

Introduction to X-ray Spectroscopy

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Max Planck Institute for Chemical Energy Conversion



Bioinorganic Chemistry Workshop, June 1-8, 2018

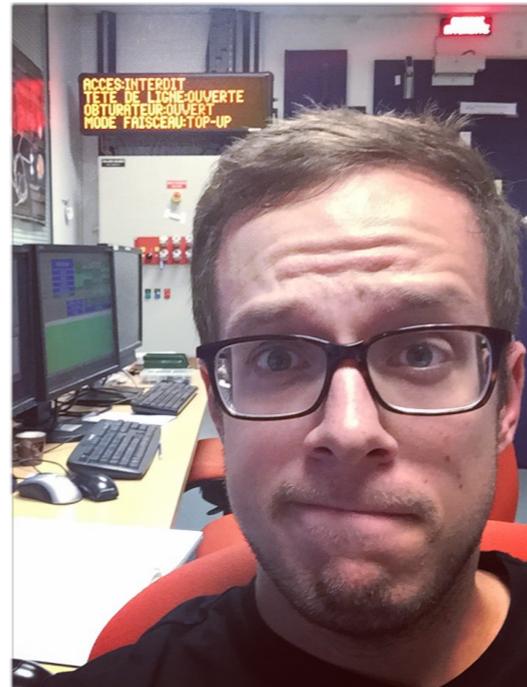
Thank you - X-ray Spectroscopy Tutors!



Rebeca Gomez Castillo



Ben van Kuiken



George Cutsail

Demeter



X-ray Absorption
Spectroscopy Using
Feff + Larch or Ifeffit.

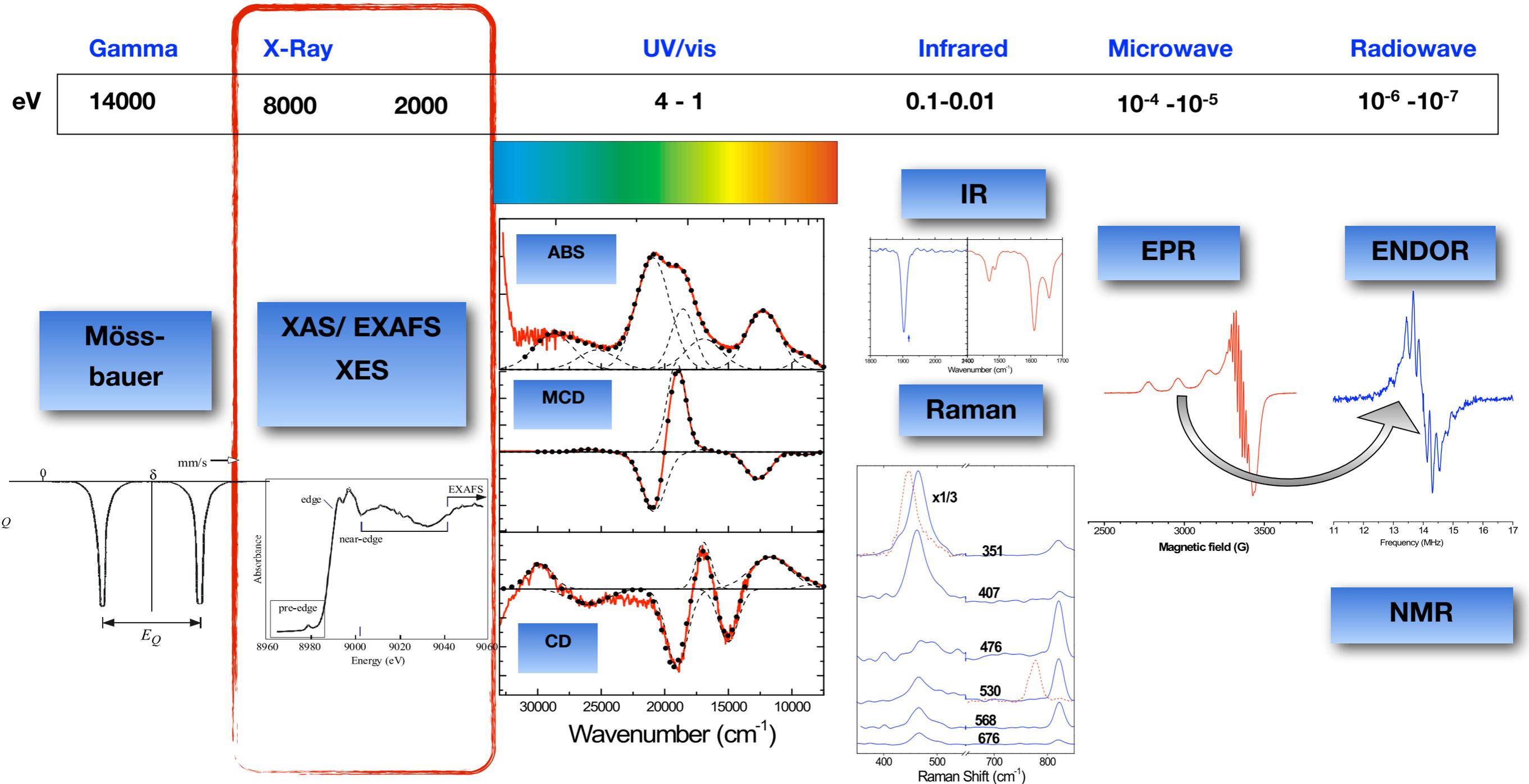
- Please install Demeter prior to the X-ray spectroscopy tutorials!
- For help with MAC installations see instruction on dropbox and/or talk to Casey!



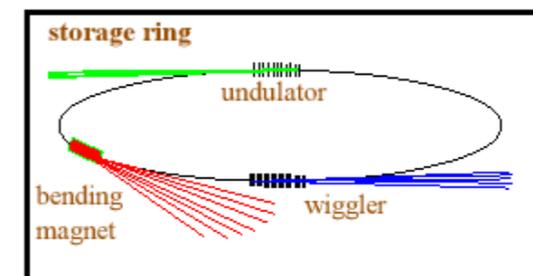
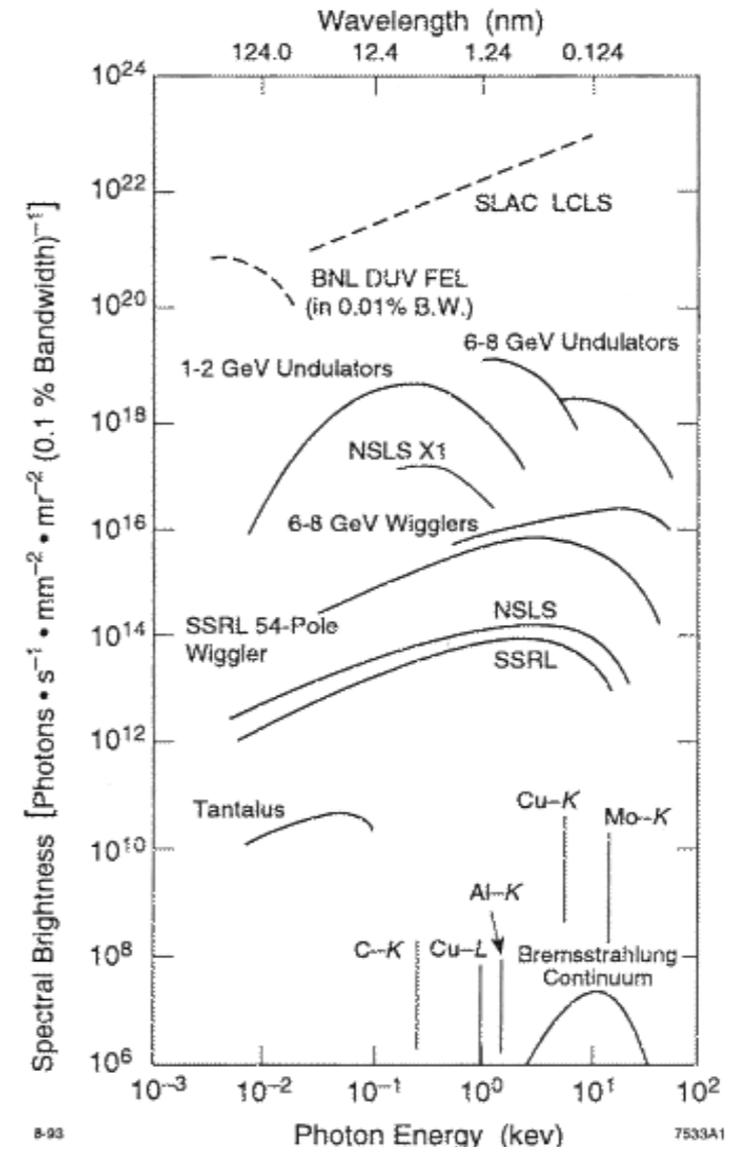
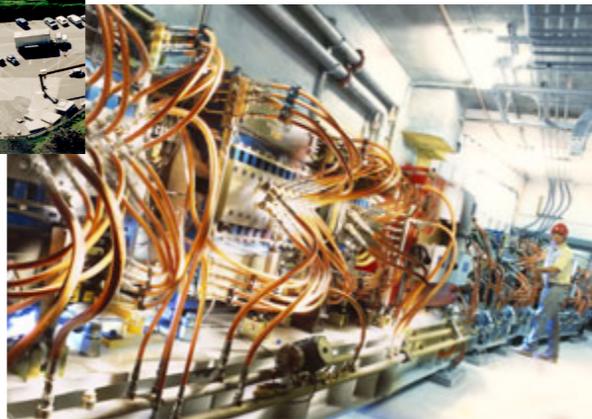
Casey van Stappen

What is x-ray spectroscopy?

the interaction between radiated energy and matter...



Intense X-ray Sources



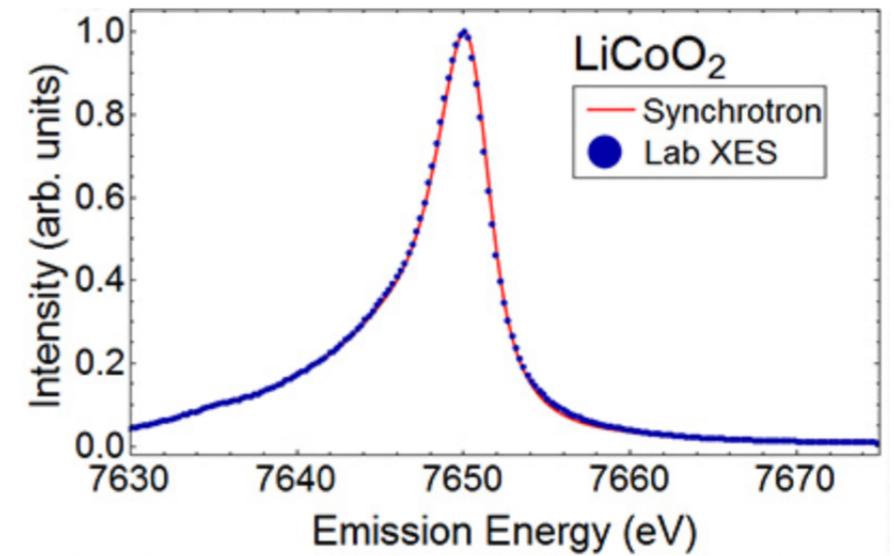
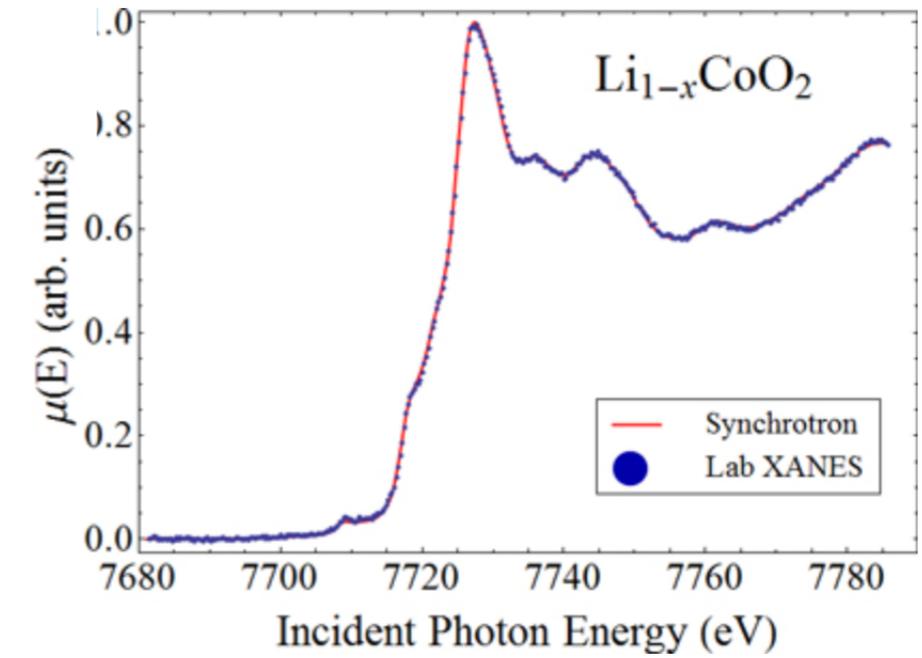
Synchrotron Sources



Key / Légende	
	Operational 3rd generation synchrotron Synchrotron de 3ème génération opérationnel
	3rd generation synchrotron under construction Synchrotron de 3ème génération en construction
	Operational 2nd generation synchrotron Synchrotron de 2ème génération opérationnel
	Proposed new synchrotron Nouveau synchrotron proposé



easyXAFS



XAFS every day in every lab.
Globally.

Outline

- **X-ray Absorption Spectroscopy (XAS)**

- 1. XAS Edge OR XANES (X-ray absorption near edge) region**

- ▶ basic definitions
 - ▶ experiment
 - ▶ information content
 - ▶ analysis - qualitative and quantitative

- 2. EXAFS**

- ▶ basic definitions
 - ▶ experiment
 - ▶ information content

Basics of X-ray Absorption Spectroscopy (XAS)

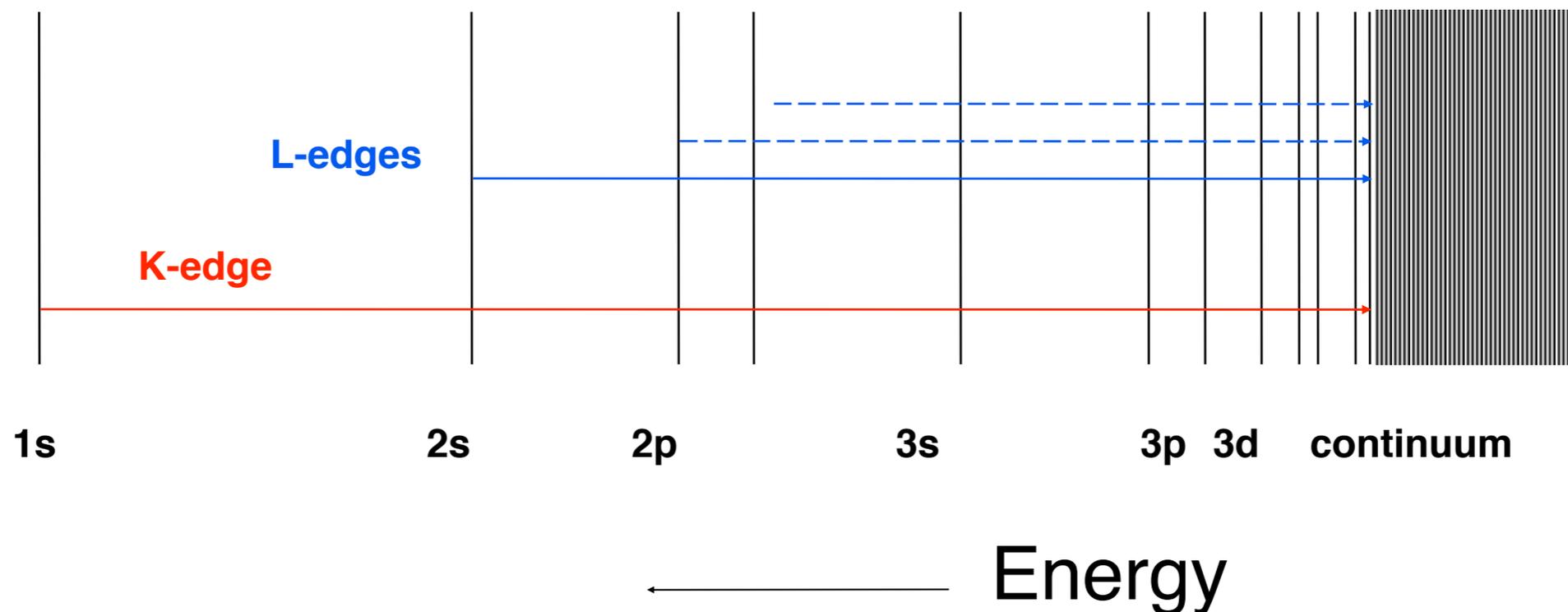
An edge results when a core electron absorbs energy equal to or greater than its binding energy.

Edges are labeled according to the shell the core electron originates from.

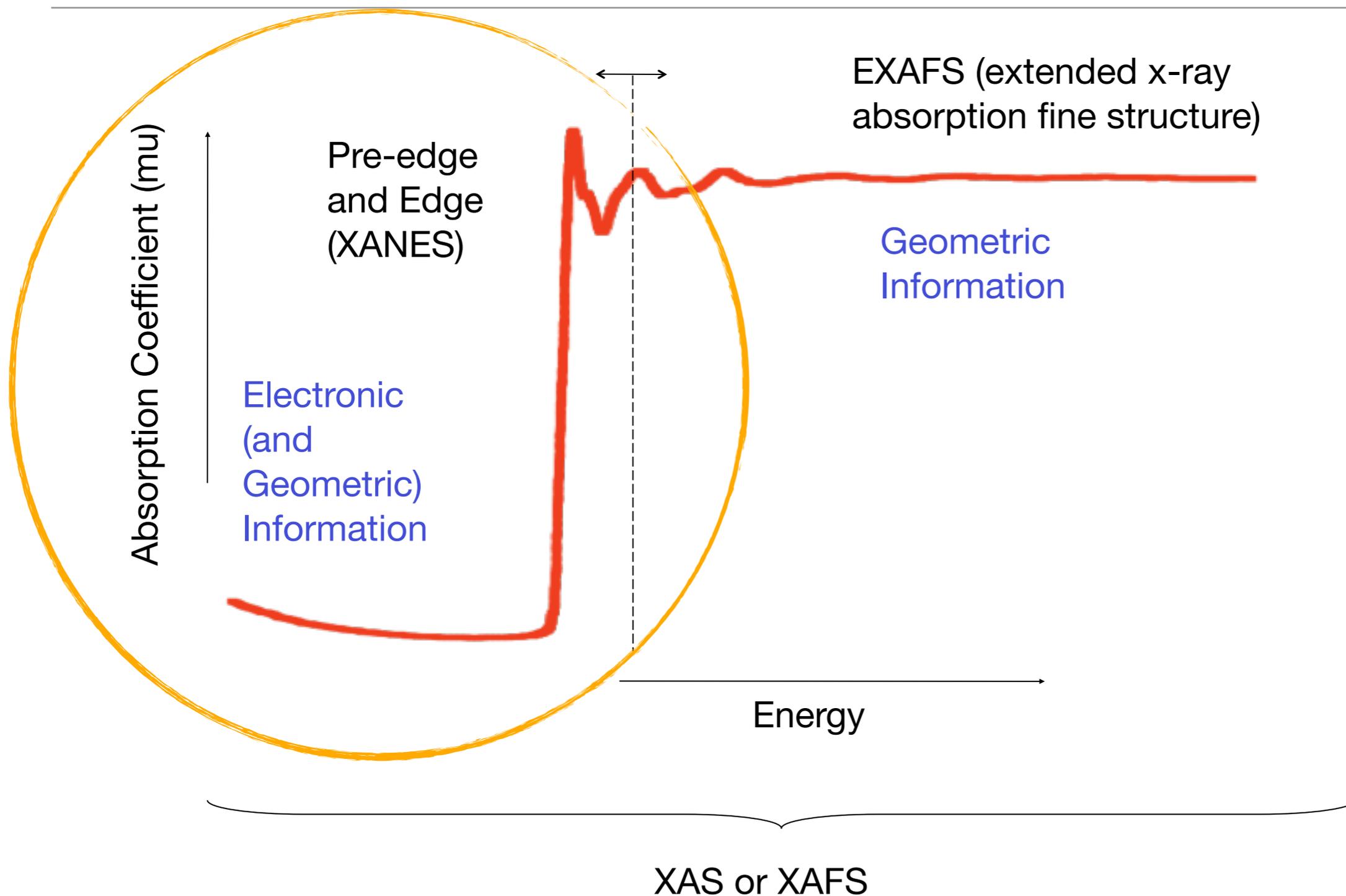
XAS is an element specific technique.

