFS – Catalysis

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

Here, EXAFS, together with XANES, was used to monitor a solid state catalyst as it performed the  $\text{NO}_x$  reduction reaction

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



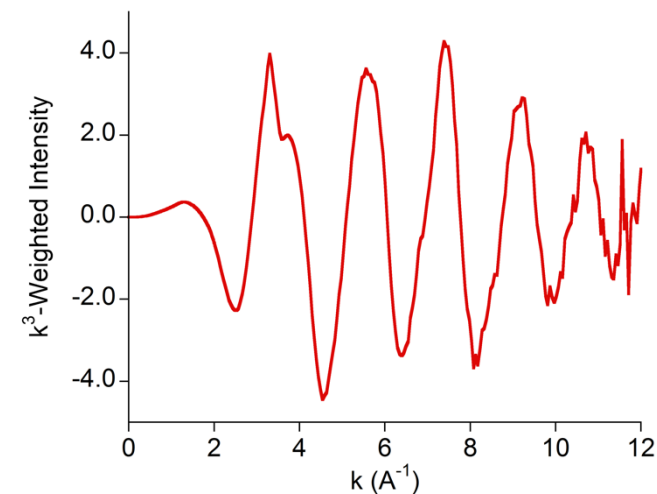
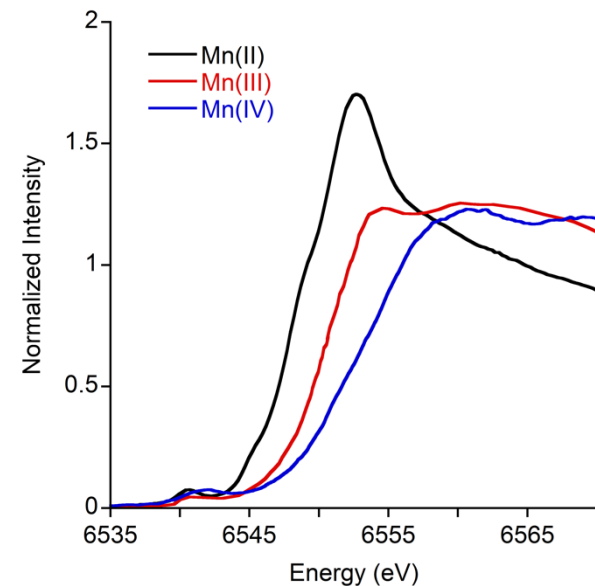
# XAS / EXAFS Cheat Sheet