Cu K-edge ~9000 eV
Cu L-edges ~930 eV
Cu M-edges ~70-120 eV

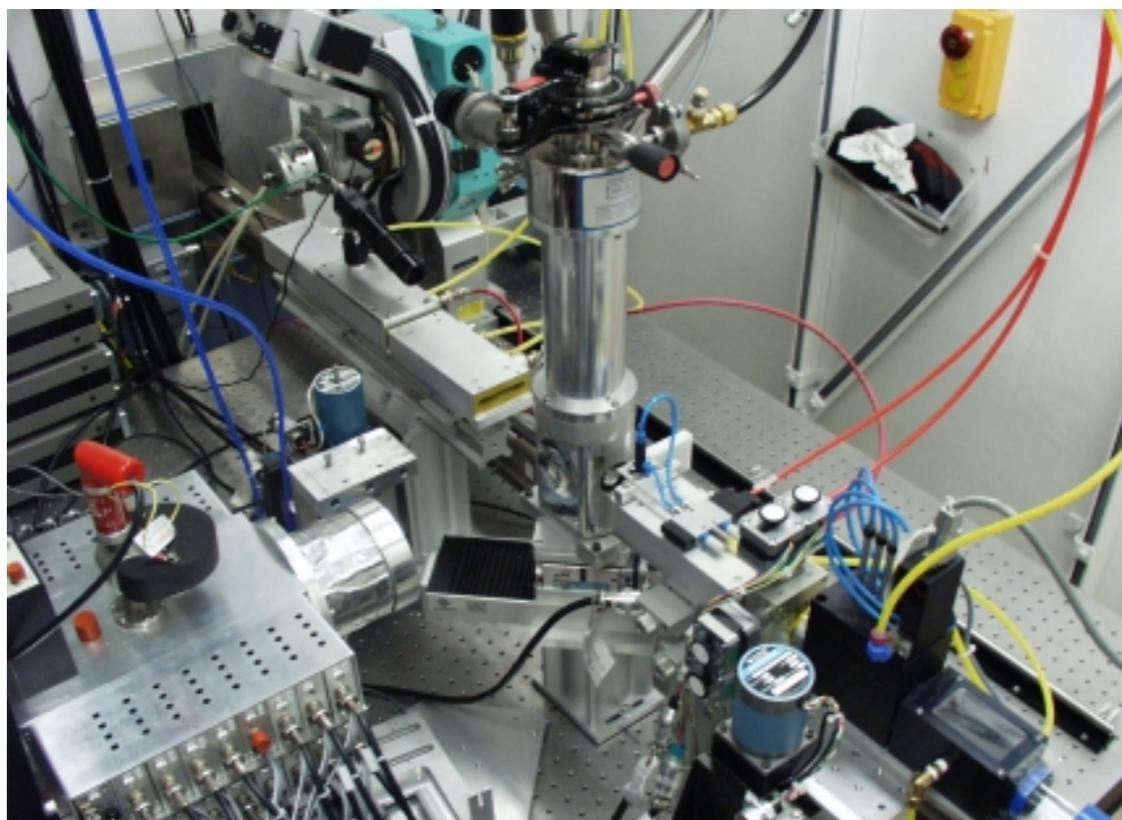
Fe K-edge ~7000 eV
Fe L-edges ~720 eV
Fe M-edges ~50-100 eV



Basics of X-ray Absorption Spectroscopy (XAS)



XAS: the experiment...

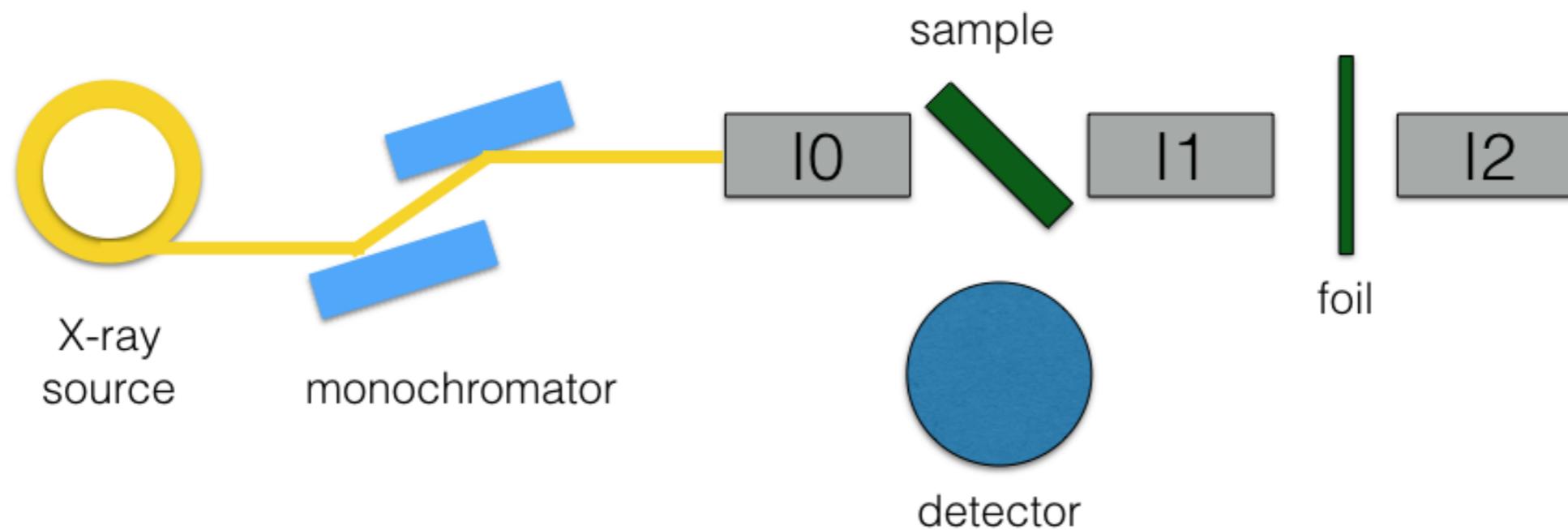


X-ray Spectroscopy Beam Lines:

XAS BLs (high energy)
5+ keV

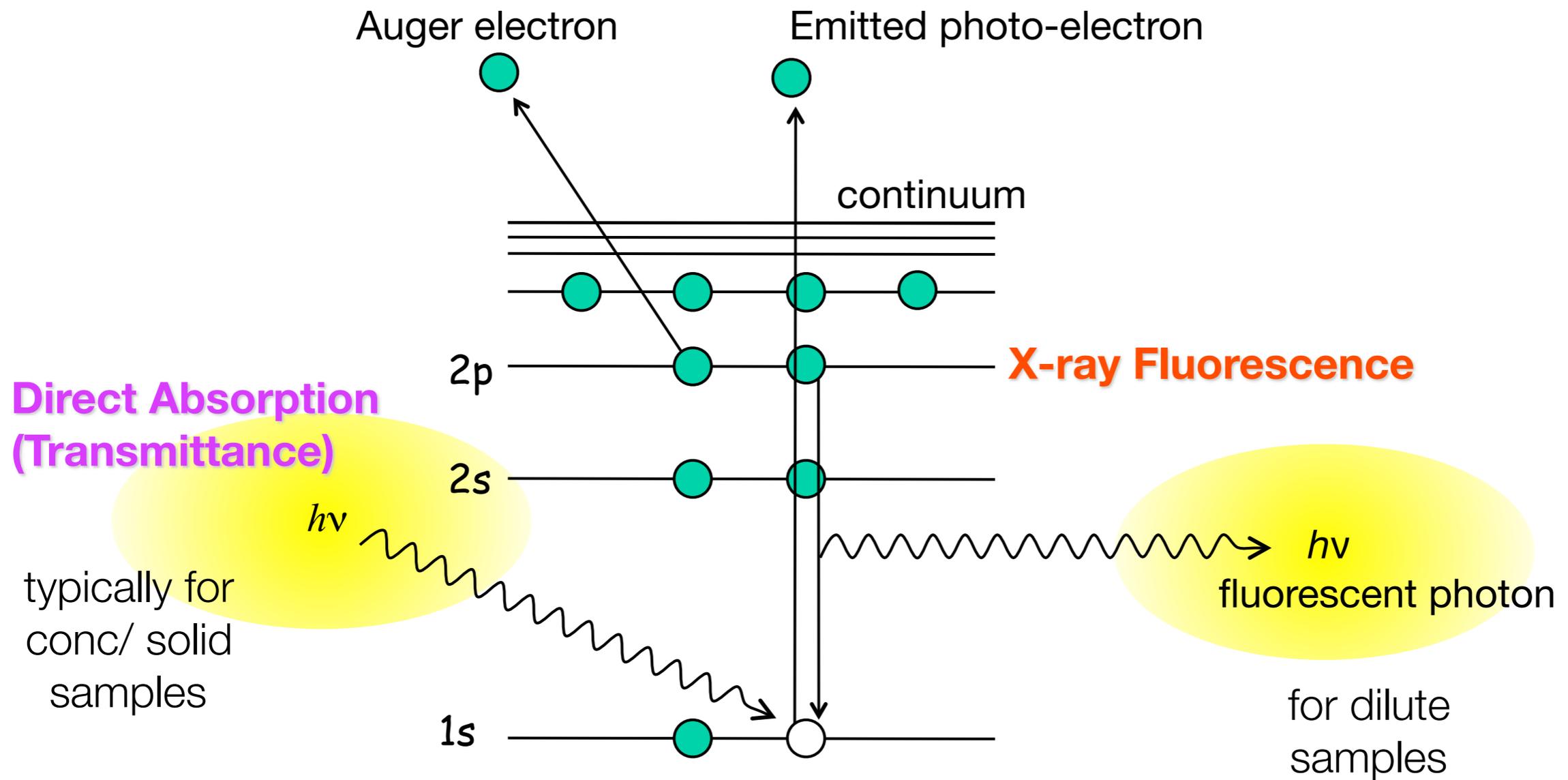
2-5 keV ("tender" X-rays)

<2 keV (soft X-rays)

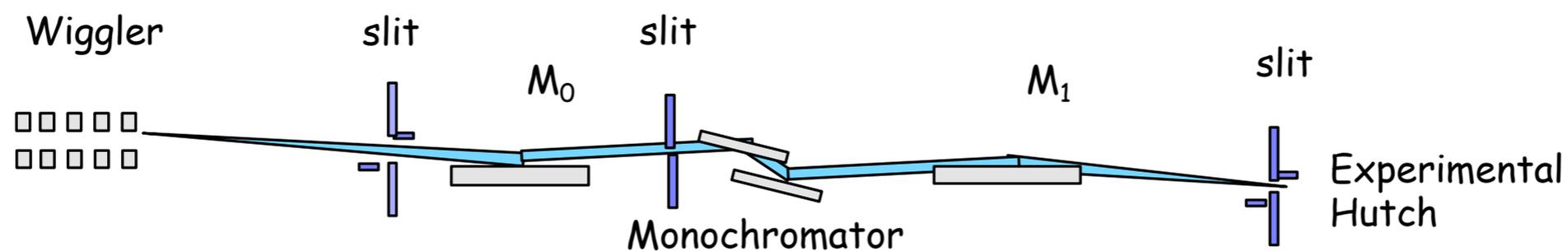


Methods of Detection

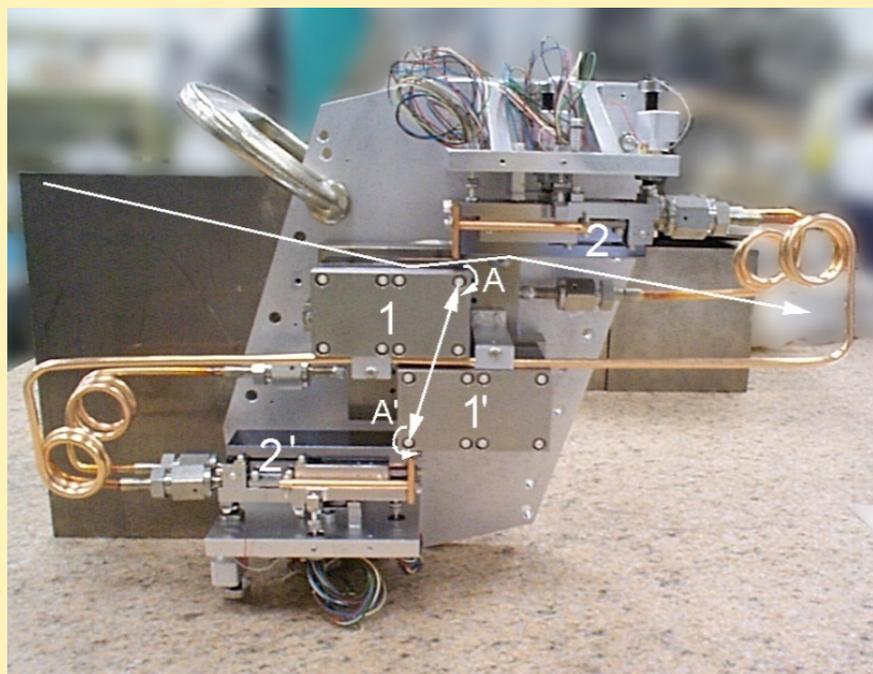
Electron Yield



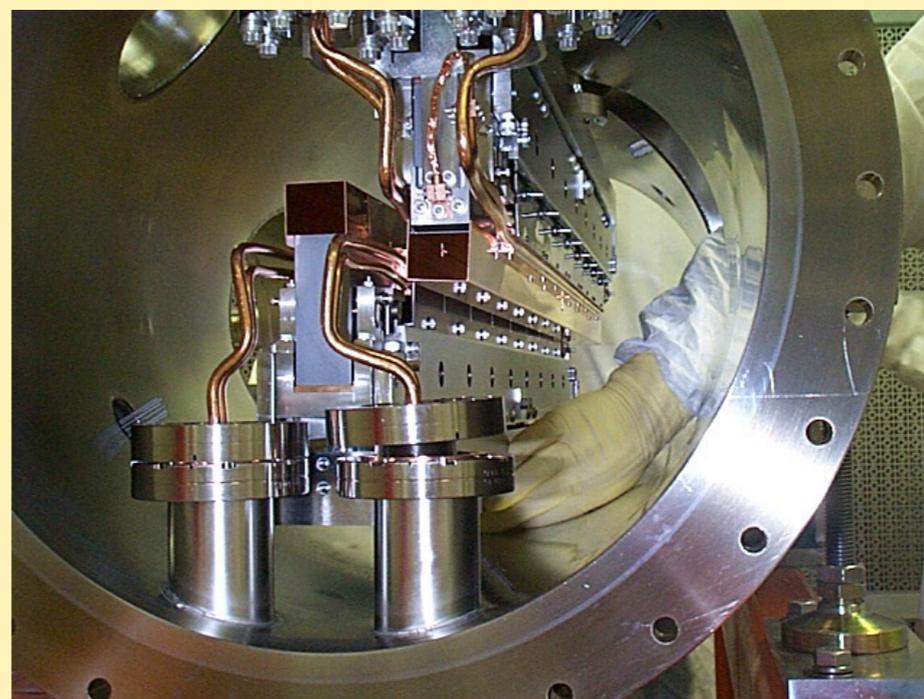
X-ray Beam Line Components



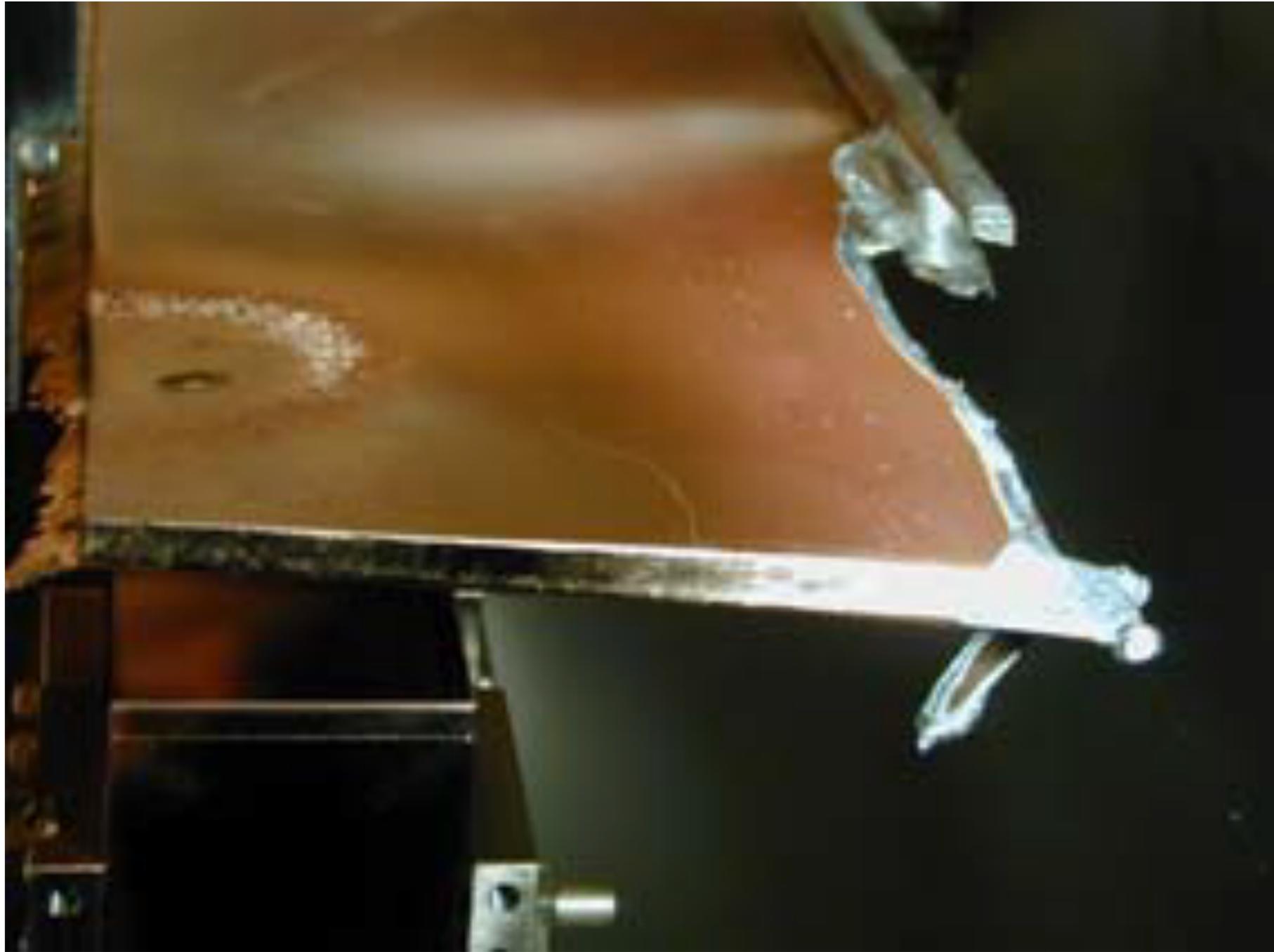
SSRL Beamline 11-2 liquid nitrogen cooled double crystal X-ray monochromator



SSRL Beamline 9-2 and 9-3 M1 X-ray Mirrors



The power of X-rays...