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

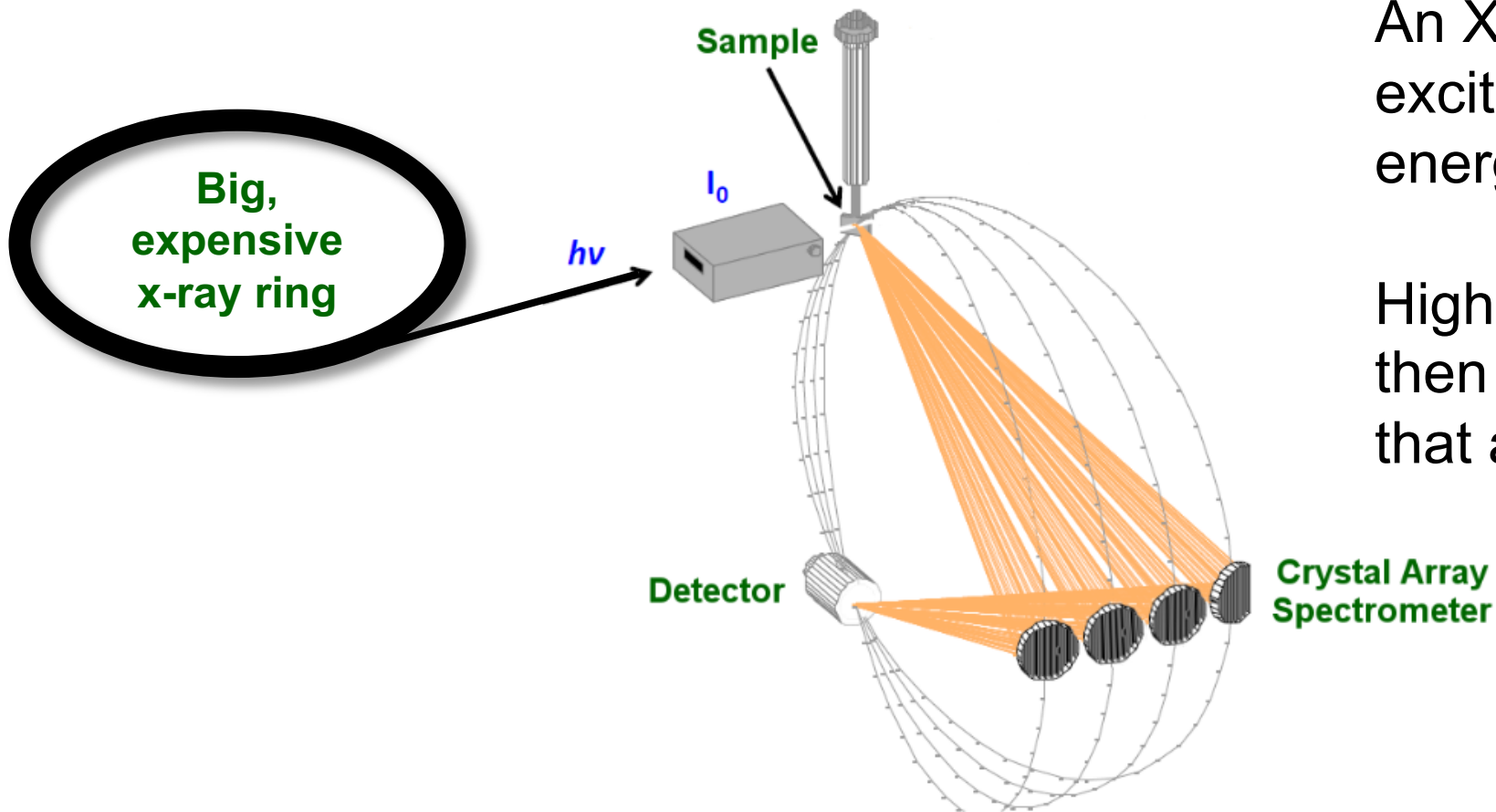


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# Part III: XES



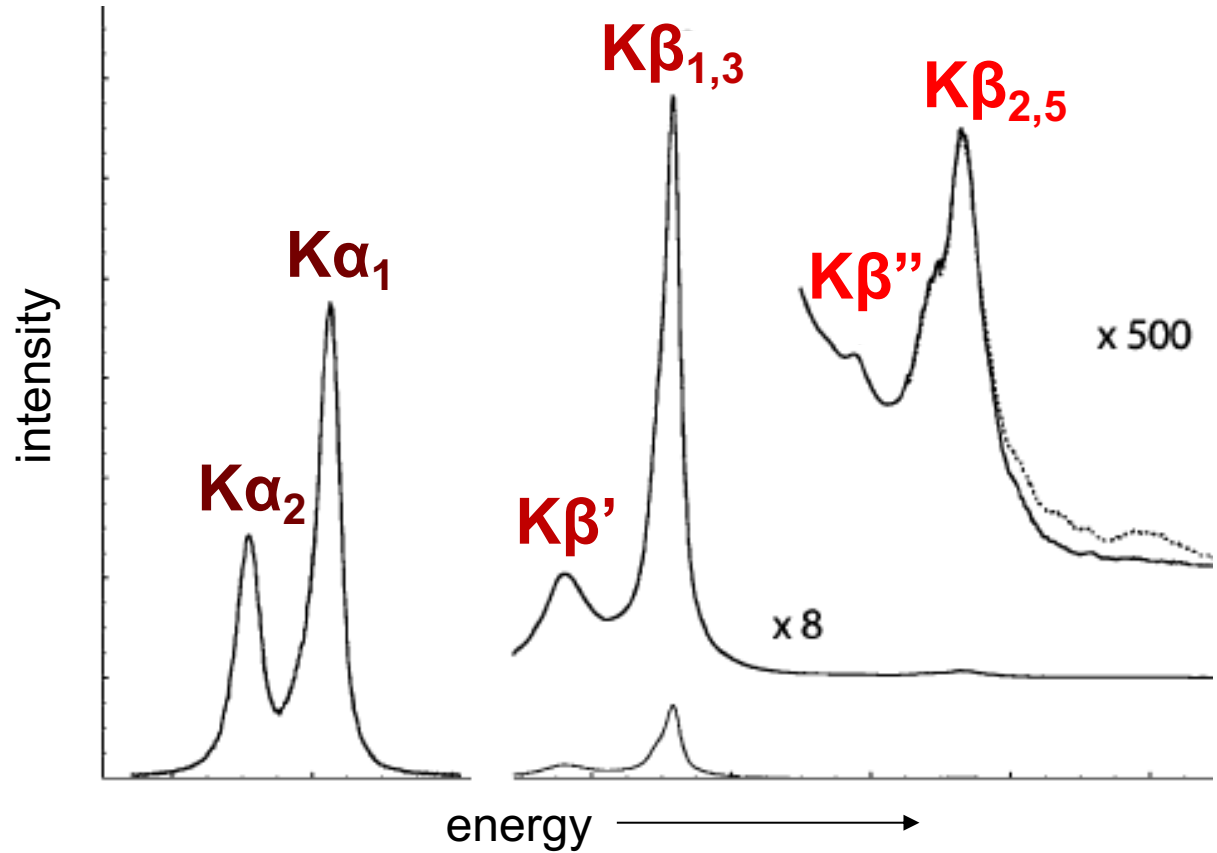
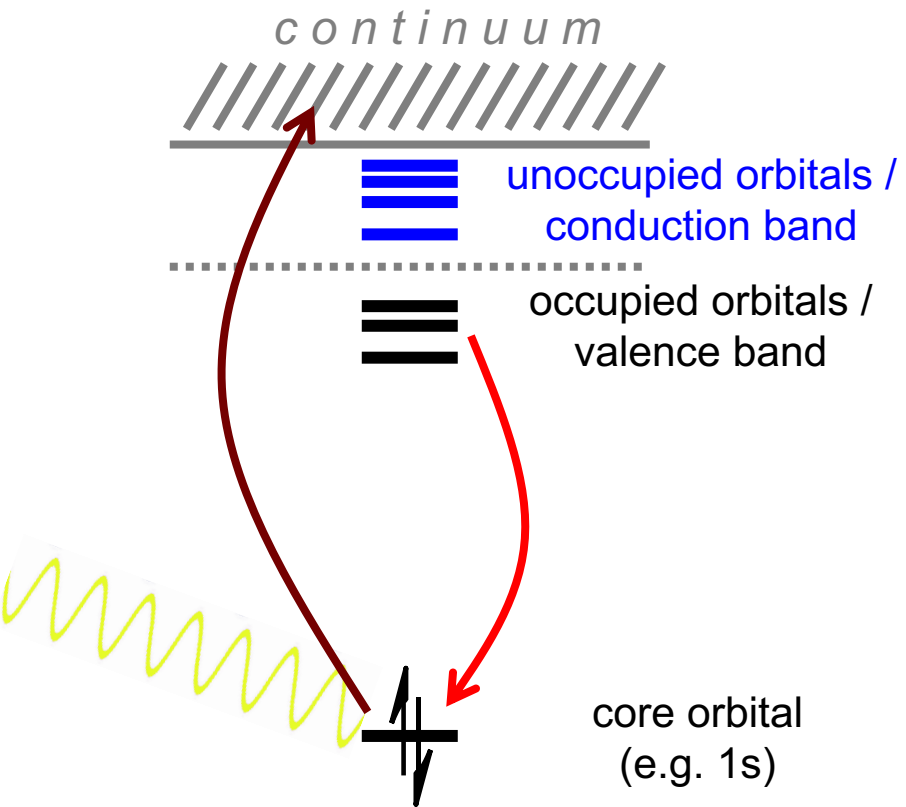
# XES Experimental Setup



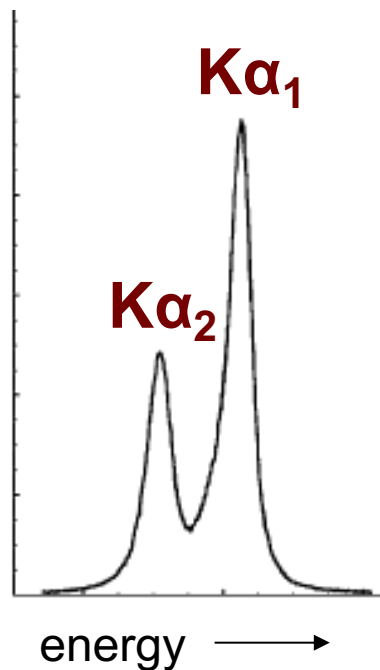
An XES experiment begins by exciting a sample with a high energy x-ray ( $\gg$  absorption edge)

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

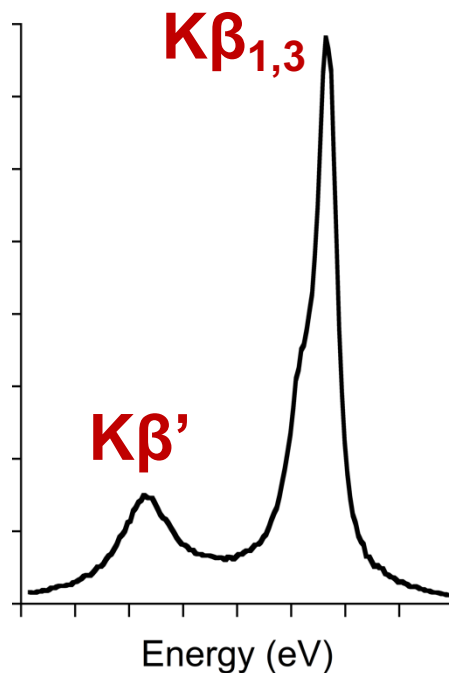
# X-ray Emission Spectroscopy (XES)



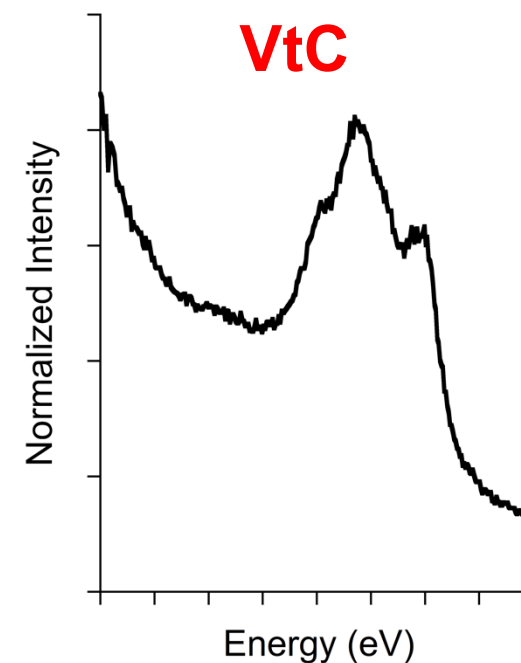
# X-ray Emission Transitions



$K\alpha$  XES are  $2p \rightarrow 1s$  transitions; they are intense but have limited chemical information



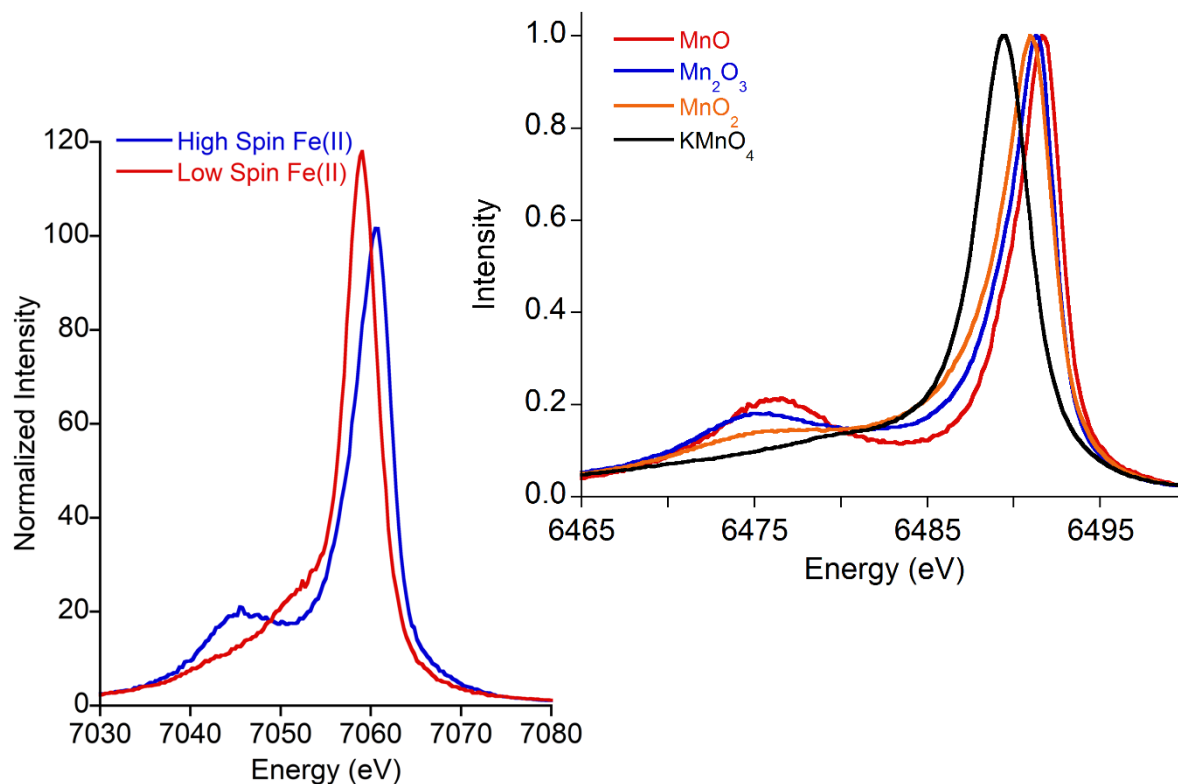
$K\beta$  XES are  $3p \rightarrow 1s$  transitions; they contain information about spin state and metal-ligand covalency