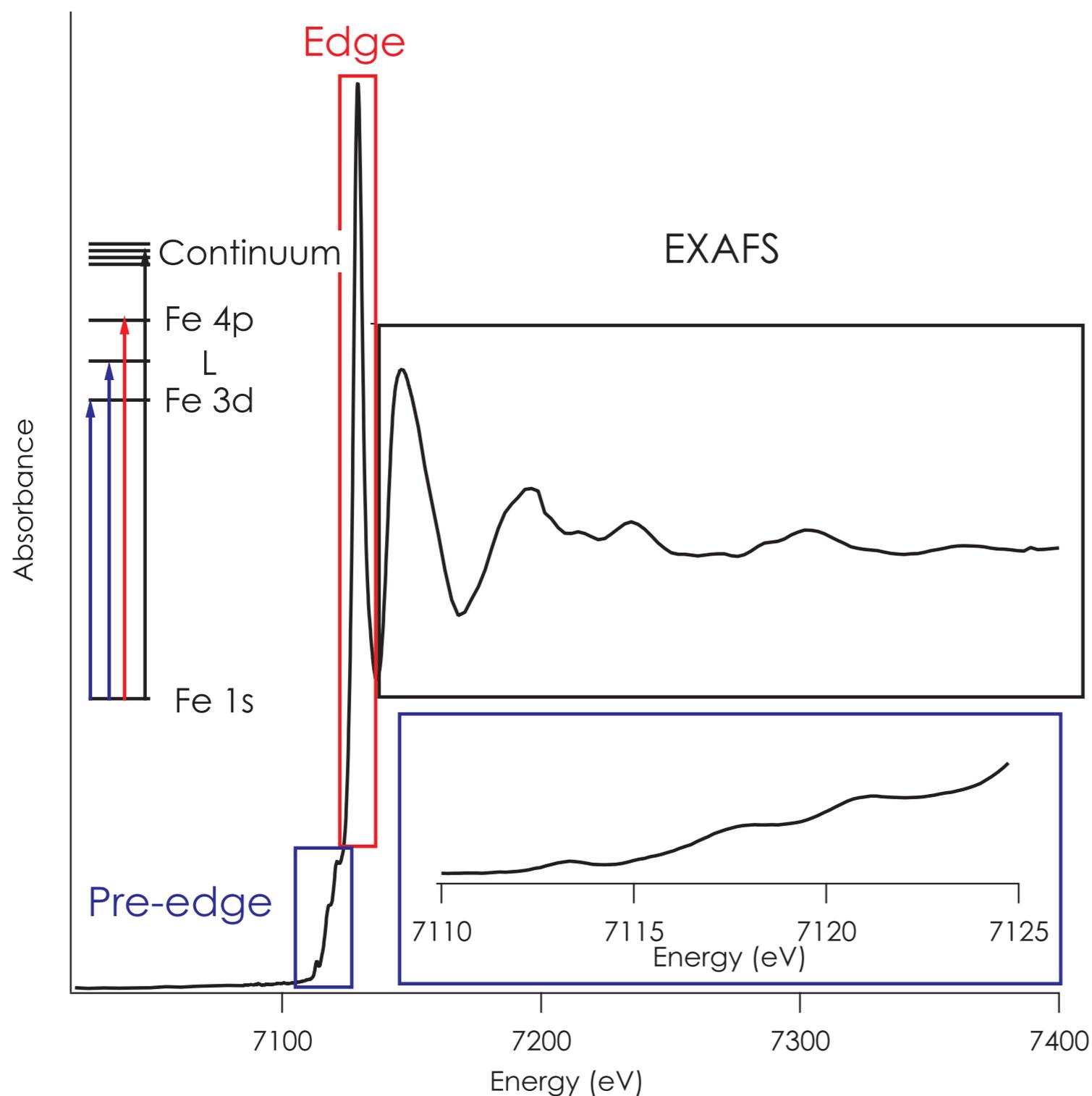


Effect of direct beam on a copper scatter shield

Sample requirements and Limitations

- ✓ Photoreduction is a **serious** issue, esp. for biological samples!
- ✓ Samples can be measured in almost any form
 - solid
 - liquid
 - gas
 - frozen solutions
- ✓ Concentration and volume requirements (depend on energy, BL an flux)
 - 1 mM (typical); 50 uM possible
 - small volume (droplets, 10 uL possible) with focused beam

Metal K-edge XAS

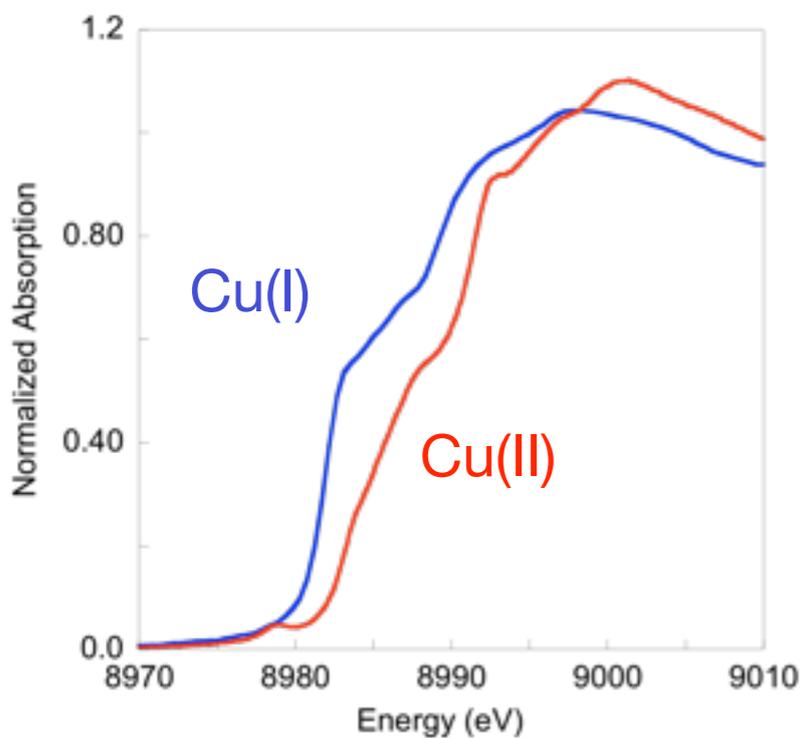


Intense edge absorption results from an electric dipole allowed $s \rightarrow p$ transition ($\Delta l = \pm 1$).

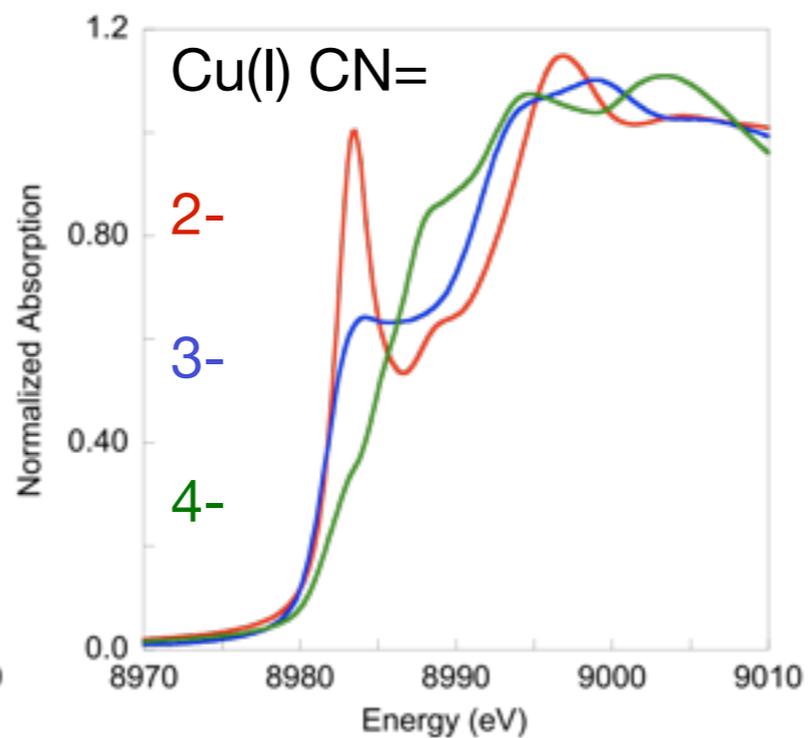
Weaker pre-edge intensity results from 3d-4p mixing in suitable symmetry or from an electric quadrupole allowed transition (~2 orders of magnitude weaker).

Edges are dependent on...

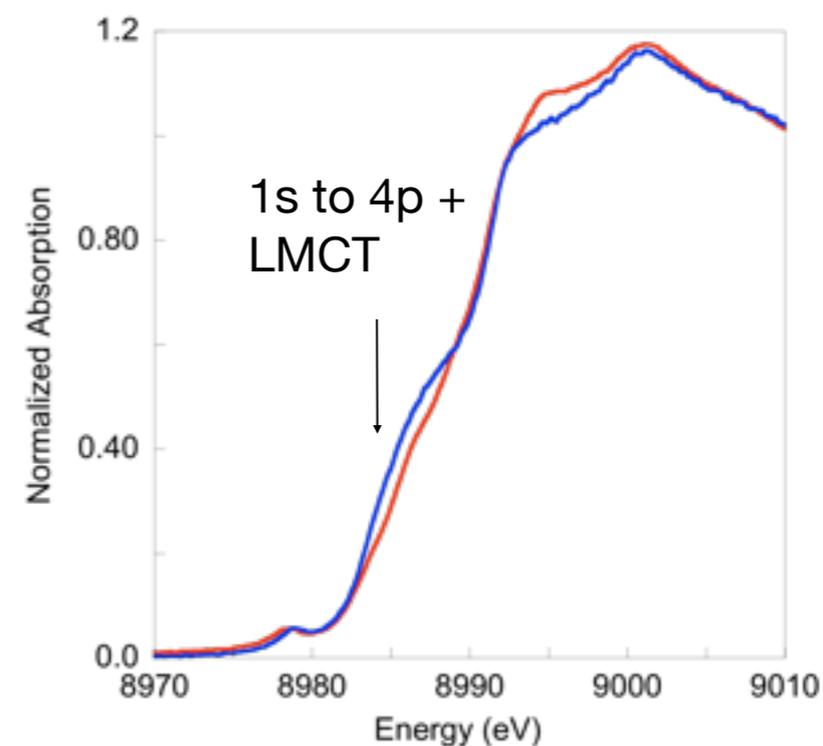
oxidation state



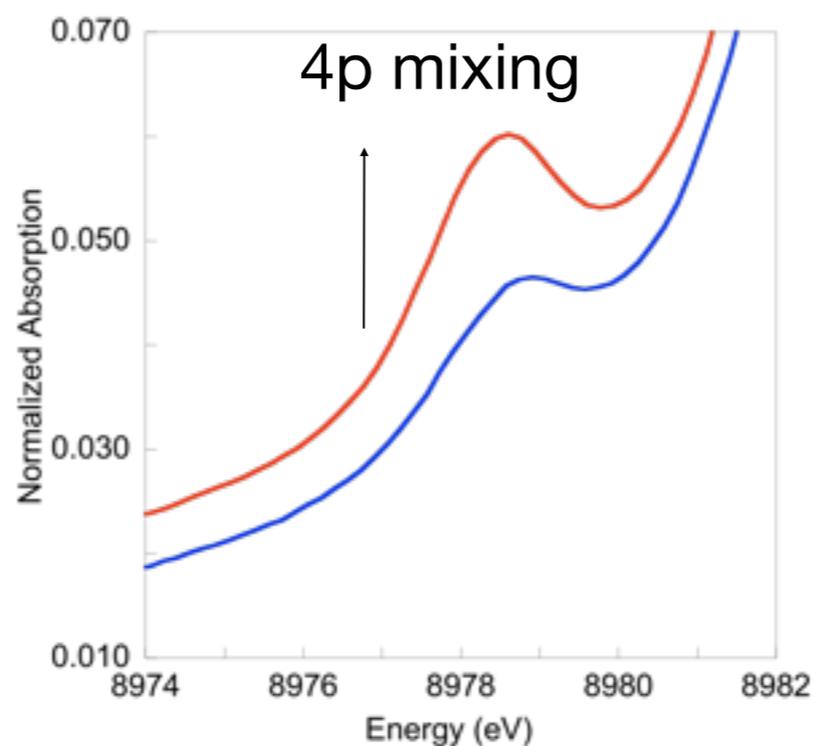
coordination number



covalency

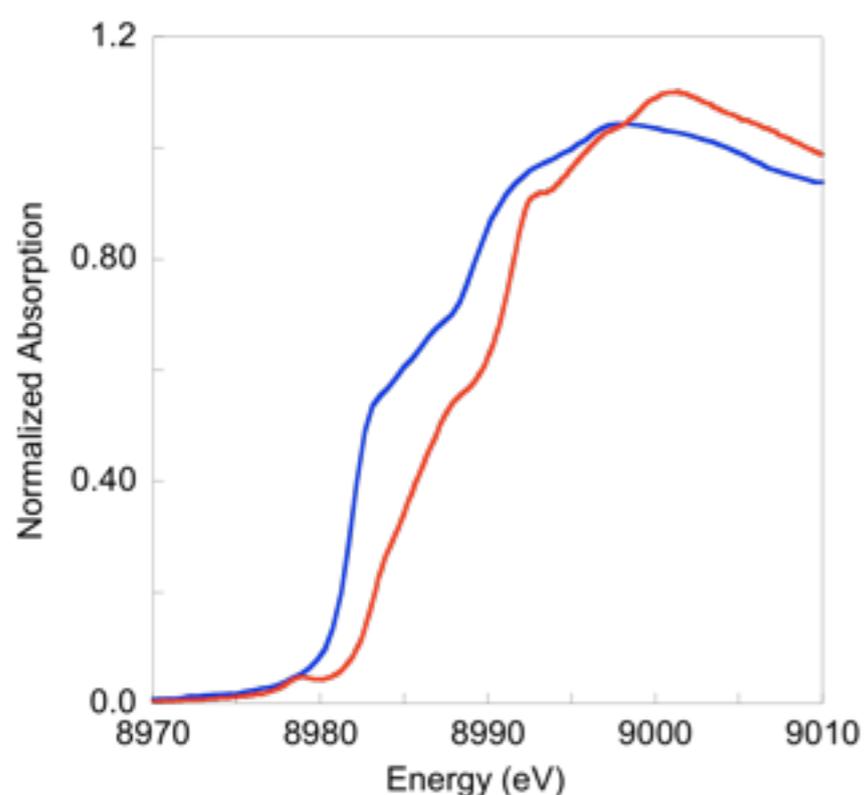


and
site symmetry
...and ligation

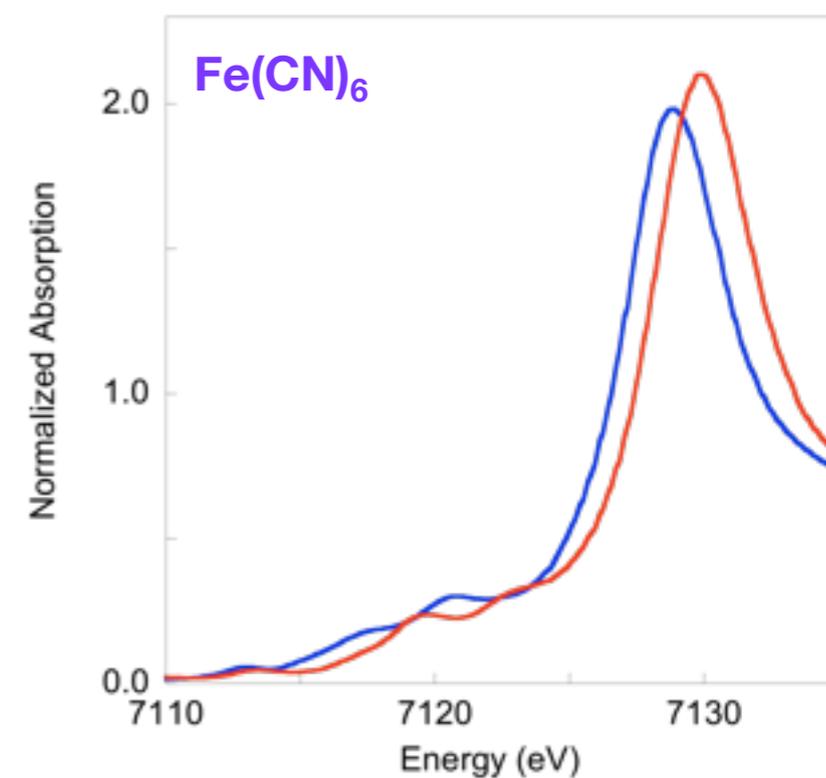
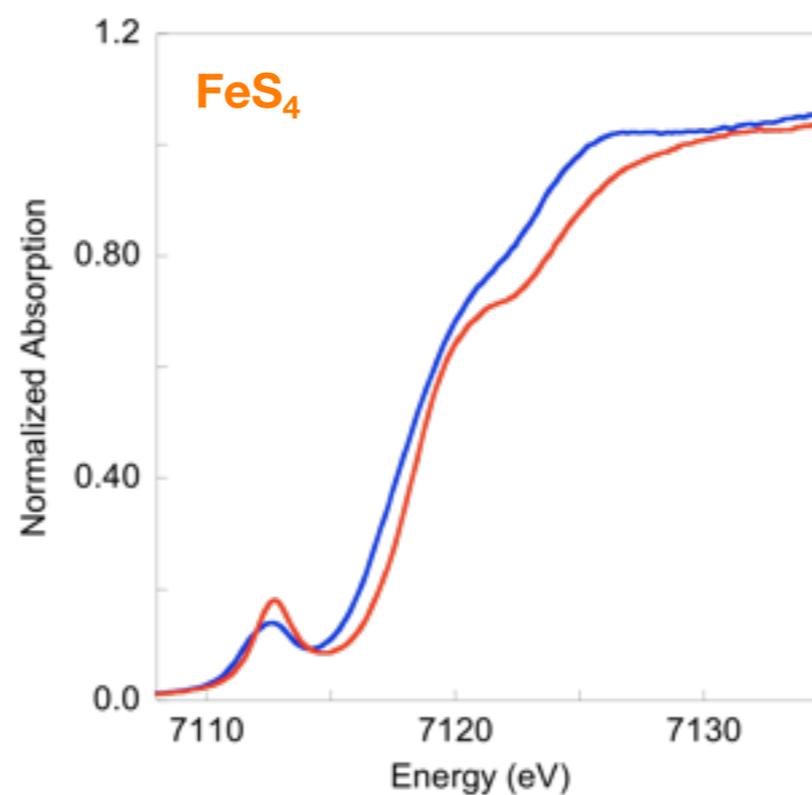