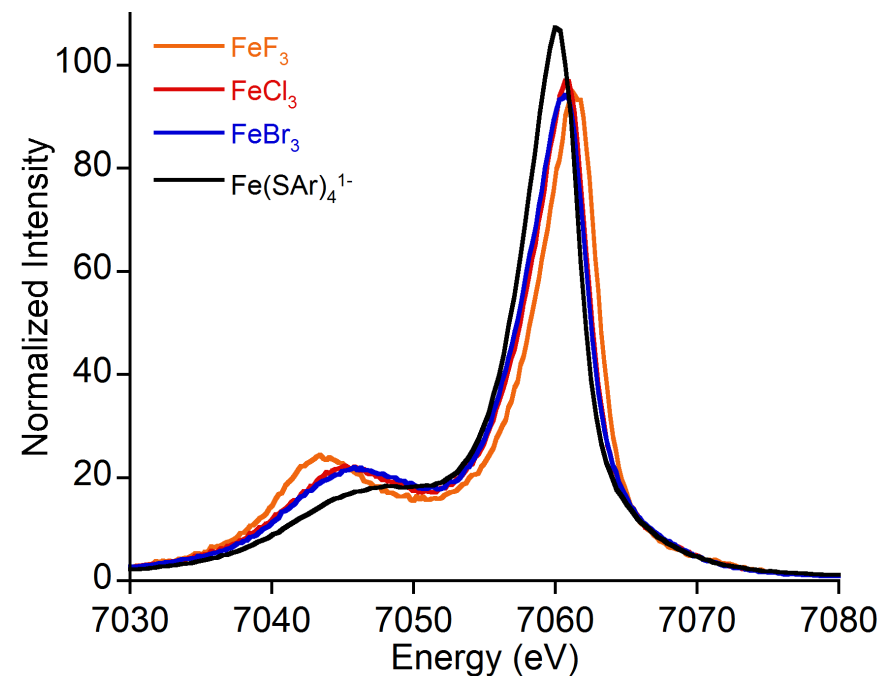
VtC XES are weak valence  $\rightarrow 1s$  transitions that directly probe the ligand electronic structure

# K $\beta$ Mainline XES

K $\beta$  mainlines are primarily sensitive to the spin state of the emitting atom



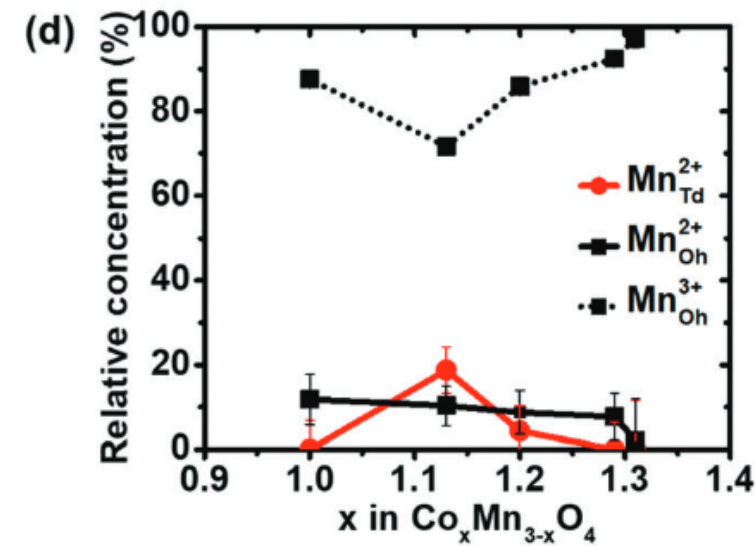
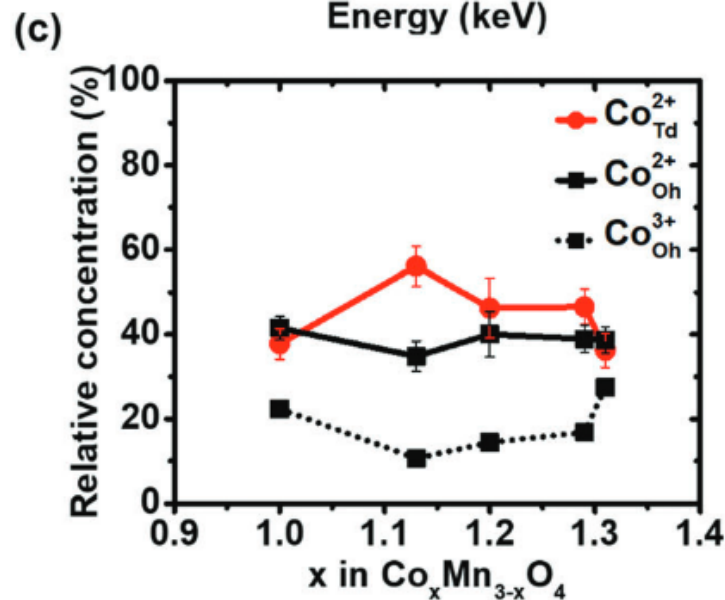
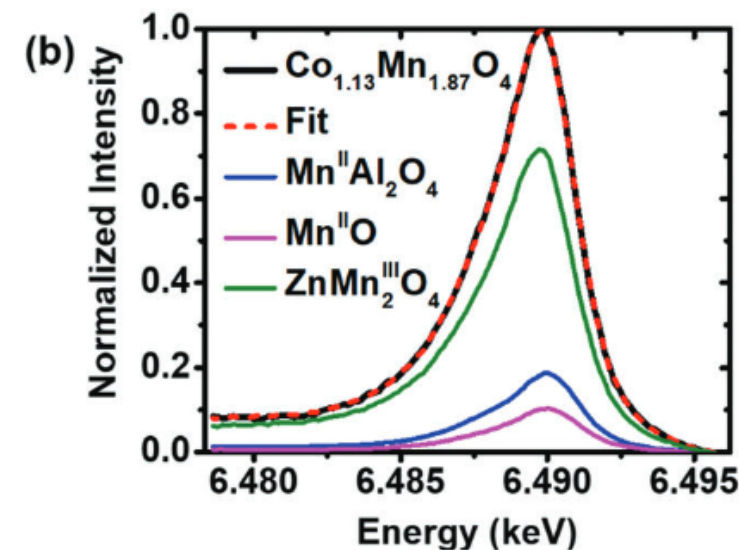
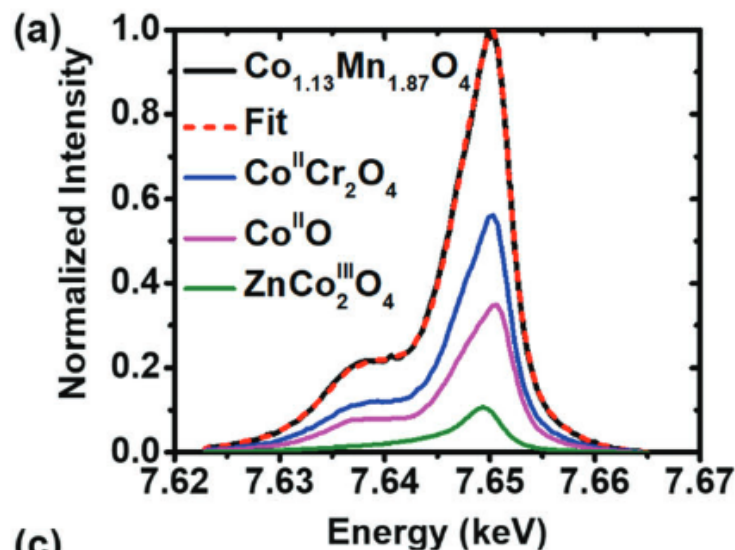
Additionally, these spectra are also affected by the covalency of the bonds between the emitting atom and its ligands



# K $\beta$ Mainline XES – Oxidation State Sensitivity

The sensitivity of K $\beta$  mainlines to metal oxidation state can be exploited to quantify mixtures with varying oxidation state

In this study, the compositions of Co/Mn oxide nanoparticles were determined using K $\beta$  mainlines



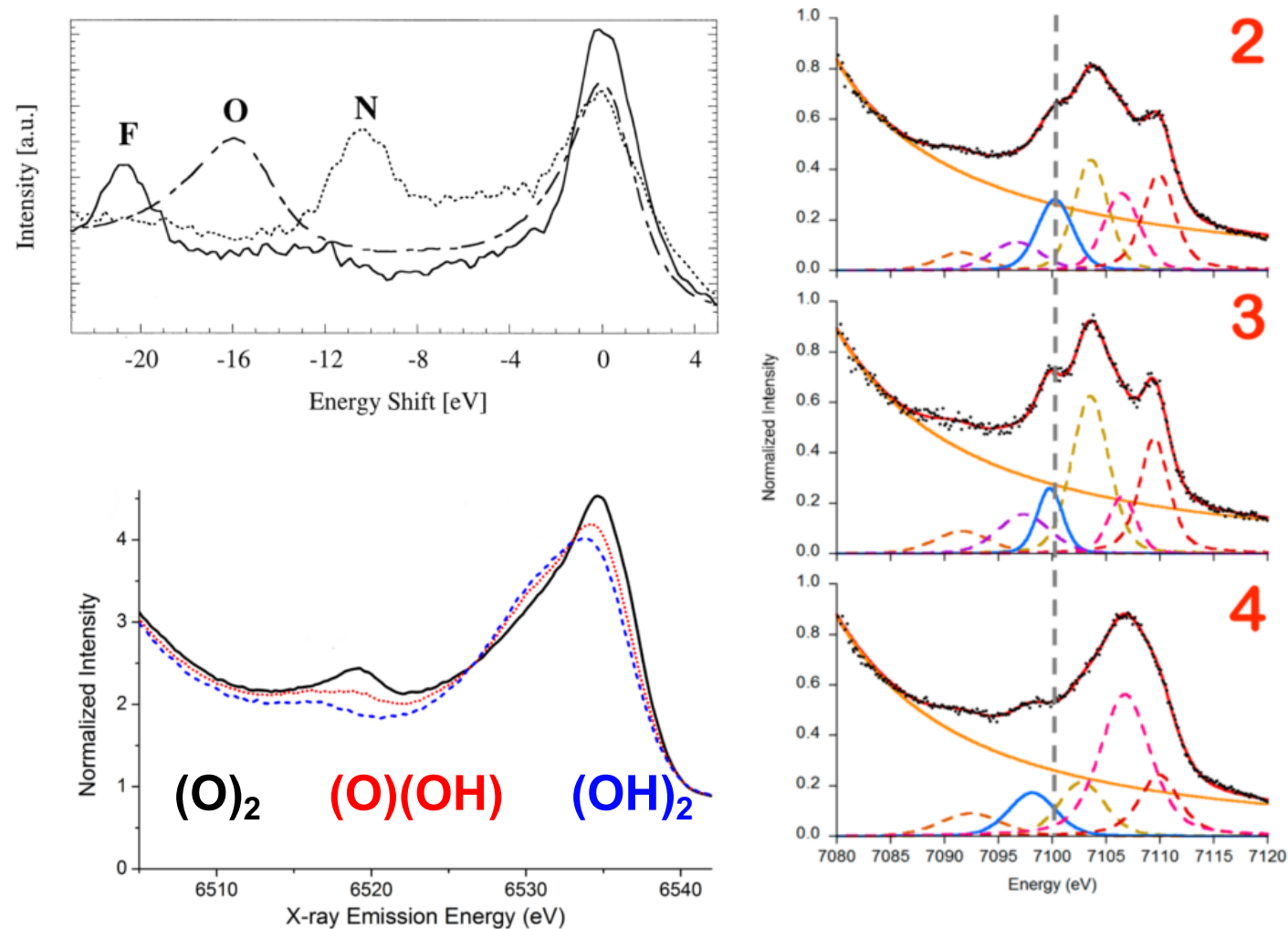


# Valence-to-Core (VtC) XES

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

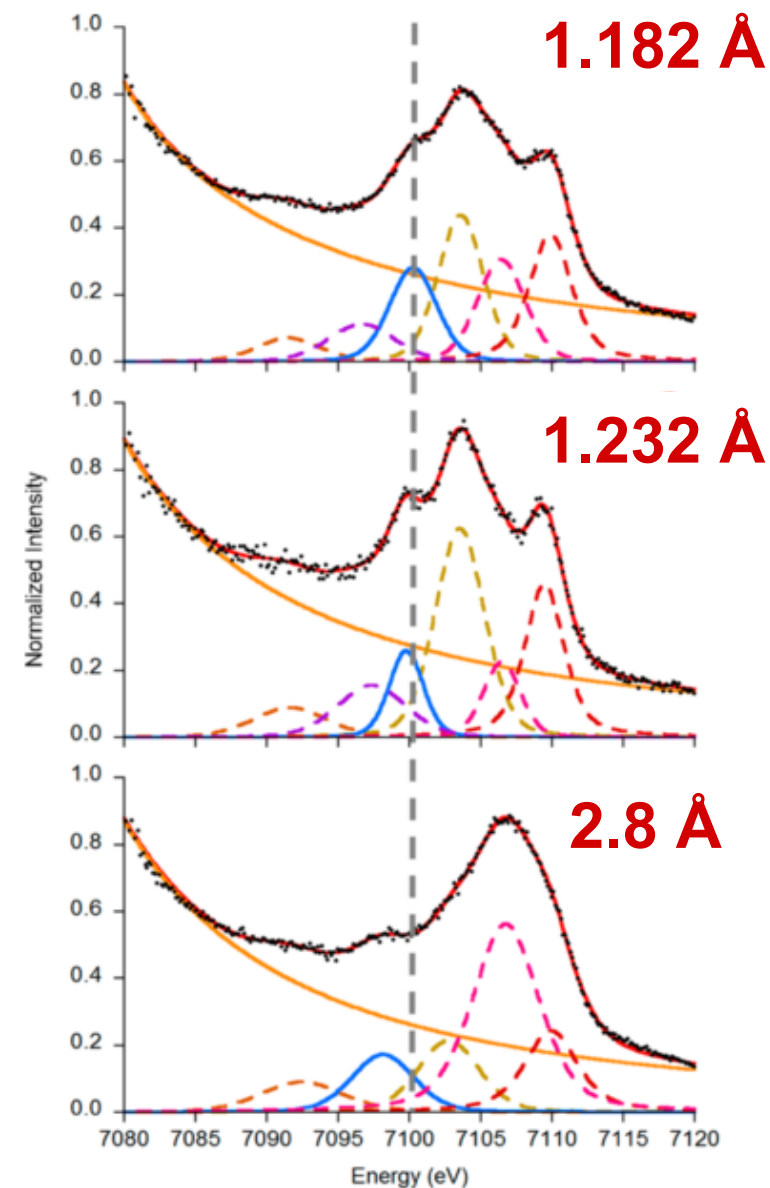
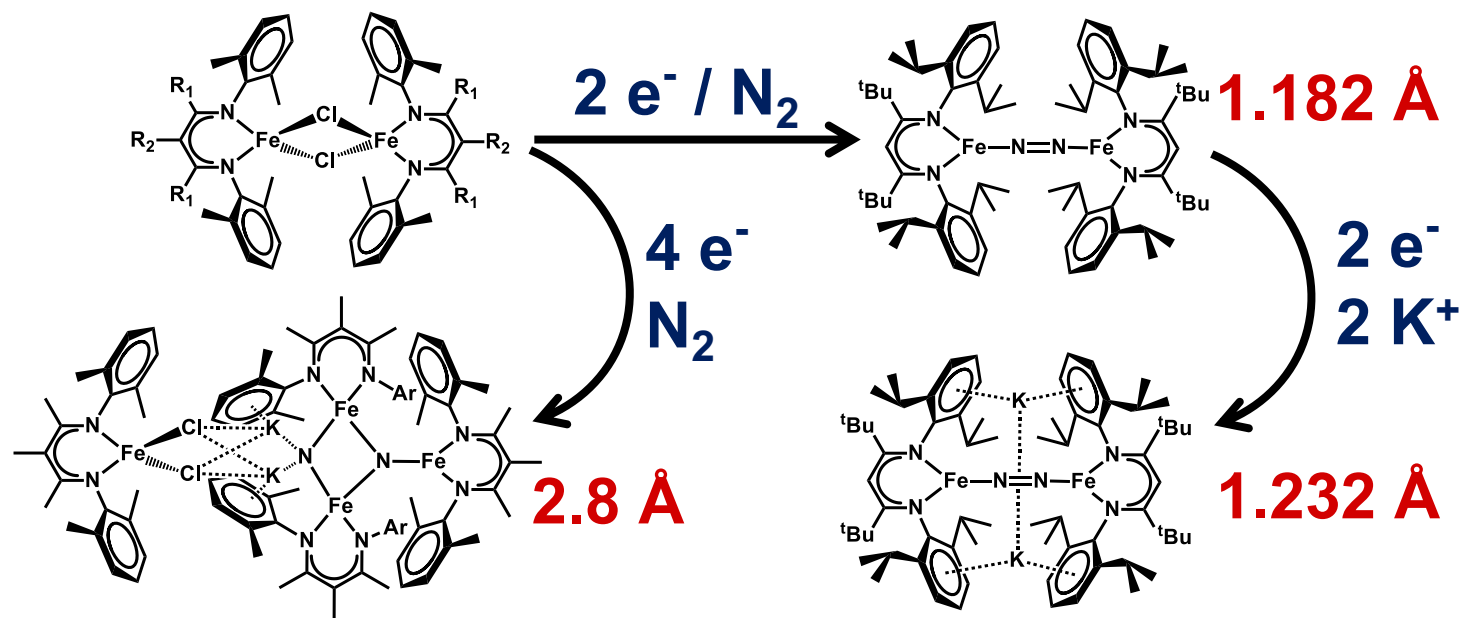