Metal K-edge XAS: Effect of Oxidation State

Cu(I) vs Cu(II) K-edges



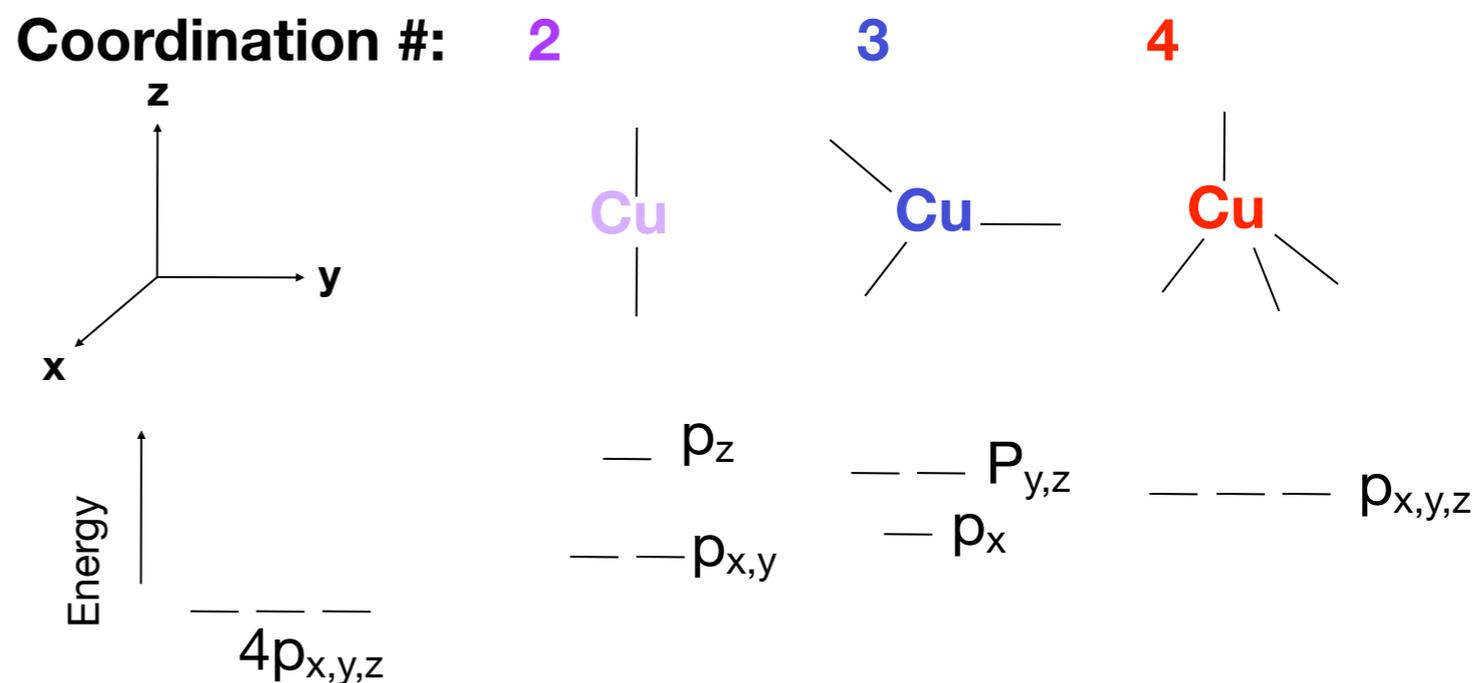
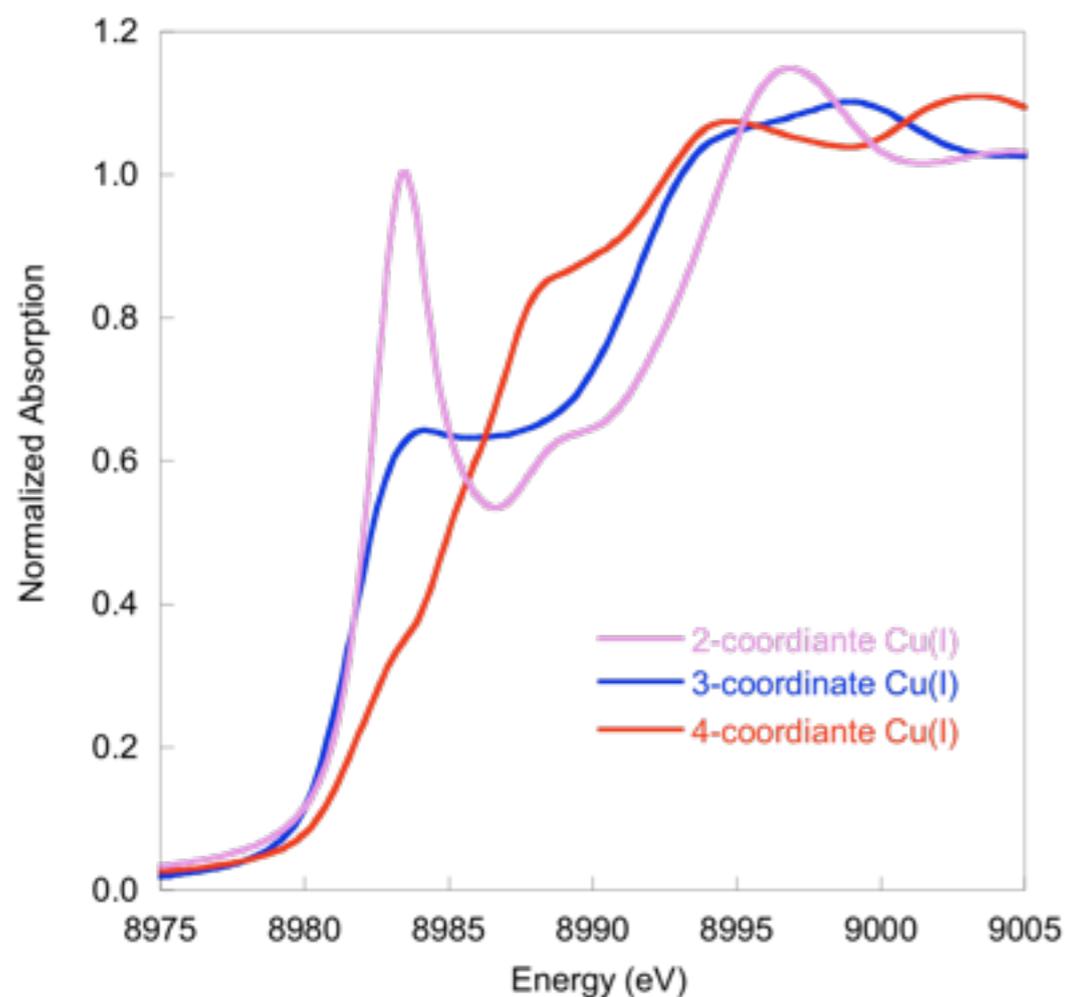
Fe(II) vs Fe(III) K-edges



“1s to 4p” transition energy increases as effective nuclear charge on metal increases

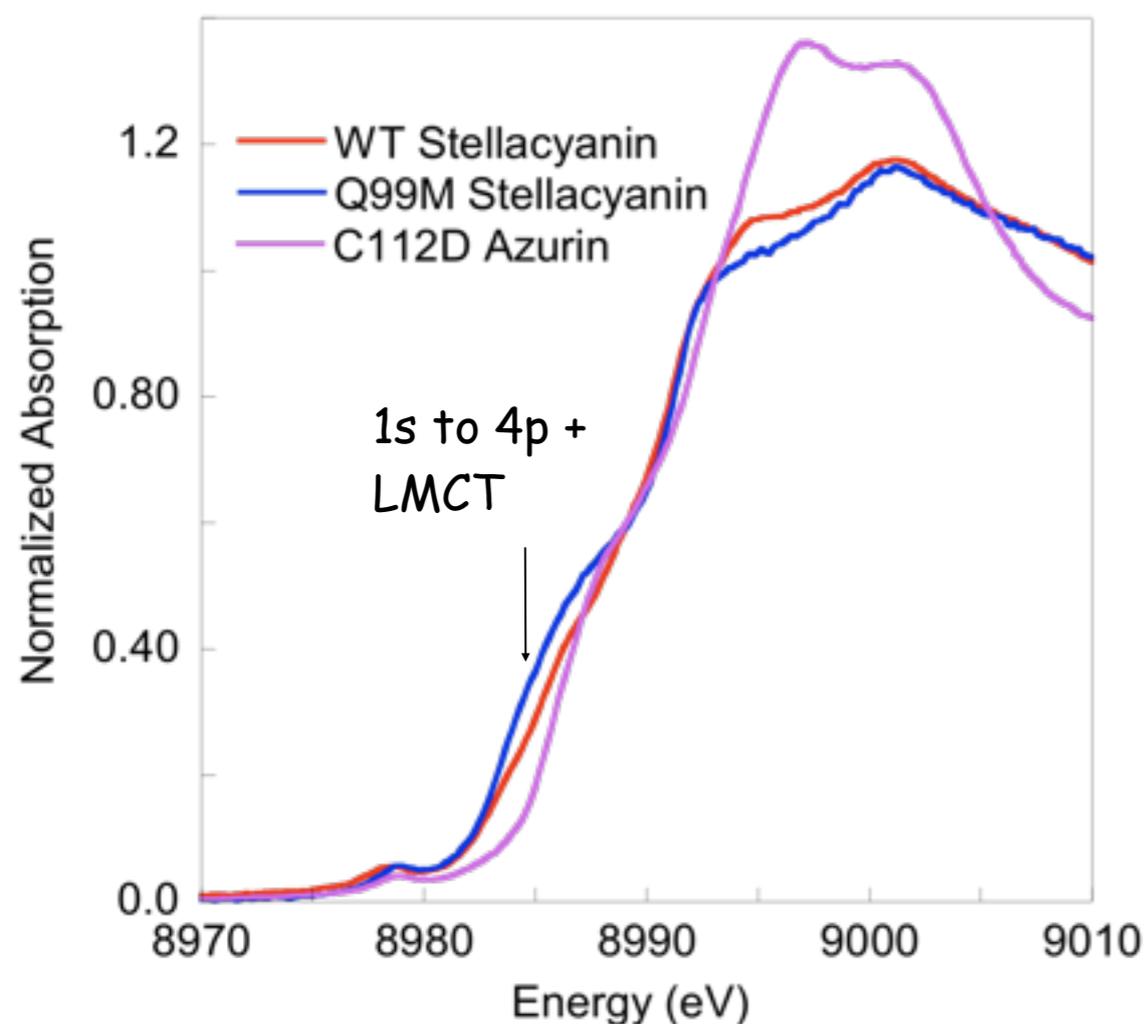
However, need to compare oxidation state trends within similar ligand environments

Metal K-edge XAS: Effect of Coordination Number



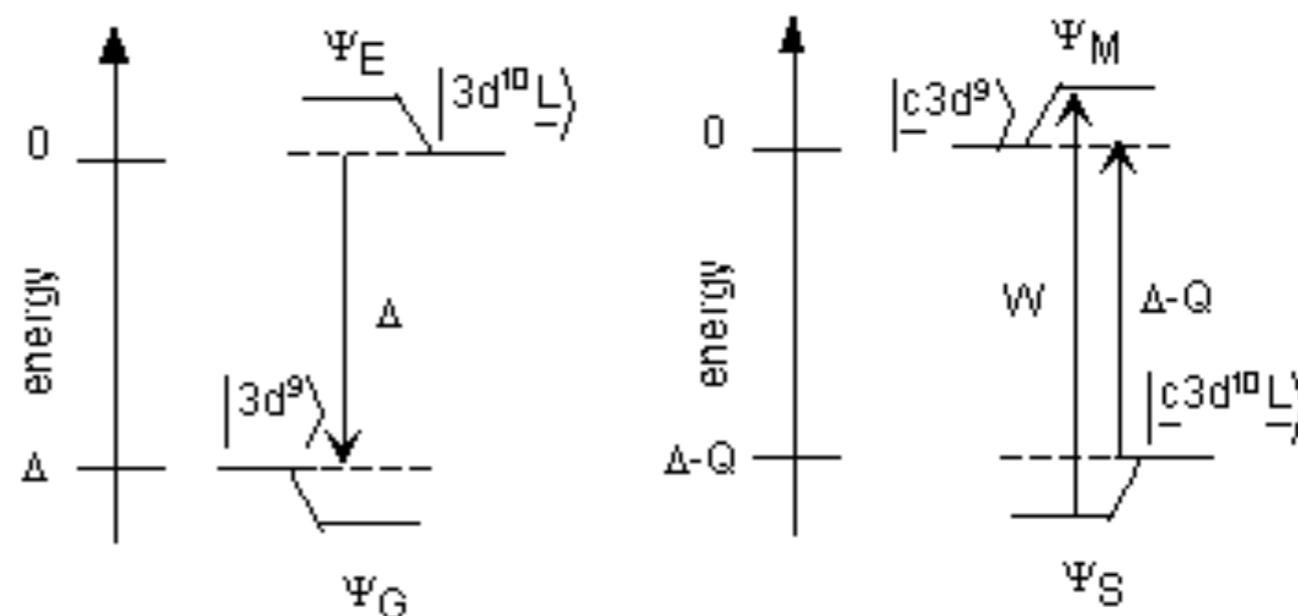
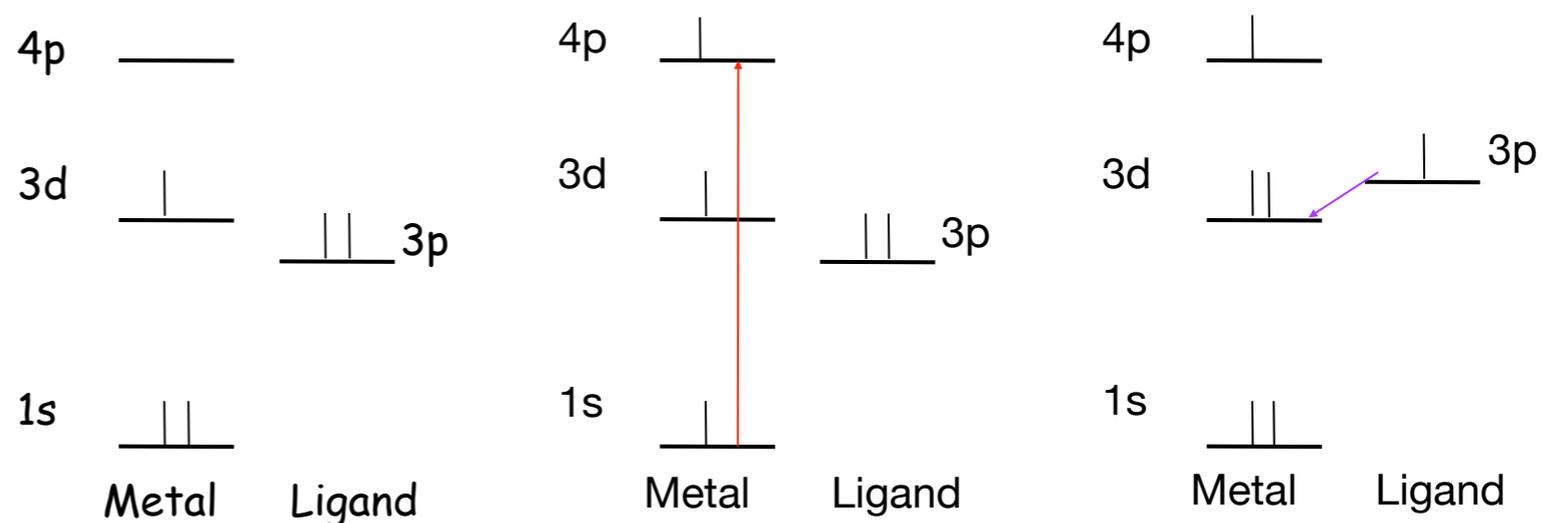
The rising edges of Cu(I) complexes can be easily understood in terms of a simple LF model.