# N-N Bond Activation

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



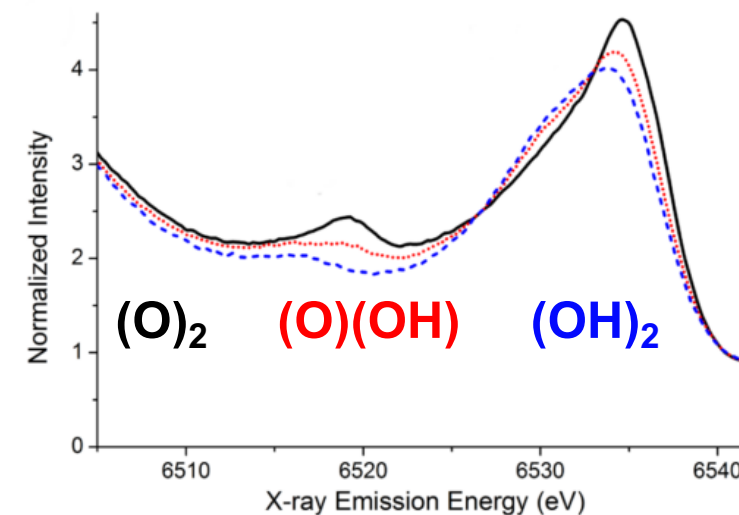
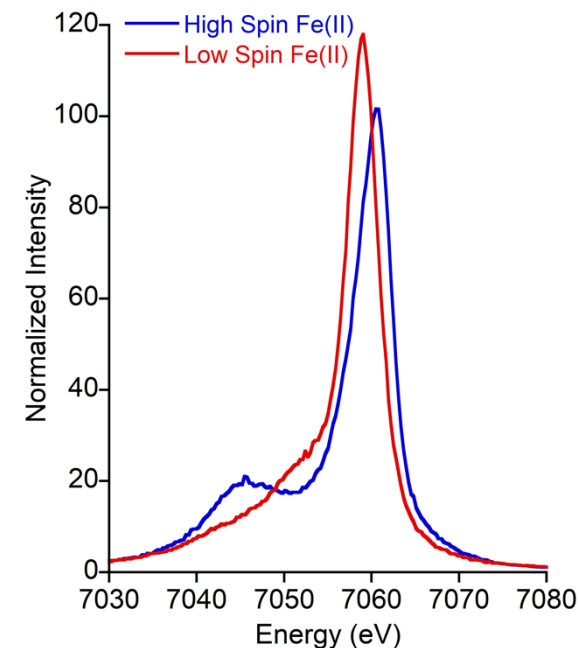
# XES Cheat Sheet

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

K $\alpha$  lines are intense but have **limited chemical information**

K $\beta$  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**

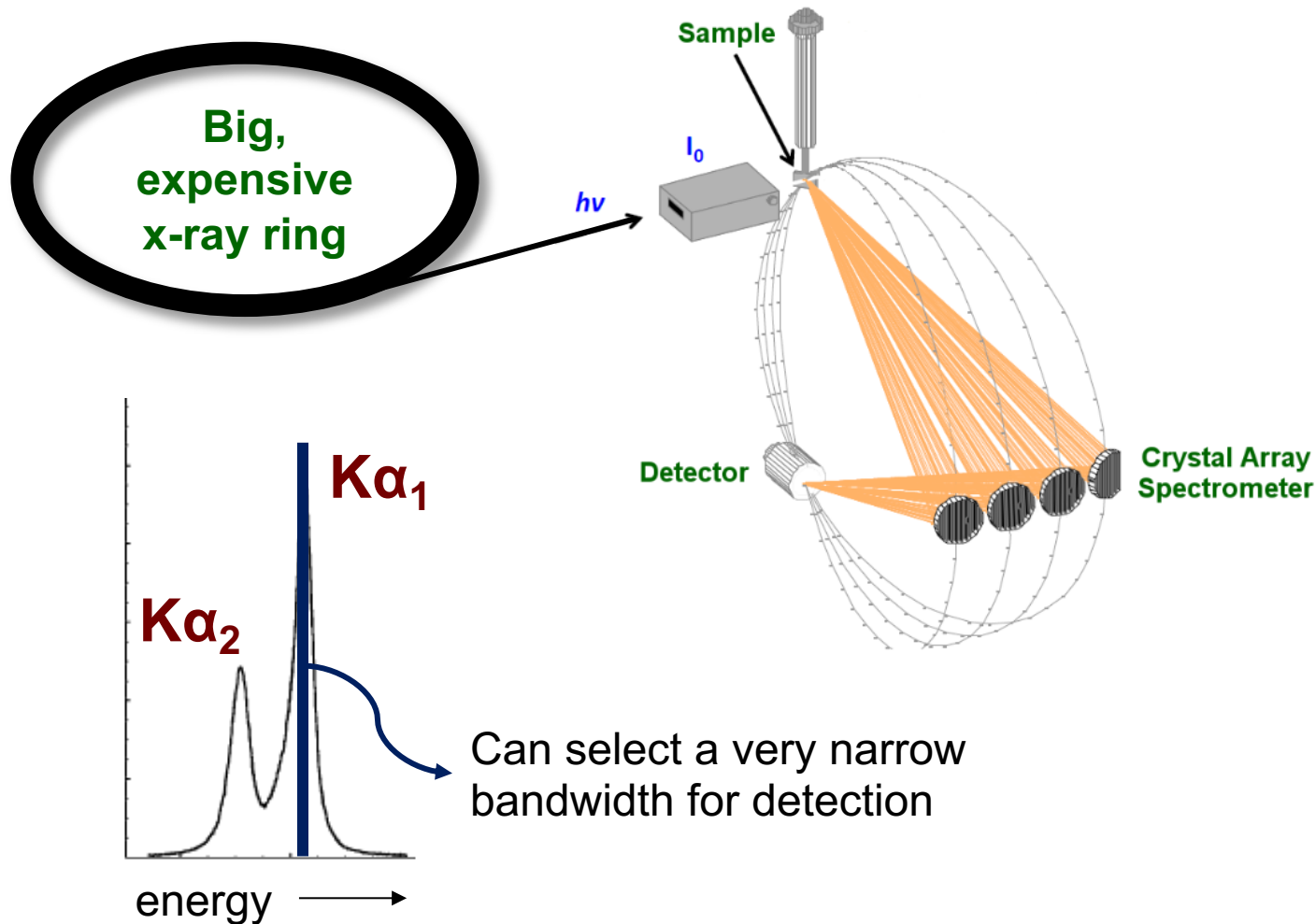


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# Part IV: HERFD



# High Energy Resolution Fluorescence Detected (HERFD) XAS

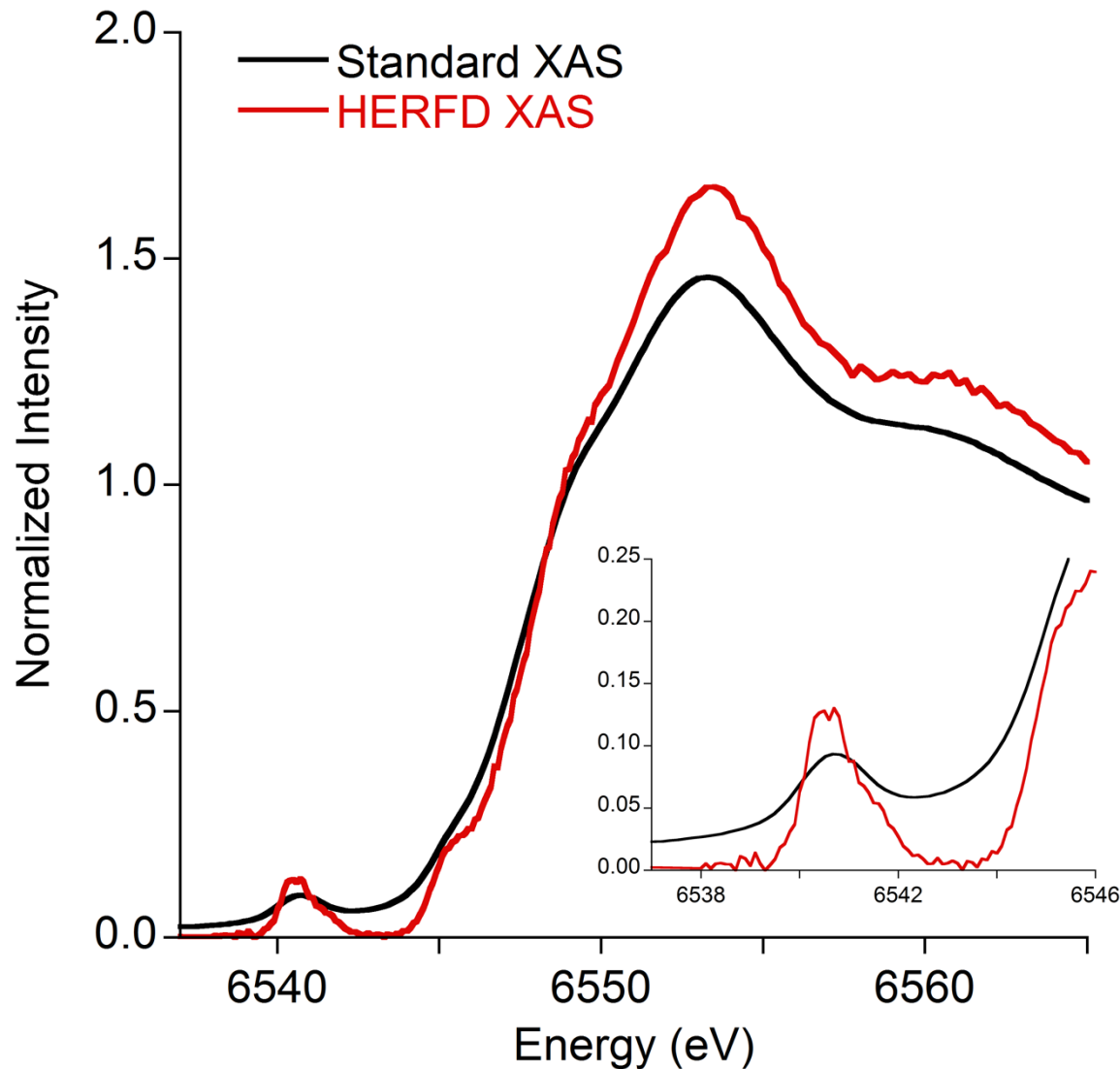


HERFD XAS is fluorescence-detected XAS with a twist— instead of using a solid state detector, a high resolution crystal spectrometer is used

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

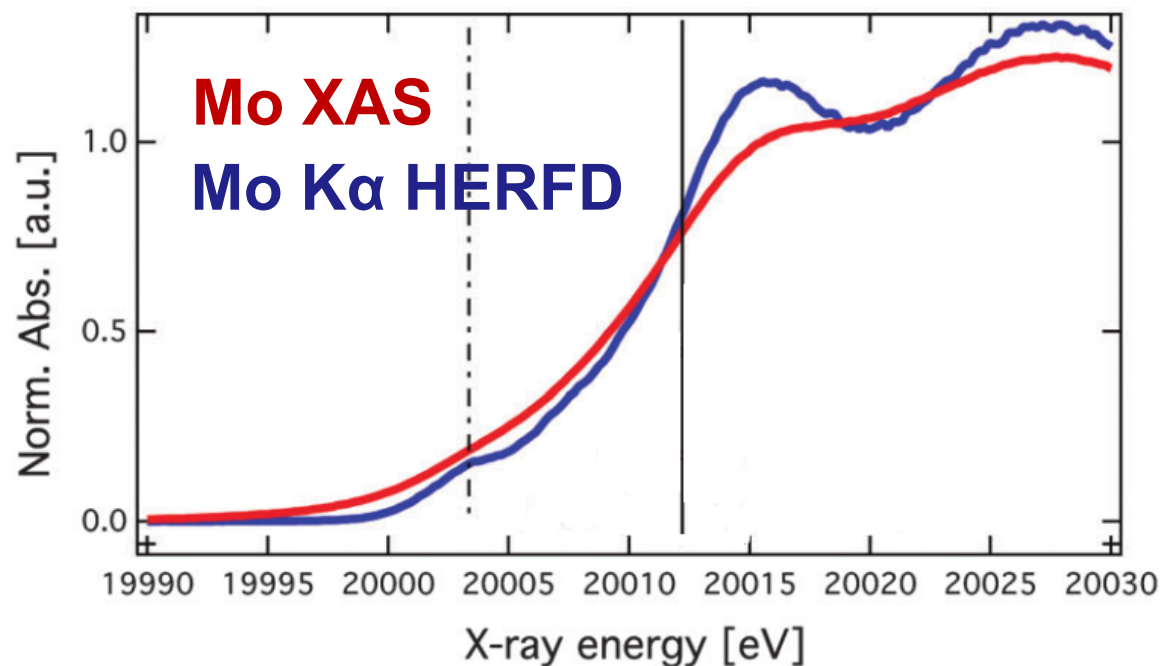
- Also lower signal!

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

# Improved Resolution for Heavy Atoms

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

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

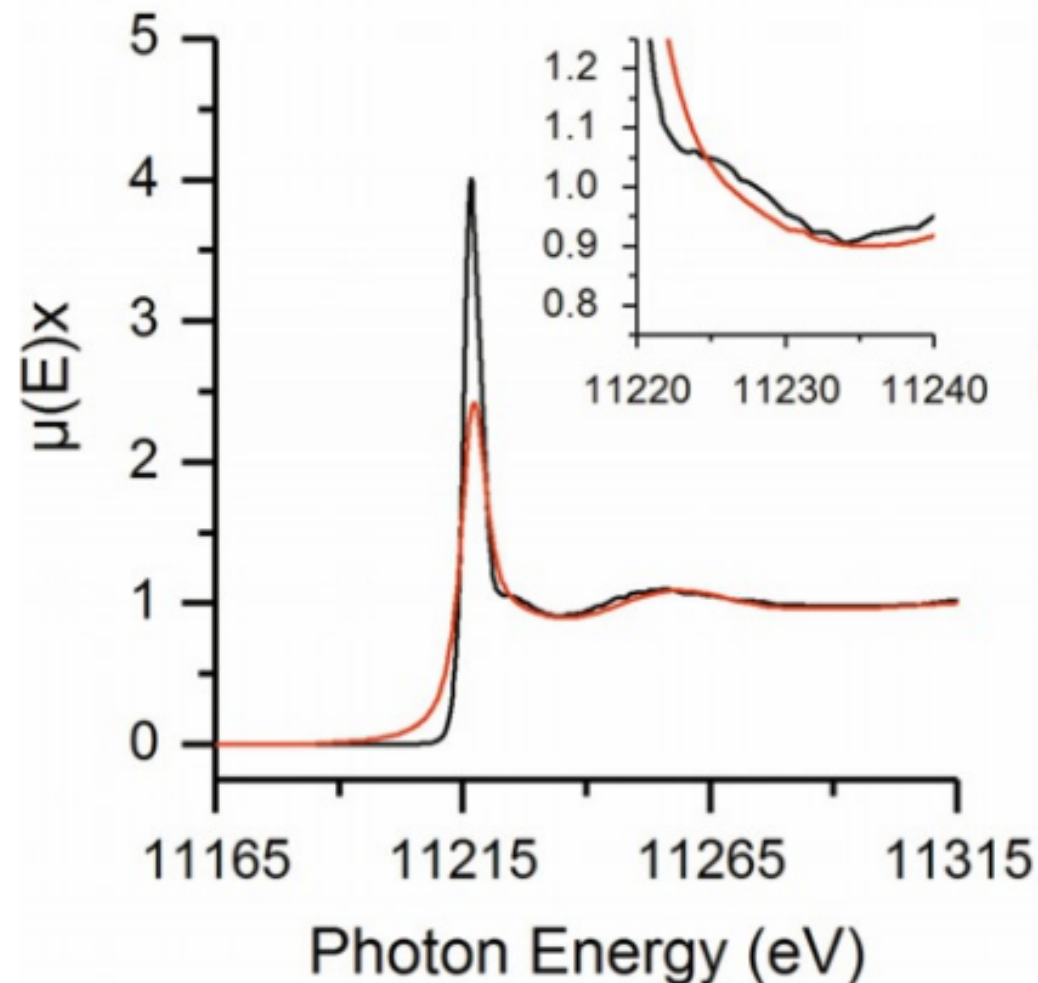
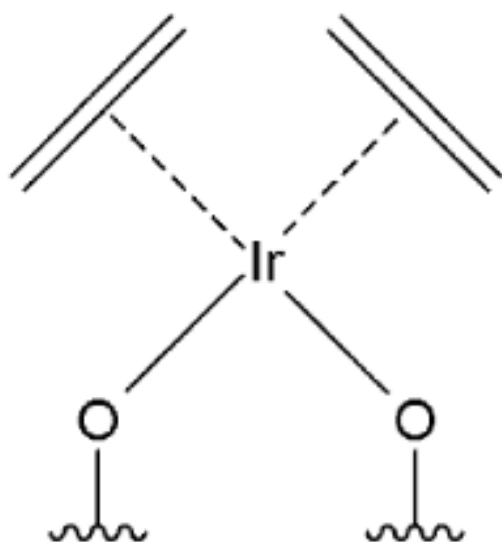