Metal K-edge XAS: Effect of Covalency



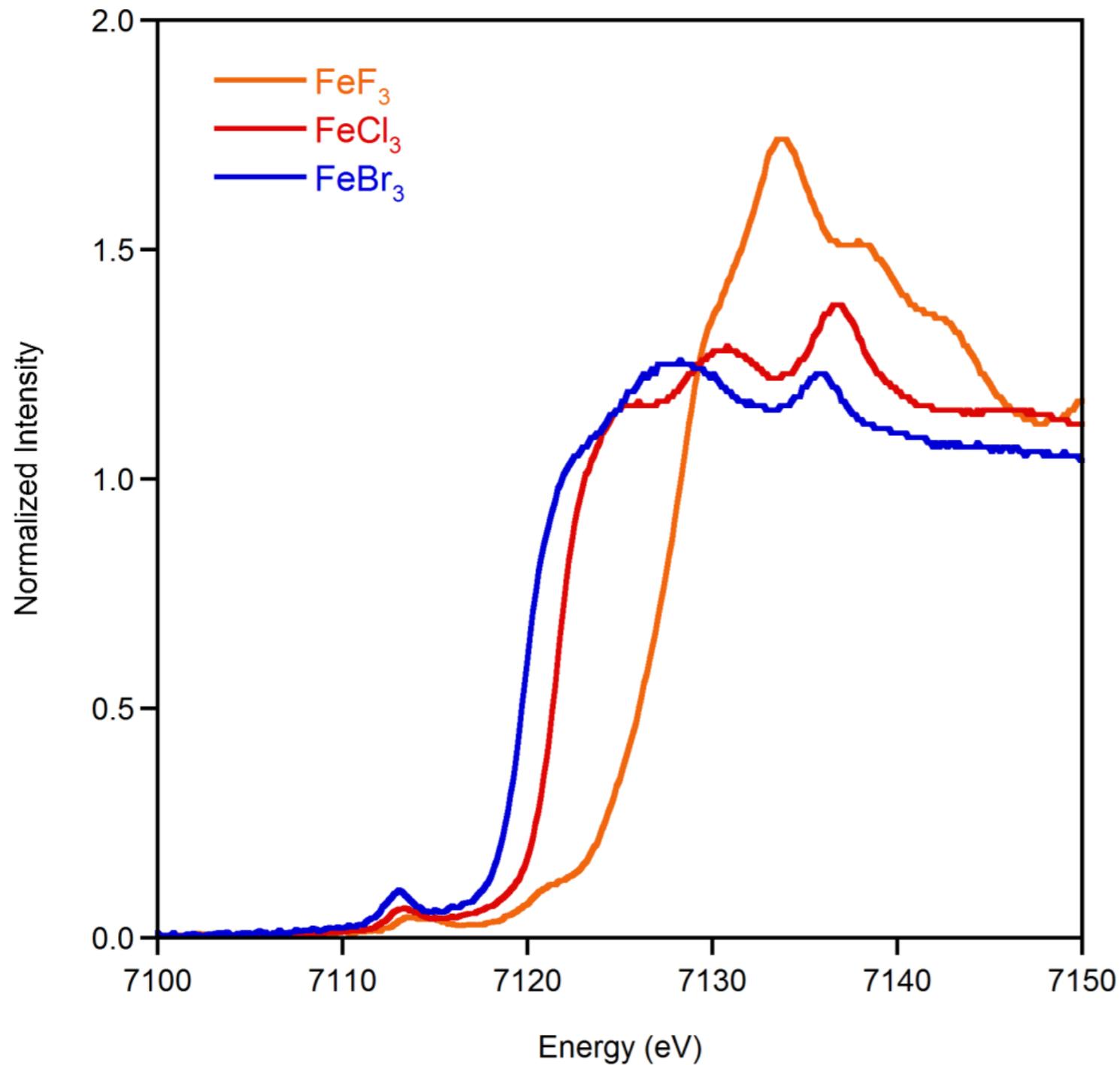
Shoulder on rising edge: Formally a 2-electron LMCT-"shakedown"-transition

"Main" Peak "Shakedown" Peak



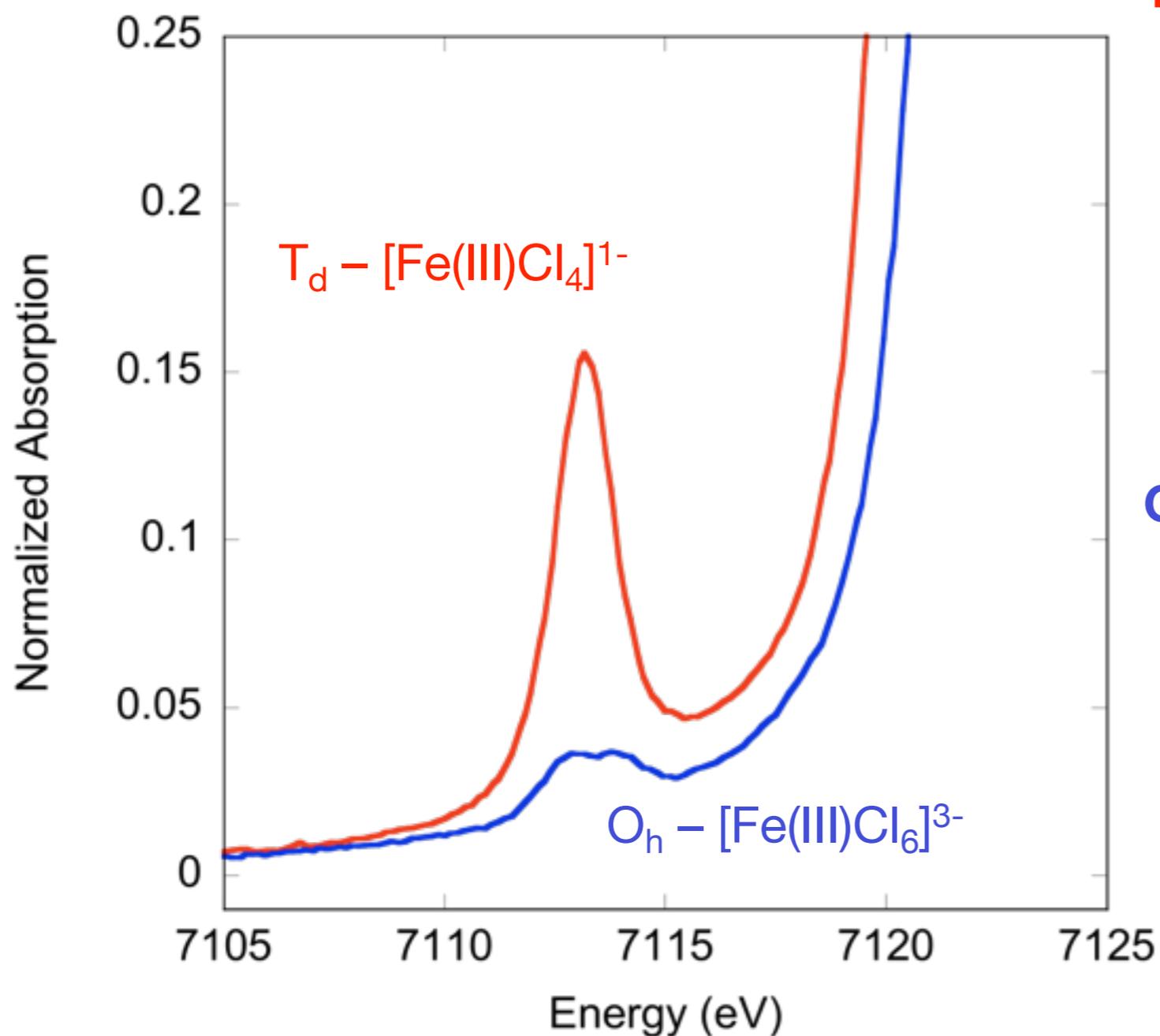
Energy and intensity can be correlated with covalency using a VBCI model

Metal K-edge and Covalency...



- ✓ All Fe(III), but ionic limit appears much more oxidized
- ✓ Shakedown transitions superimposed?
- ✓ Or difference in scattering properties?
- ✓ Or both?

Symmetry-Based 3d-4p Mixing



4p orbitals transform as t_2

3dxy, xz, yz orbitals transform as t_2

allows 3p-4d mixing and intense pre-edge



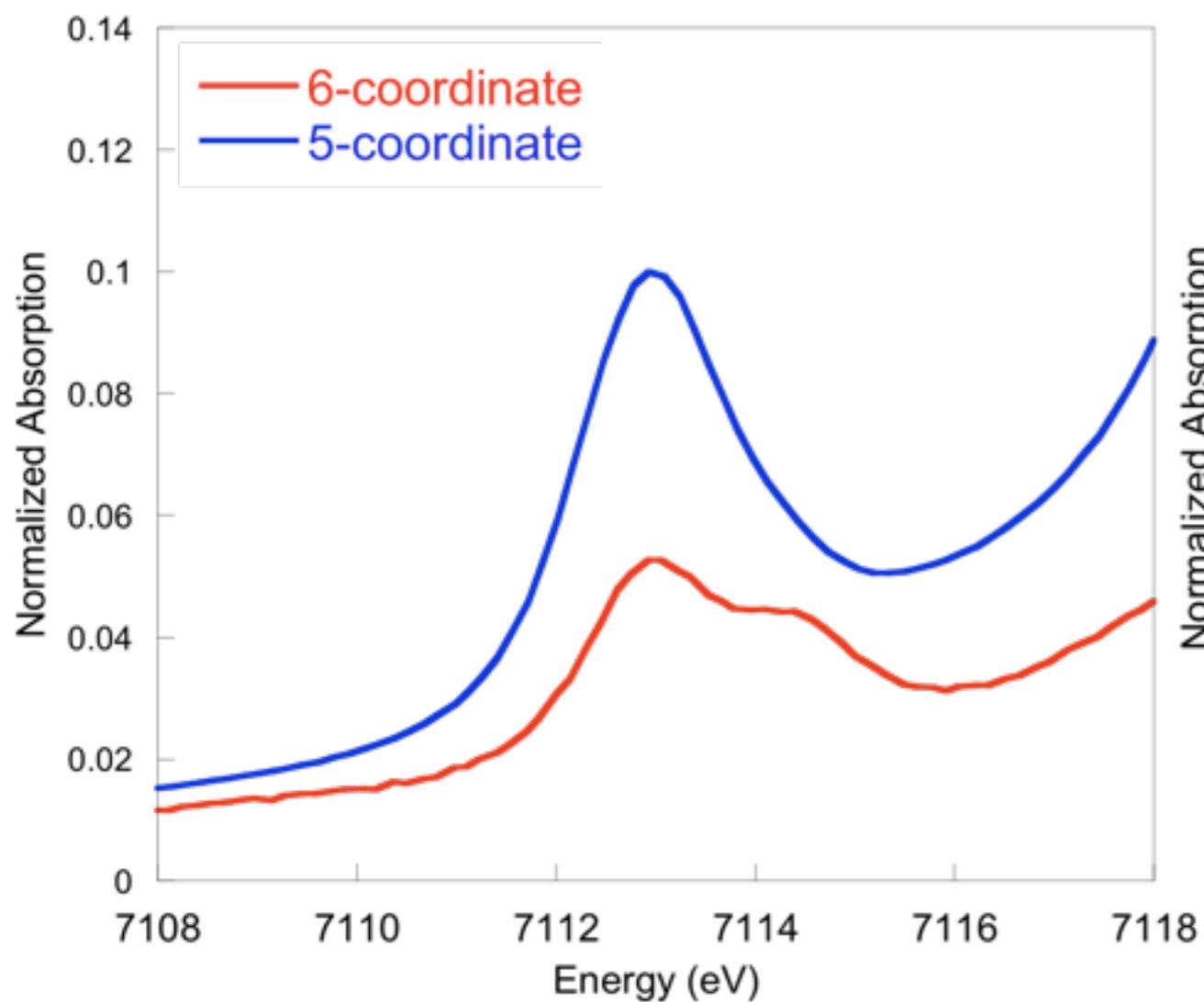
4p orbitals transform as t_{1u}

d-orbitals transform as t_{2g} and e_g

No 3d-4p mixing, quadrupole Only

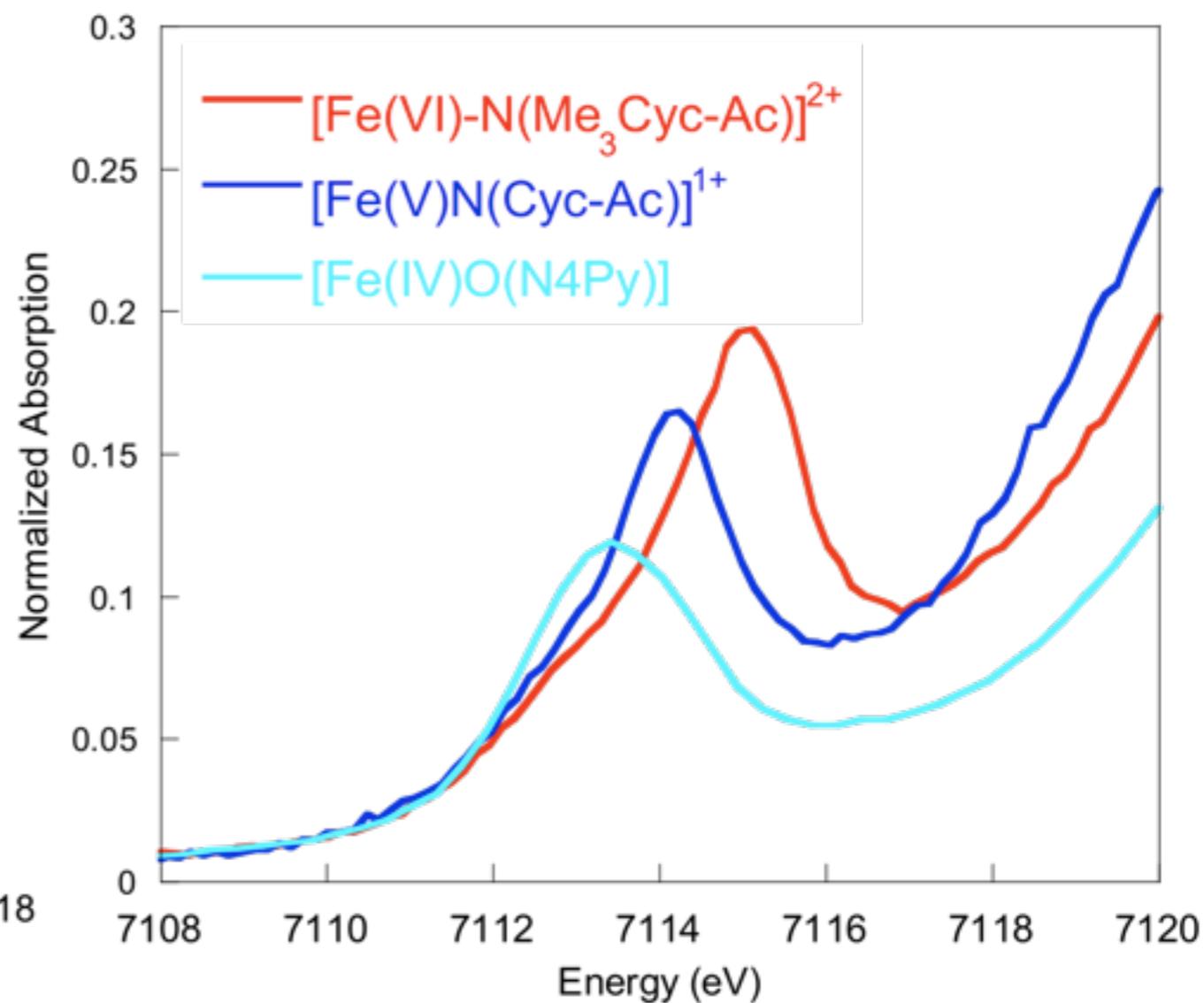
In general, the larger the distortion of the site, the greater the 3d-4p mixing.

Established Paradigms



Pre-edge area 6-coordinate < area of 5-coordinate complexes

Westre, et al, J. Am. Chem. Soc. 1997, 119, 6297.



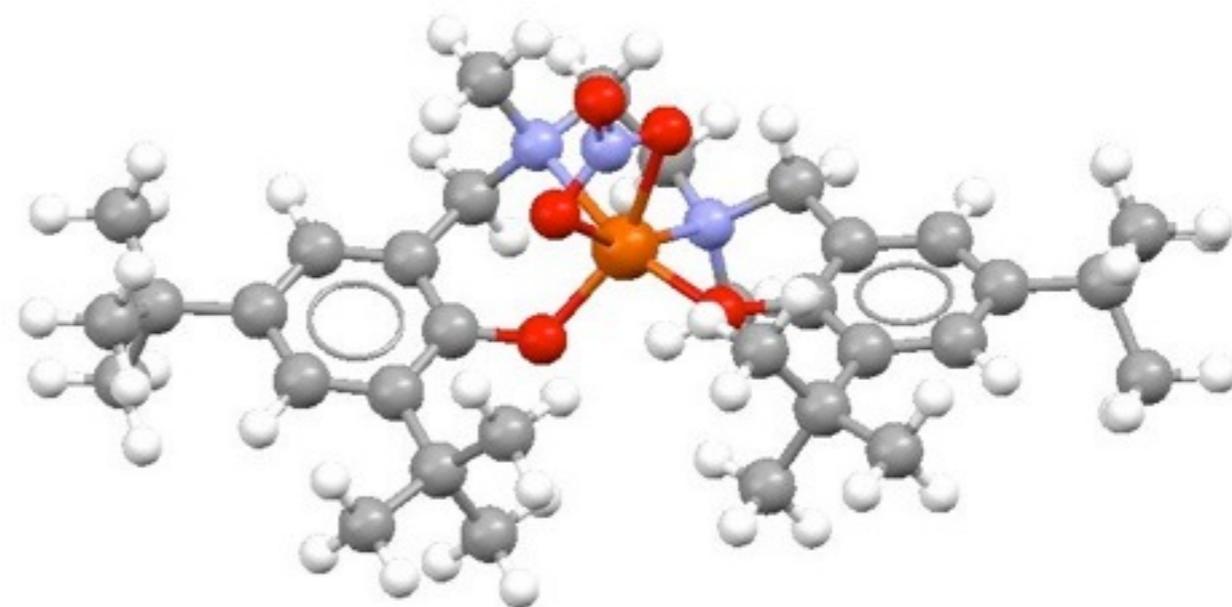
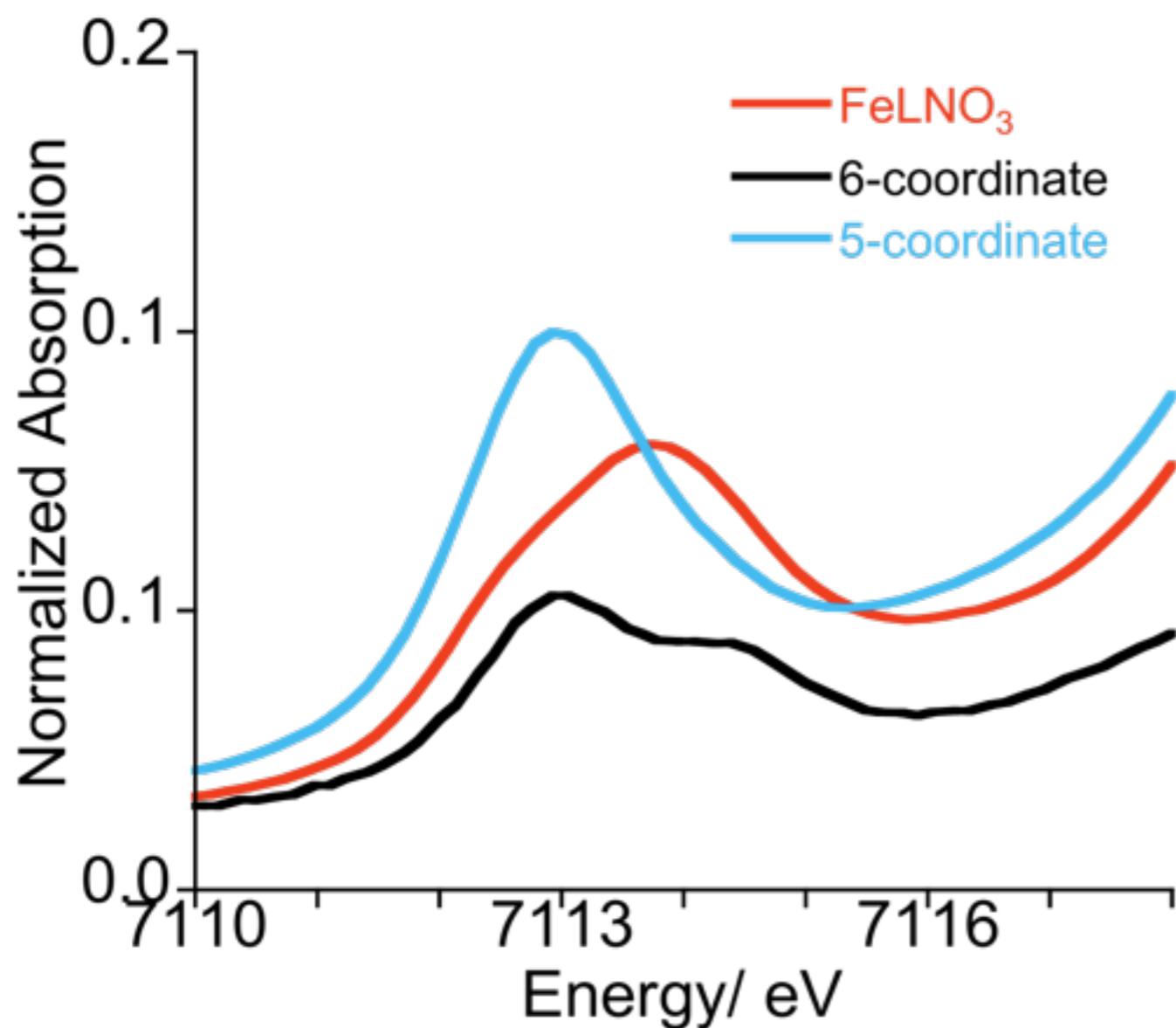
~1 eV per oxidation state

Lim et al, PNAS, 2003, 100, 3665.

Aliaga-Alcalde et al., Angew. Chem., 2005, 44, 2908.

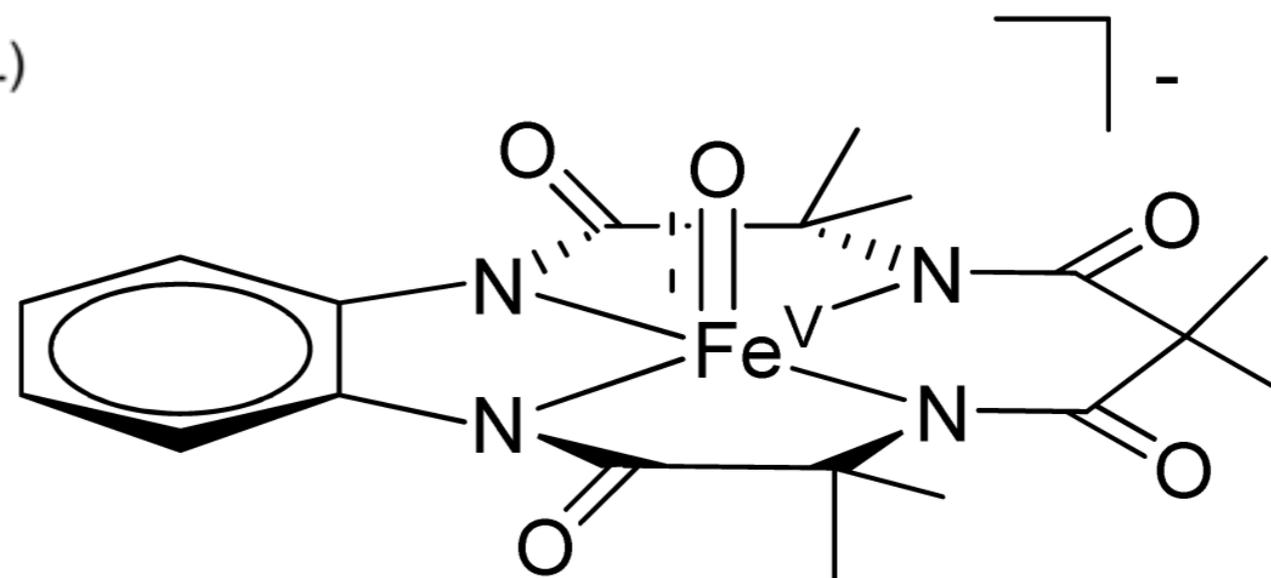
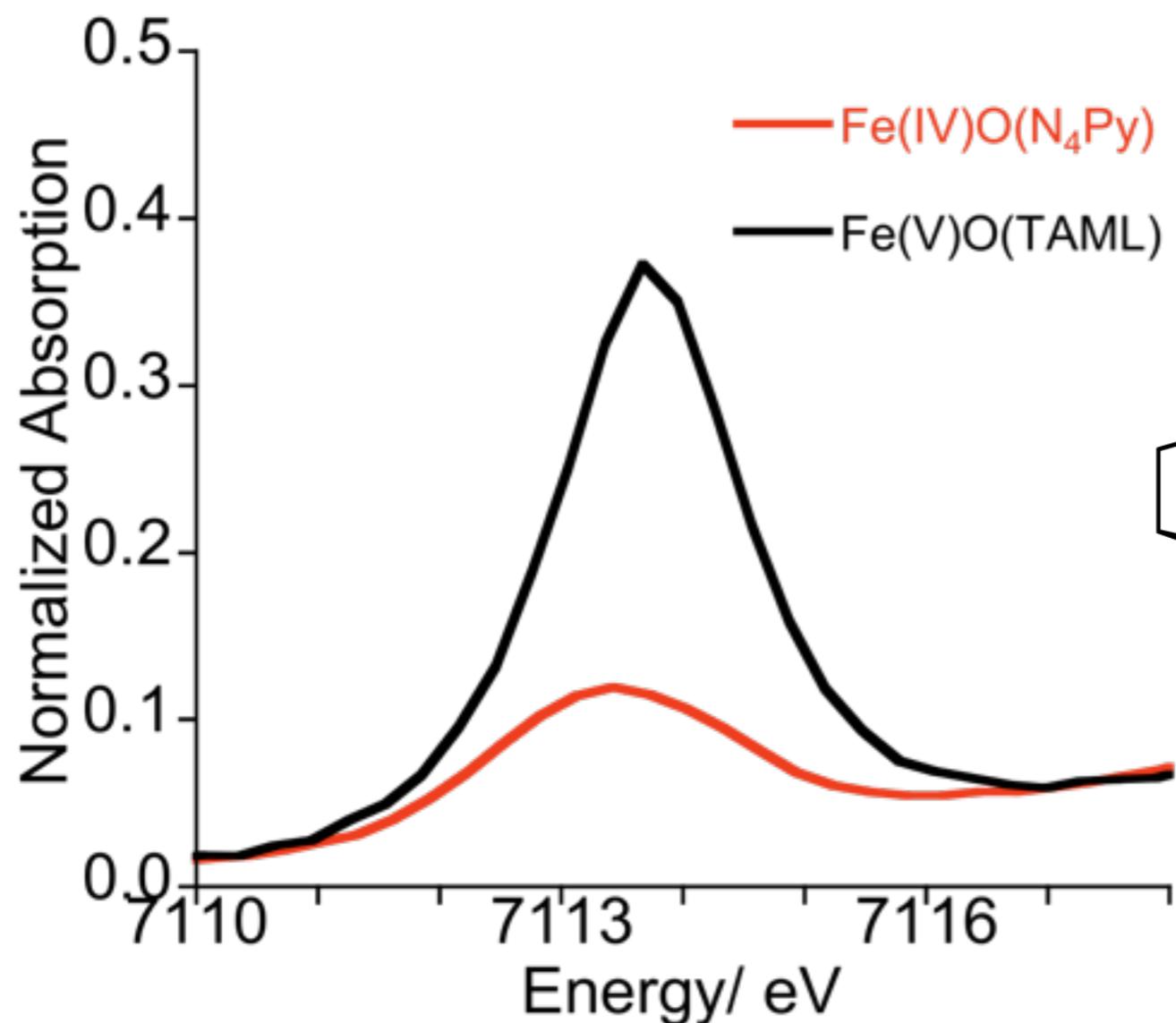
Berry et al., Science 2006, 312, 1937.

“Exceptions” to the Rule



Distortion of 6-coordinate site yields pre-edge area in 5-coordinate range

“Exceptions” to the Rule



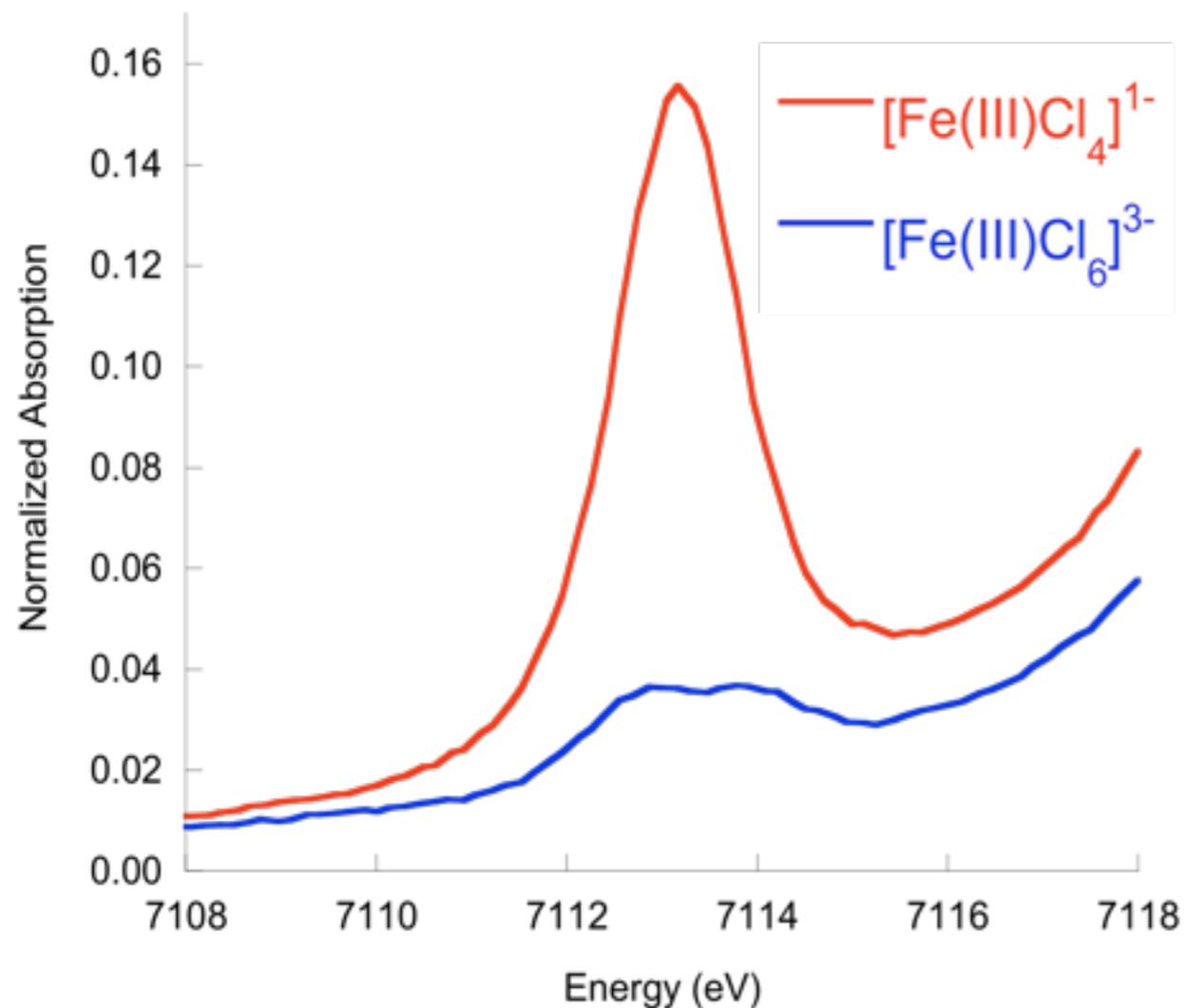
F. T. de Oliveira, A. Chanda, D. Banerjee, X. P. Shan, S. Mondal, L. Que Jr., E. L. Bominaar, E. Münck and T. J. Collins, *Science*, 2007, 315, 835.

What's missing?

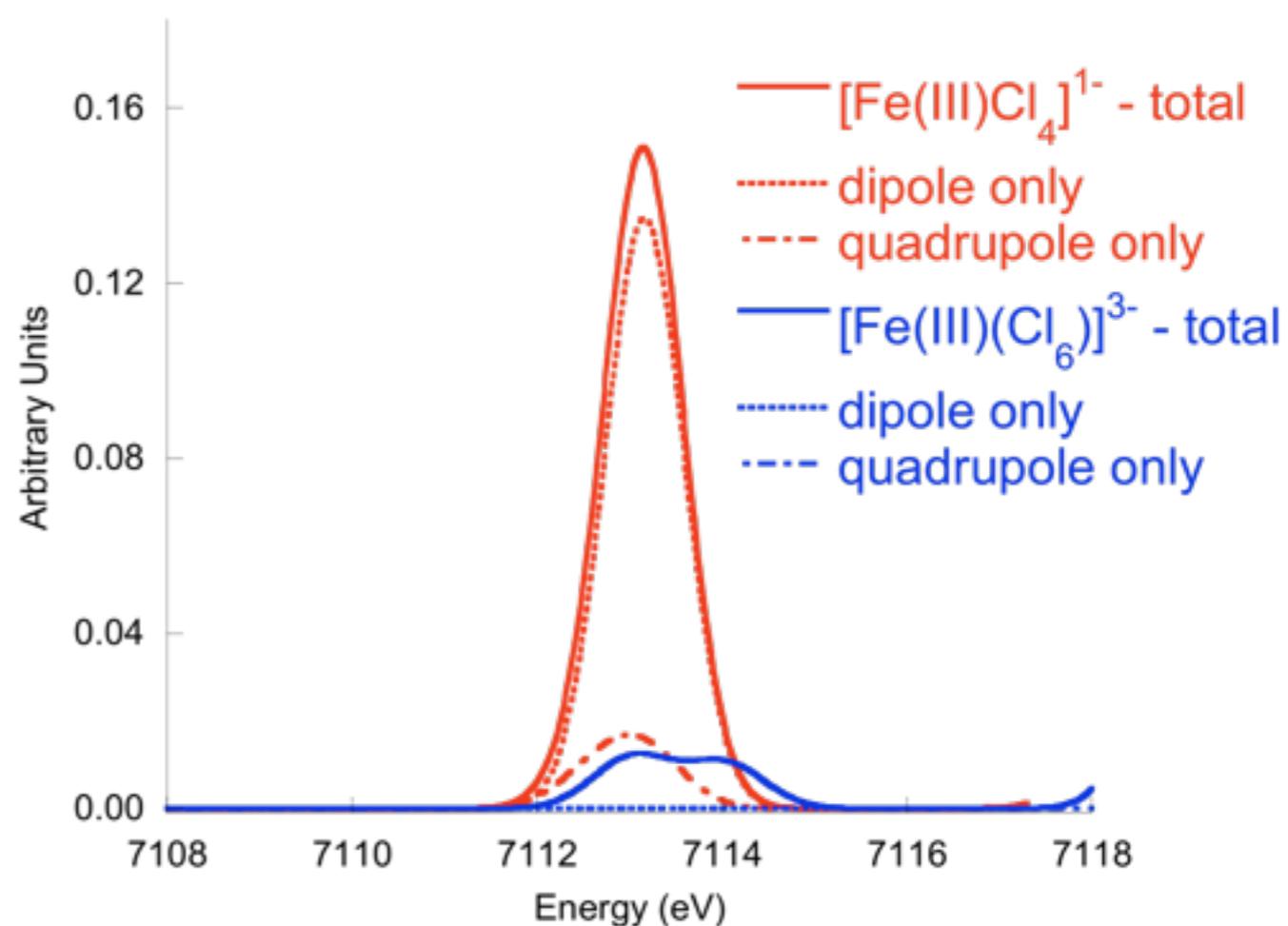
Systematic approach that includes dipole and quadrupole contribution, as well as pre-edge energies