Increased resolution of the HERFD measurements allows additional information to be extracted from the XAS spectra

# Improved Resolution for Heavy Atoms

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

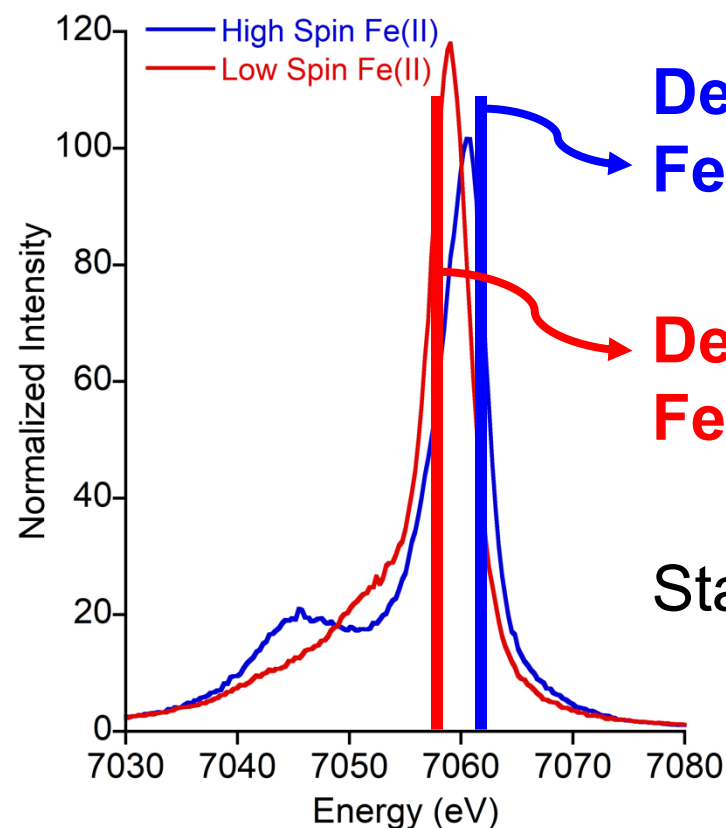
Similarly, for an Ir catalyst, features appear in the HERFD XAS spectra that are invisible in the conventional XAS experiment





# 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**

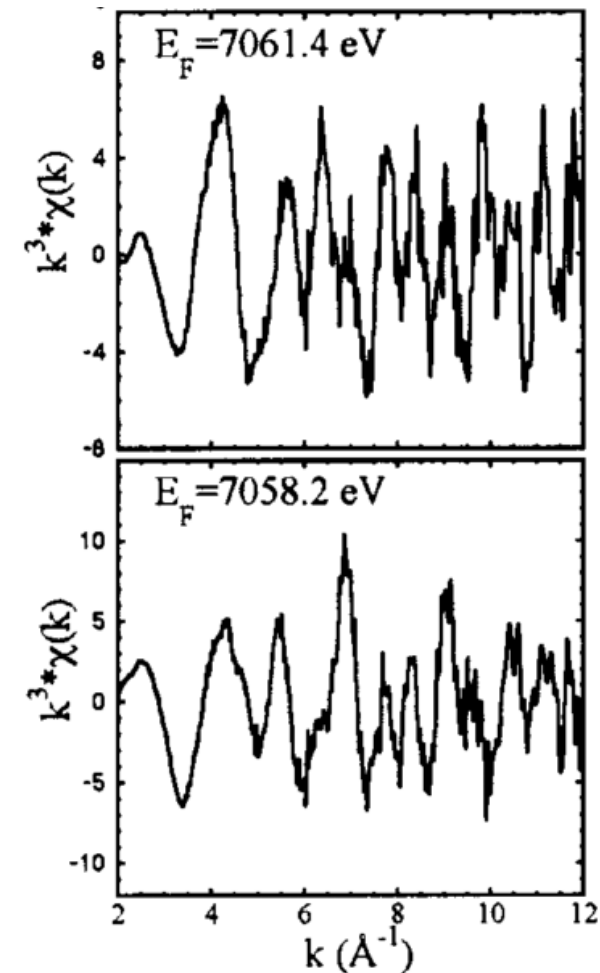
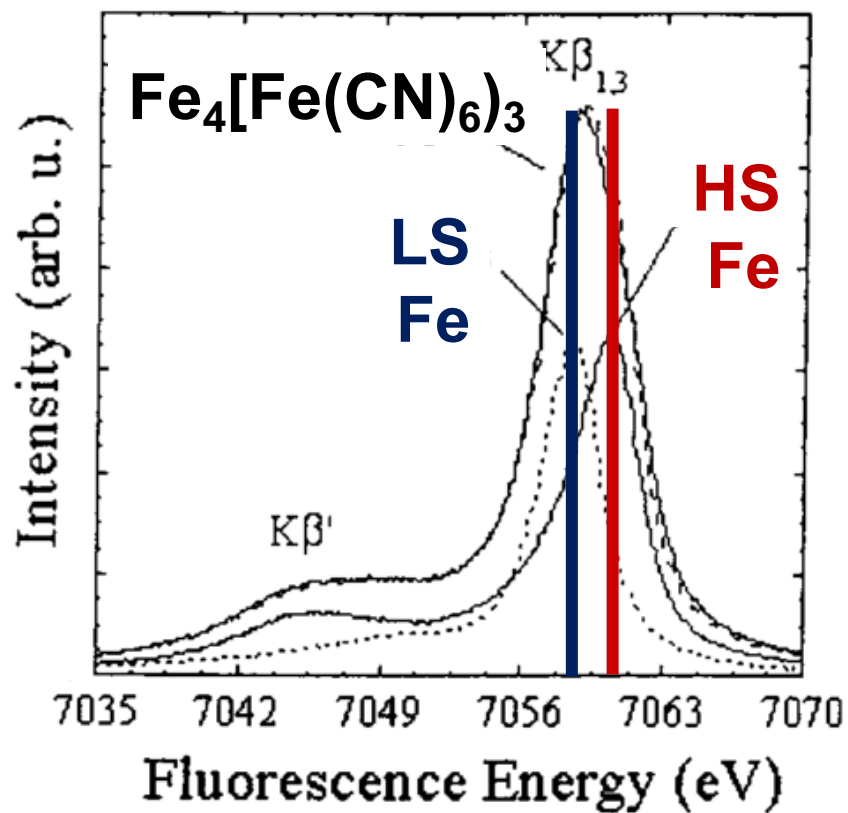
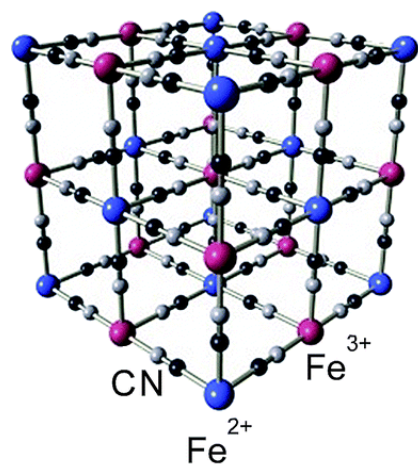
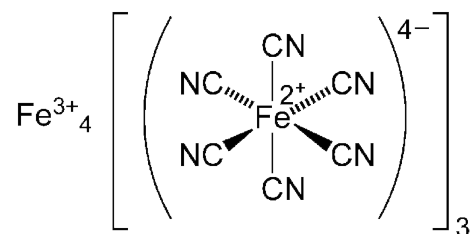
Standard XAS would only see an average of both species!