TD-DFT with inclusion of Quadrupole

experiment



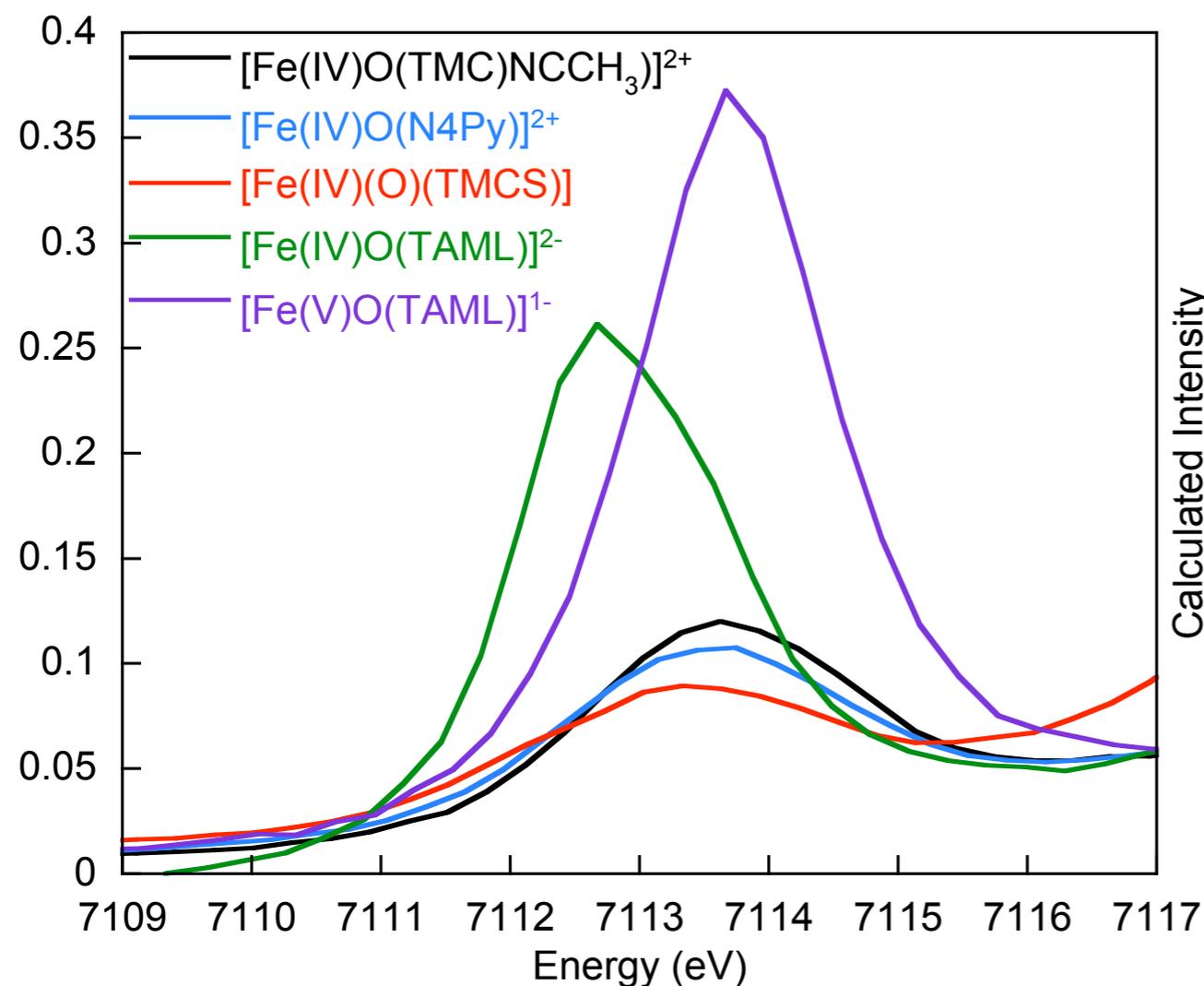
calculation



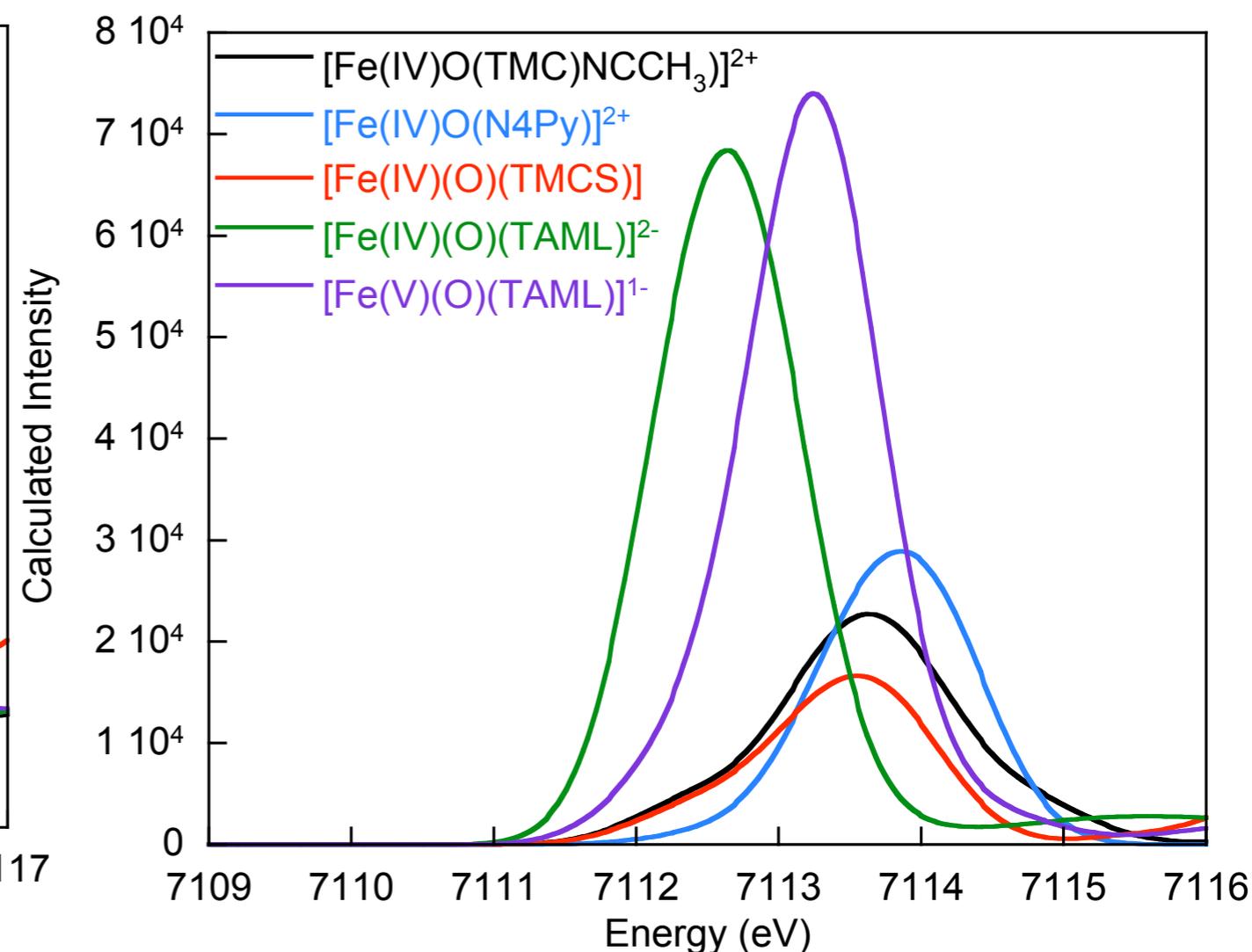
DeBeer George, S.; Petrenko, T.; Neese, F. *Inorg. Chem. Acta*, 2008, 361, 965.
DeBeer George, S.; Petrenko, T.; Neese, F., *J. Phys. Chem. A*, 2008, 112, 12936.

Fe(IV), Fe(V)-oxo Model Complexes

experiment



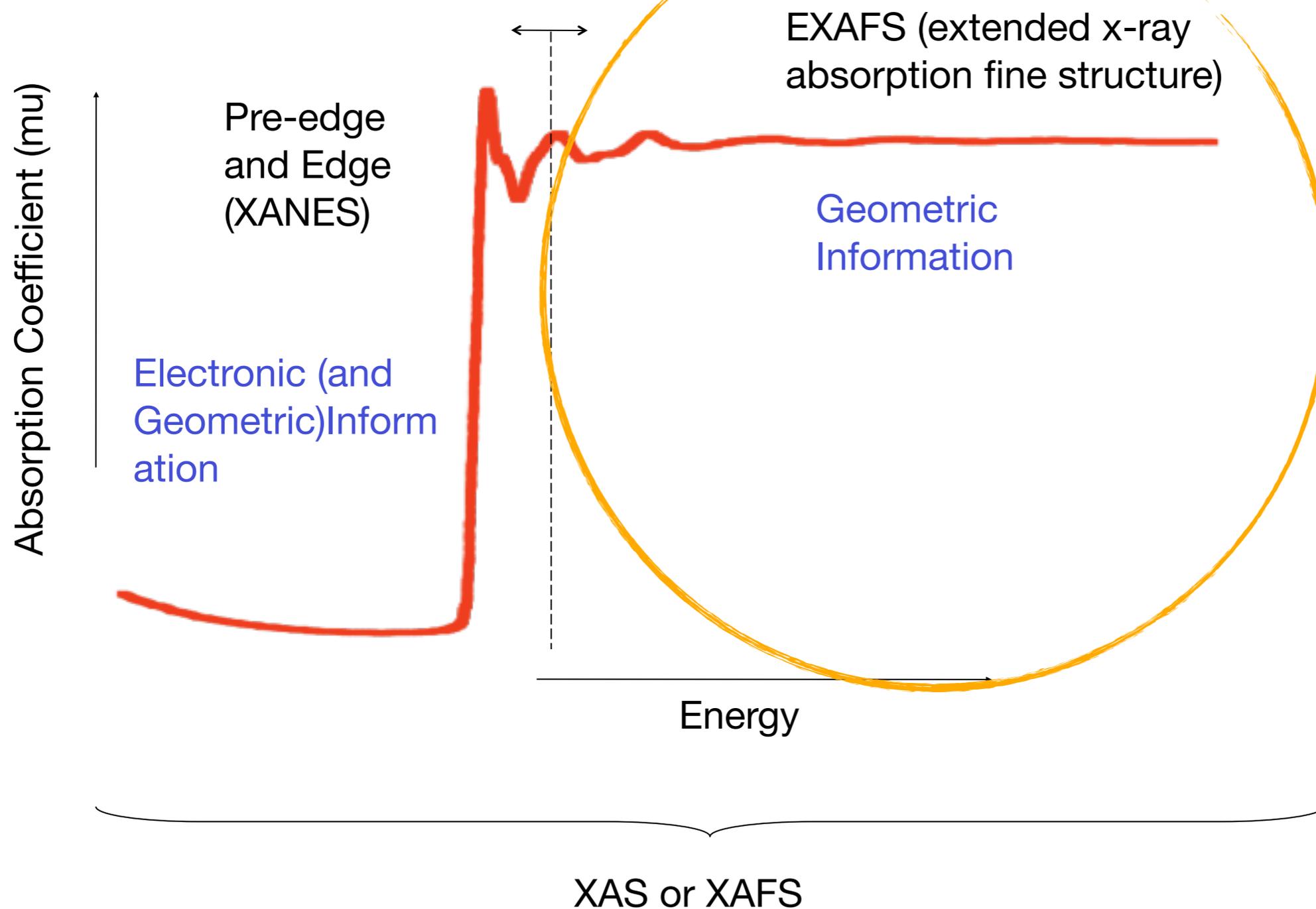
theory



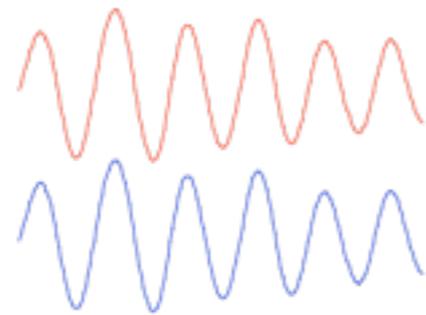
P. Chandrasekaran, S. C. E. Stieber, L. Que, Jr., T. Collins, F. Neese, S. DeBeer, Dalton Trans., 2011.

Pre-edge Calculations can be used in a predictive fashion!

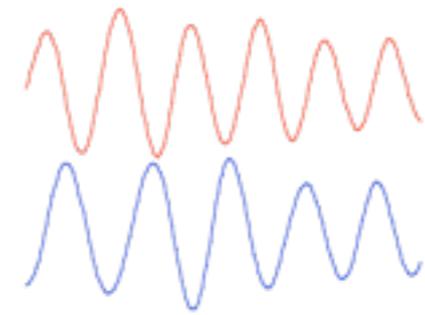
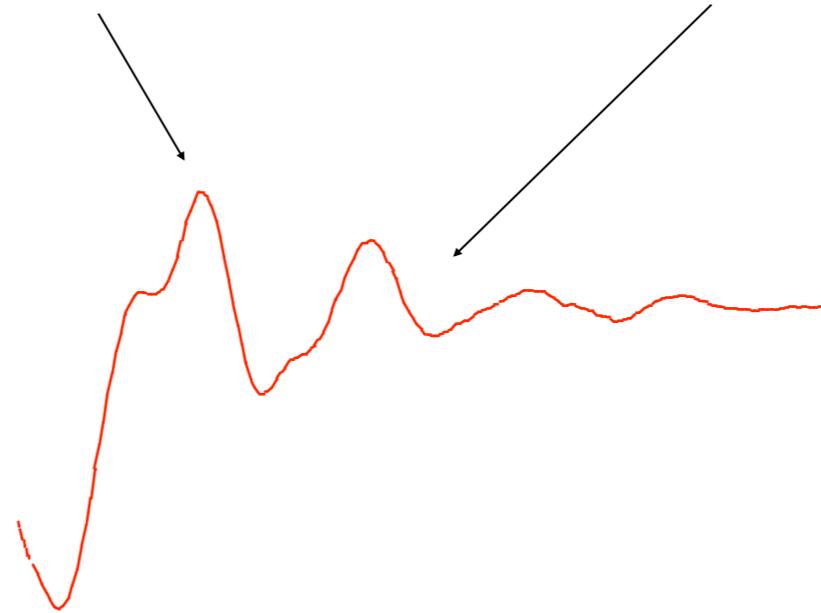
Basics of X-ray Absorption Spectroscopy (XAS)



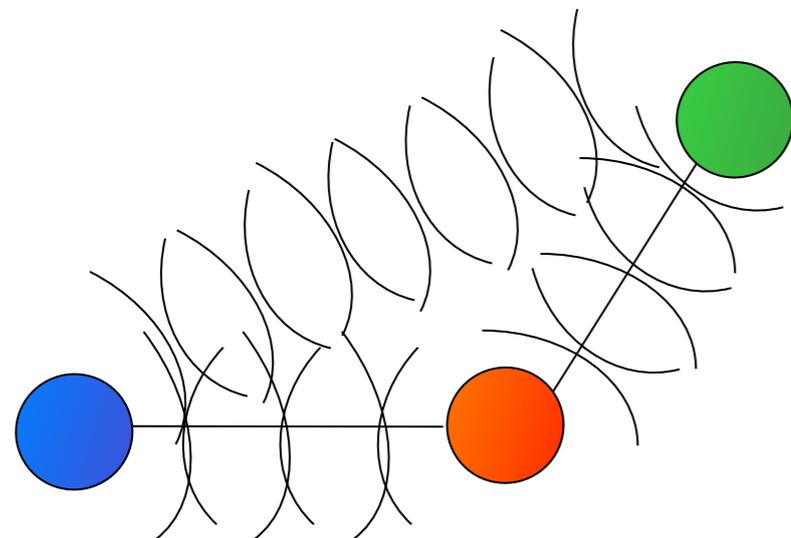
Geometric Structural Insight from XAS: EXAFS



constructive interference
results in a maximum



destructive interference
results in a minimum

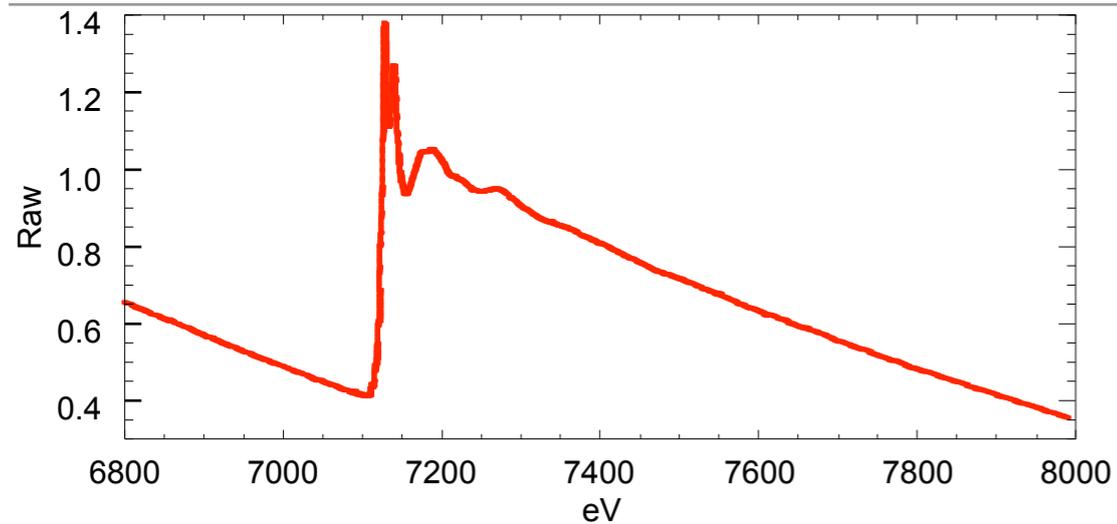


multiple scattering - photoelectron may be scattered
by more than one atom before returning to the absorber

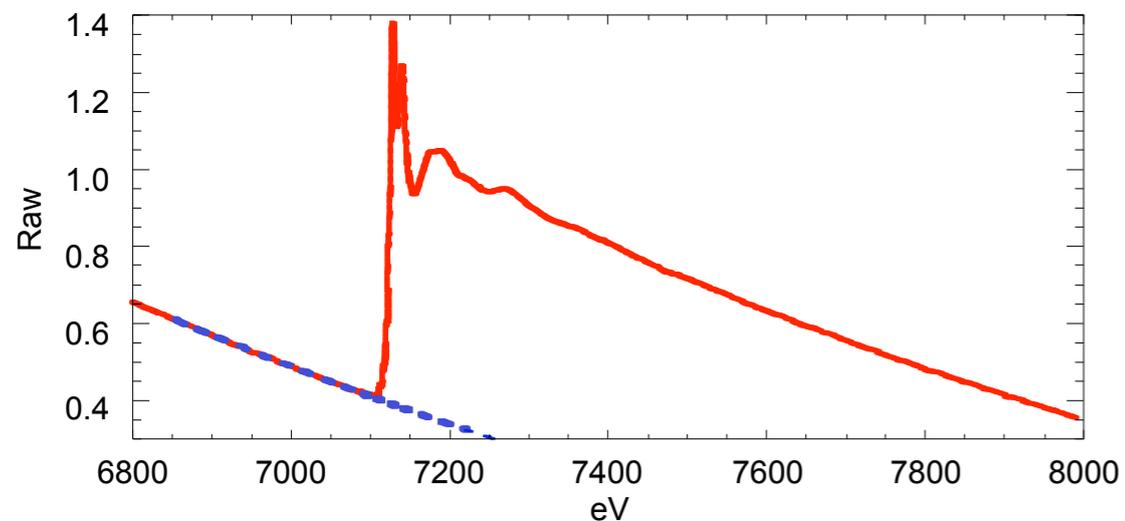
EXAFS: what information can I get?

- distances (± 0.01 - 0.02 \AA)
- coordination numbers (± 20 - 25%)
- types of ligands (within $z = \pm 1$)
- some nearest neighbor (with in $\leq 6.0 \text{ \AA}$)
- bond angle information (in certain cases)
- **EXAFS “sees” the average of all photoabsorbers**

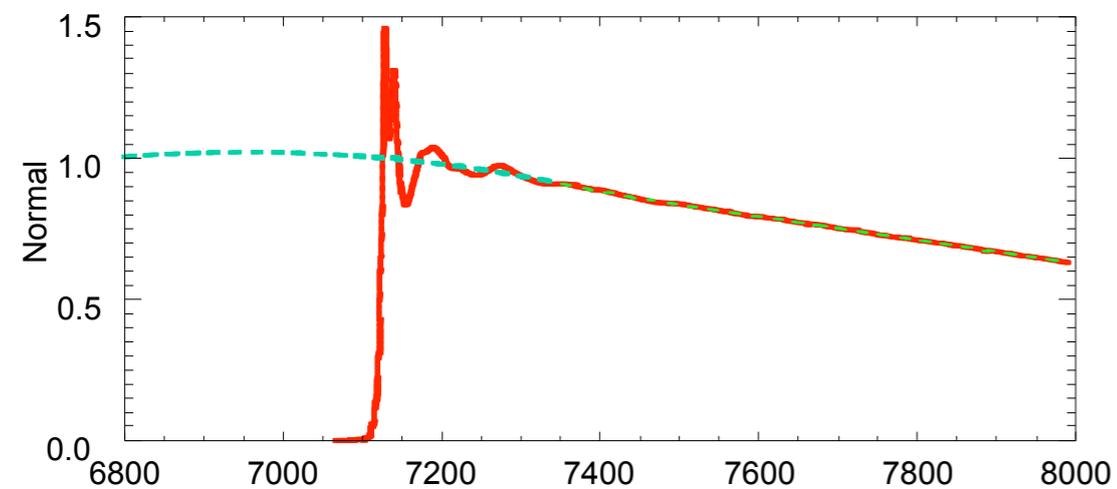
Processing XAS data to extract EXAFS



Raw data: This is the way that the XAS transmission mode spectrum looks, right off the beam line.