# 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)

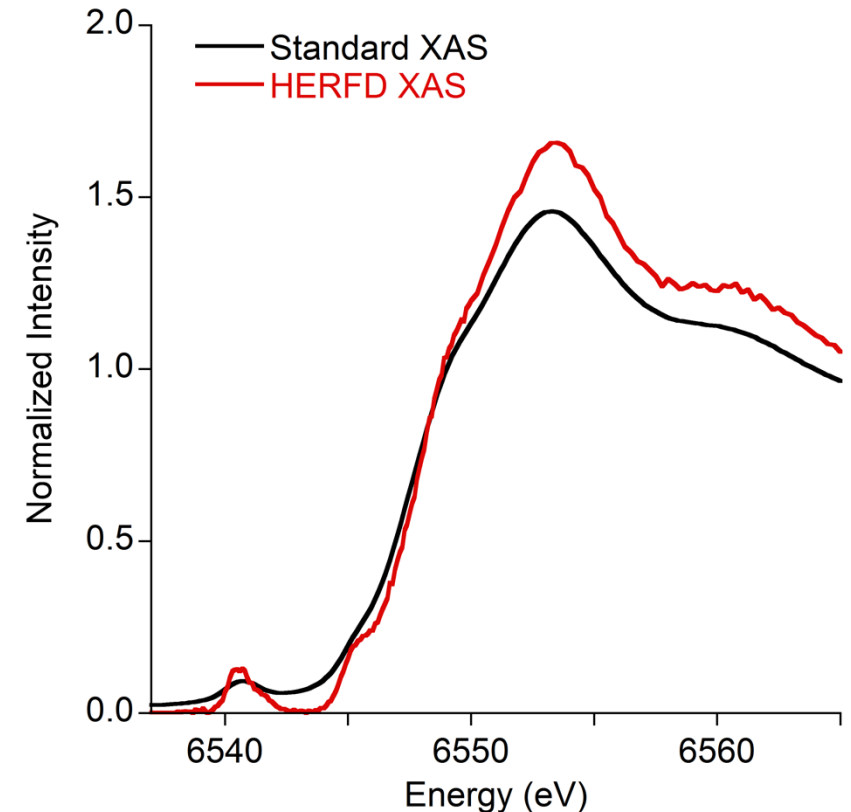


# HERFD XAS Cheat Sheet

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



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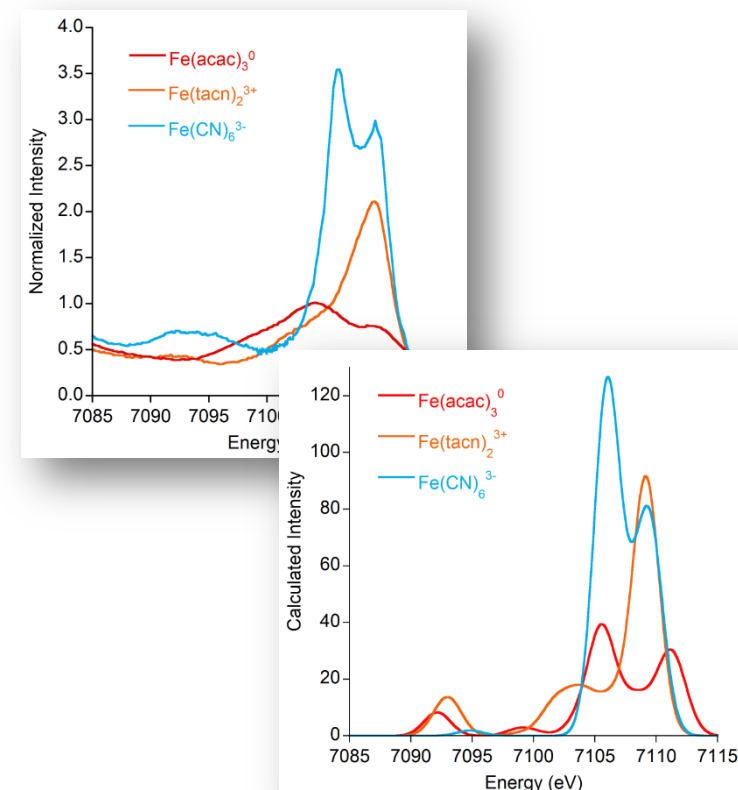
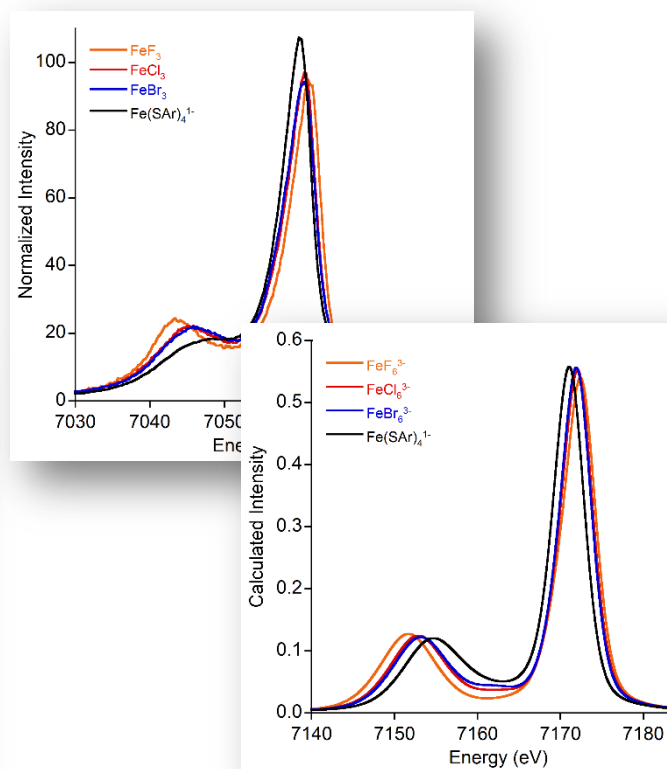
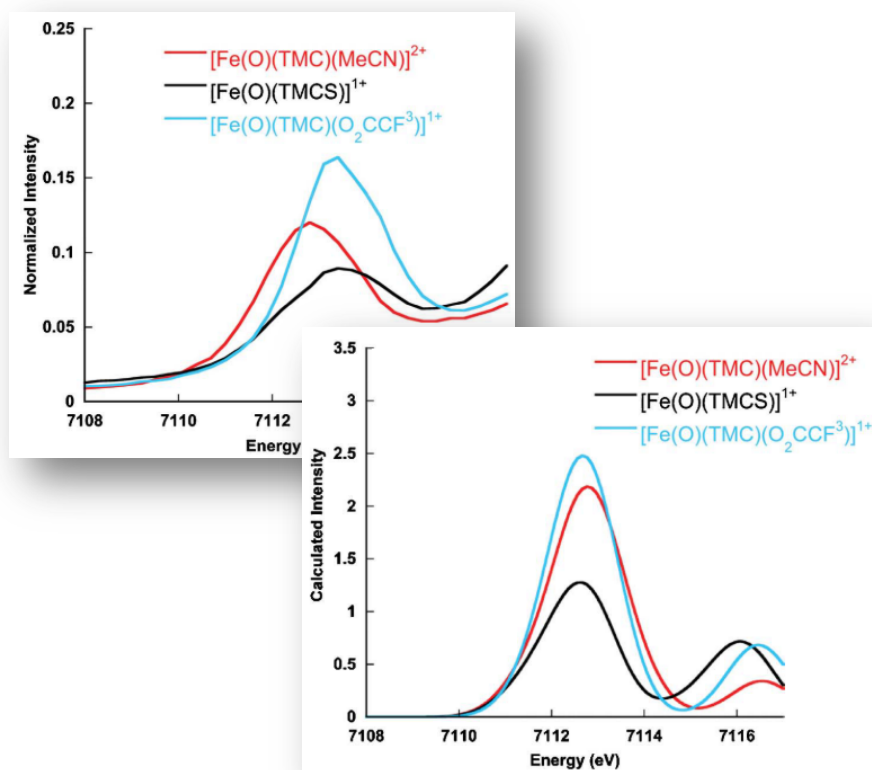
# Part V: Calculations



# Help from DFT

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

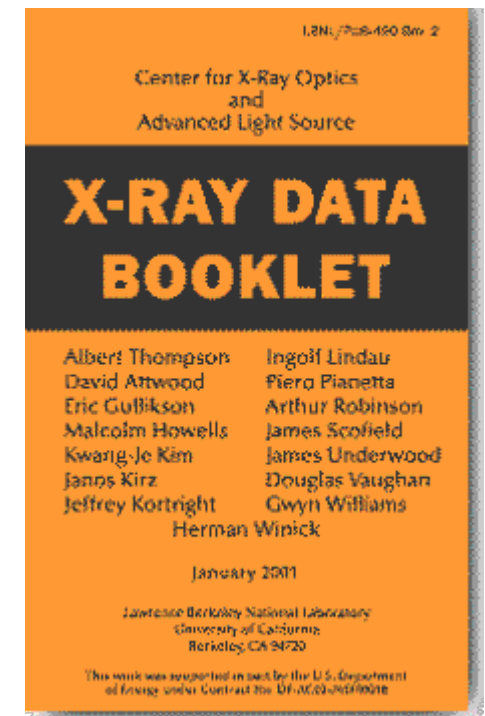
Calculations can help with analysis and interpretation of x-ray spectra



# 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



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# Questions?

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



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