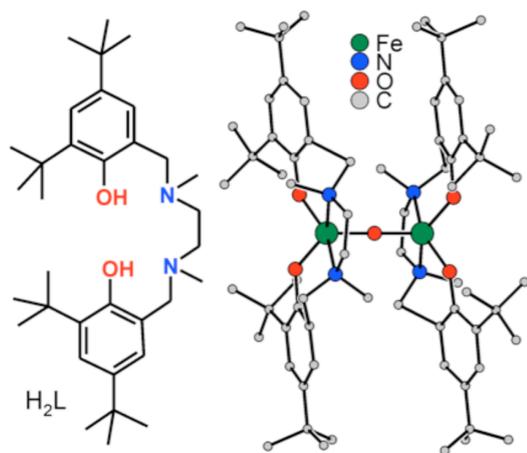
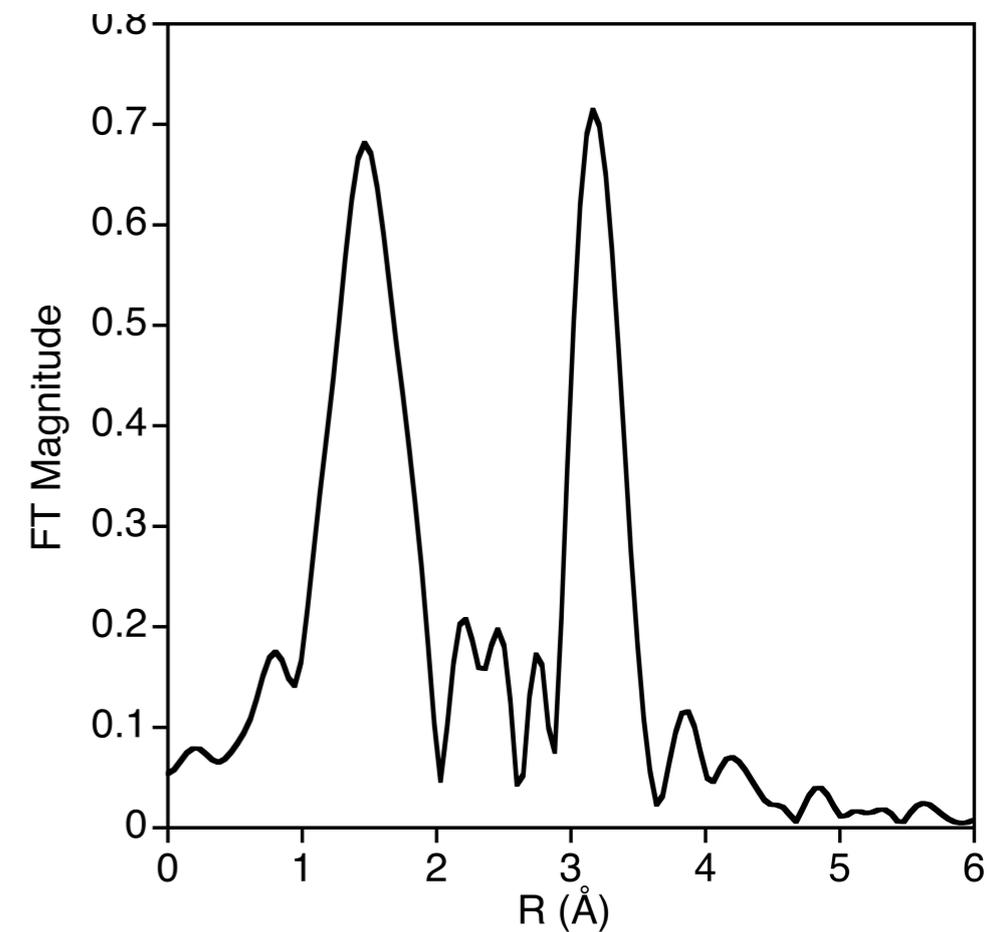
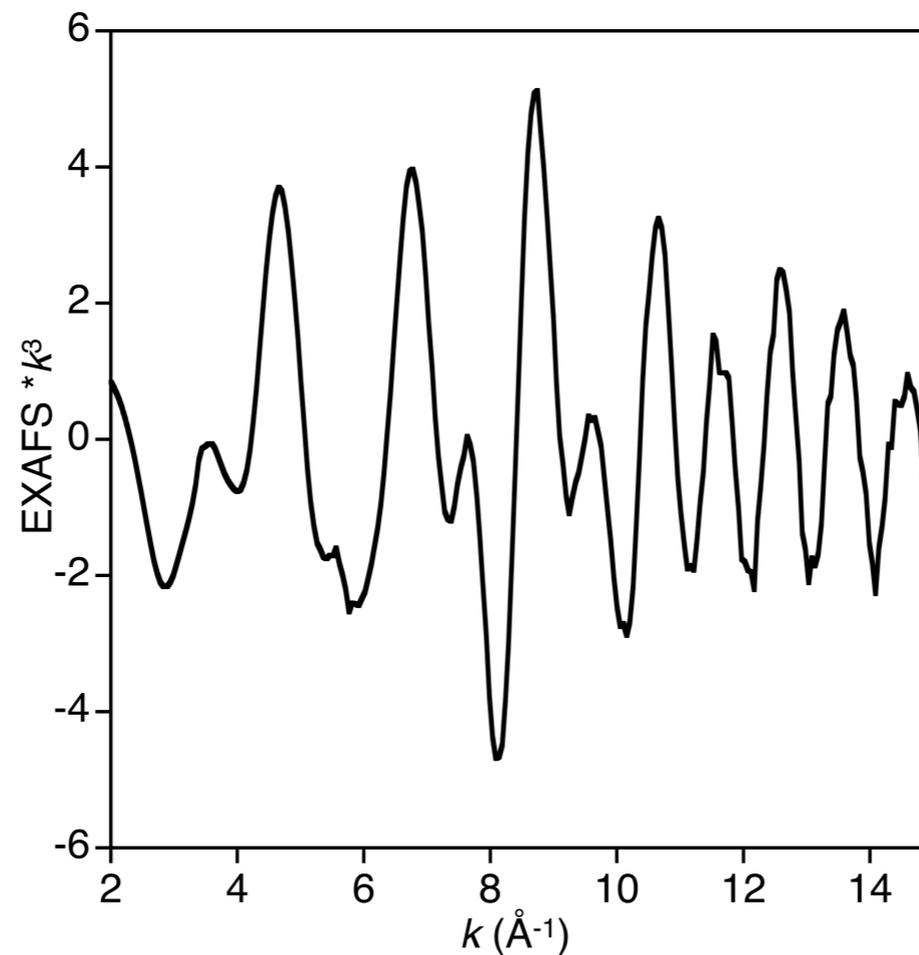
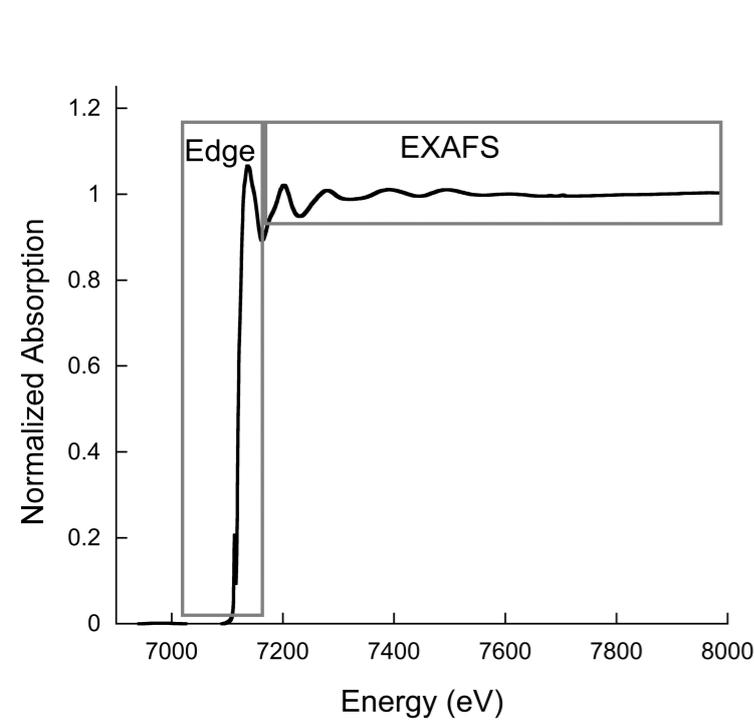


Pre-edge subtraction: A procedure performed to subtract the total absorption from the absorption of the edge in interest.



Spline: A method for removing the atomic background from the absorption curve (i.e. the absorption due to the photoabsorber alone, with out any neighboring atoms).

From k-space to the Fourier Transform



Note:

$$k = (2m(E - E_0)/\hbar^2)^{1/2}$$

EXAFS data are k -weighted to enhance oscillations at high- k .

A Fourier transform allows you to visualize the radial distribution of atoms.

But you cannot simply read distances from an FT!!

EXAFS require fitting!

A bit more mathematically....

EXAFS: the fine structure
oscillation in $\mu(E)$

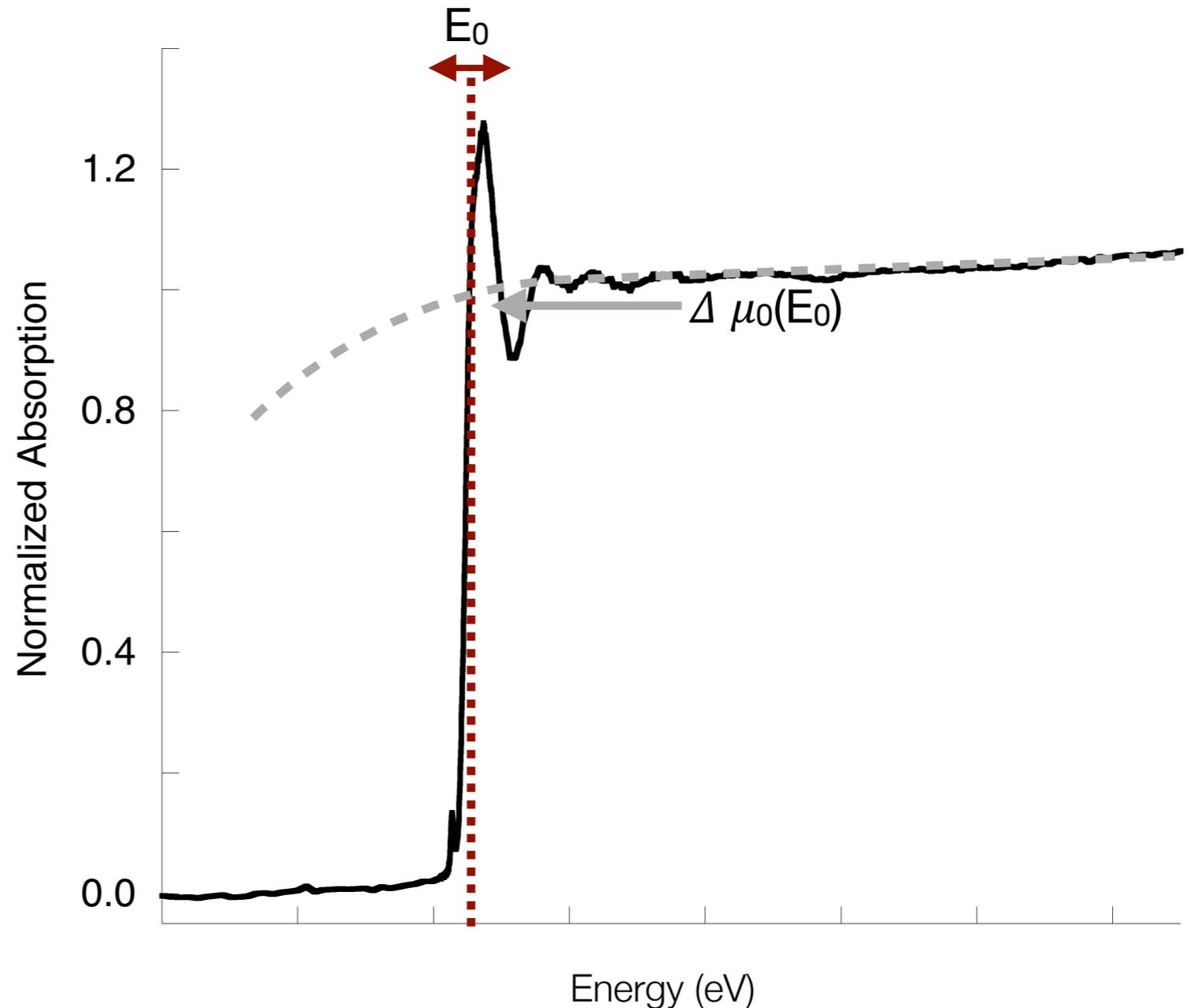
$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

$\mu(E)$ = measured absorption

$\mu_0(E)$ = atomic background

$\Delta\mu_0(E)$ = edge jump measured at

E_0 = origin of the photoelectron
wave vector

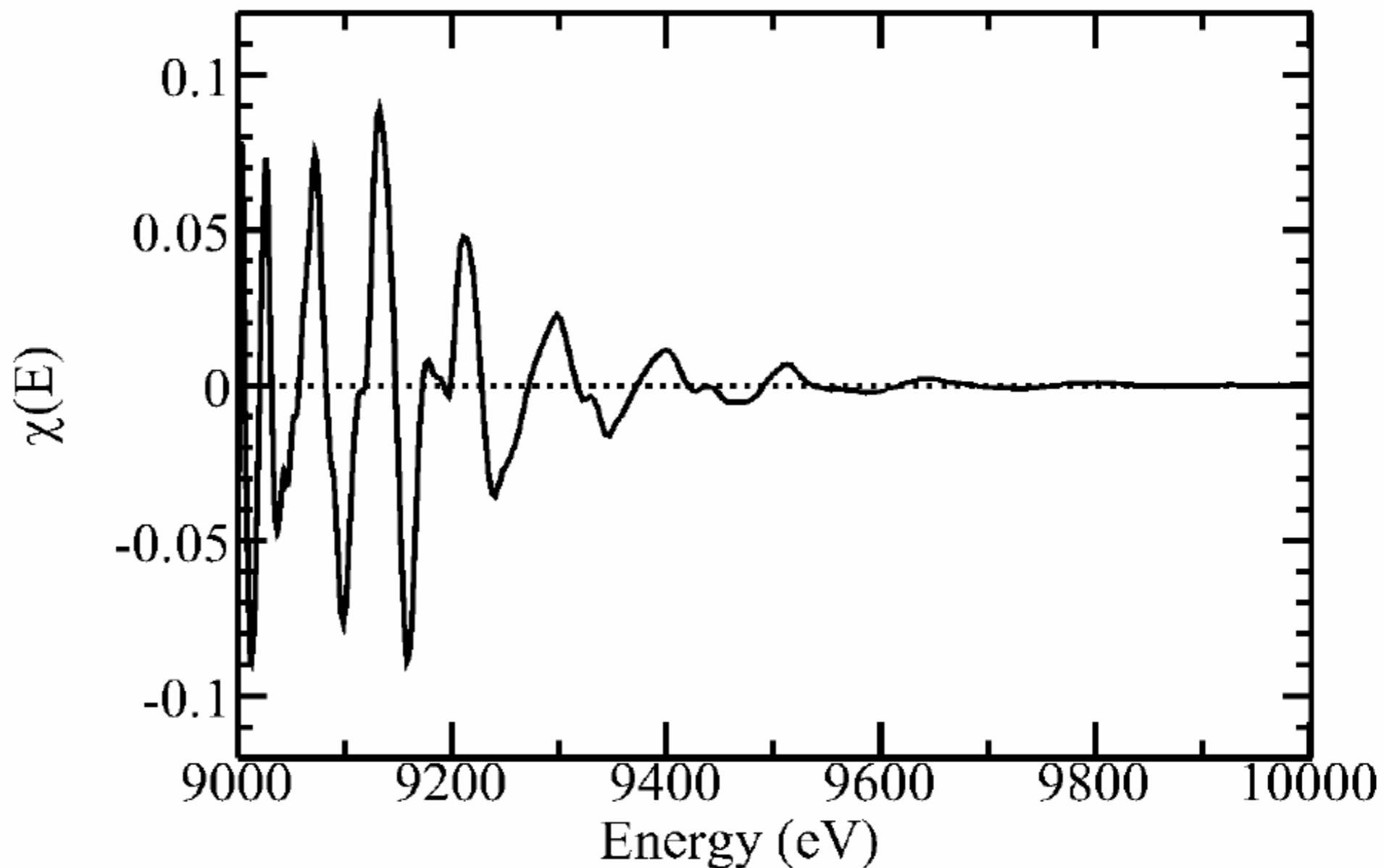


EXAFS in Energy Space

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

You will never see this in a paper!!

Oscillations are compressed and damp out at high energy.....



Converting to k-space

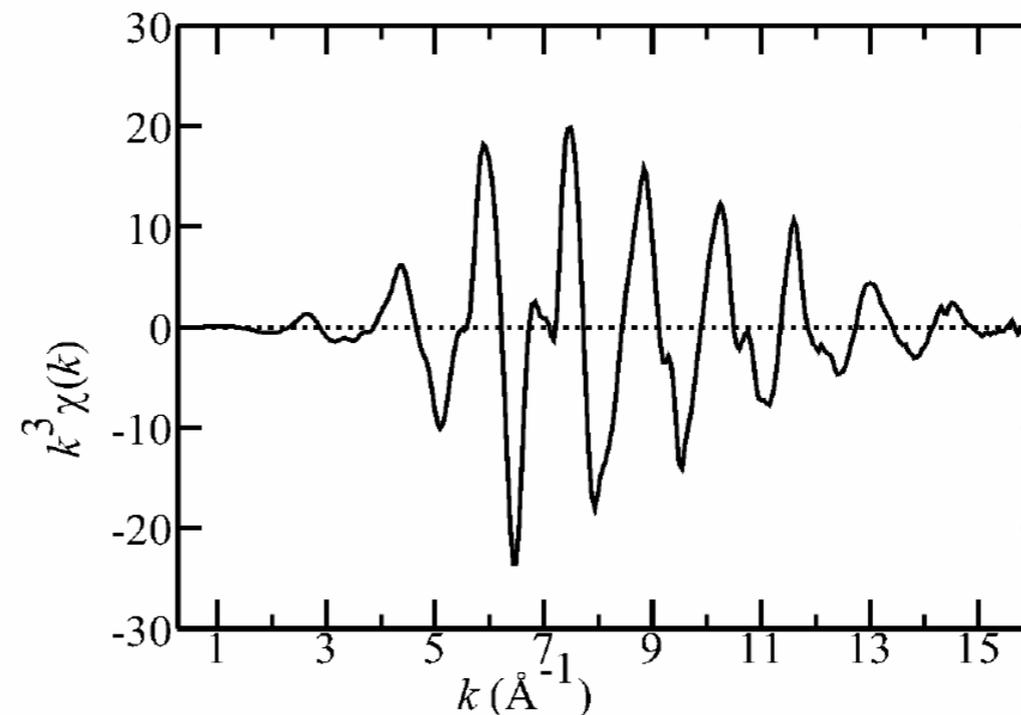
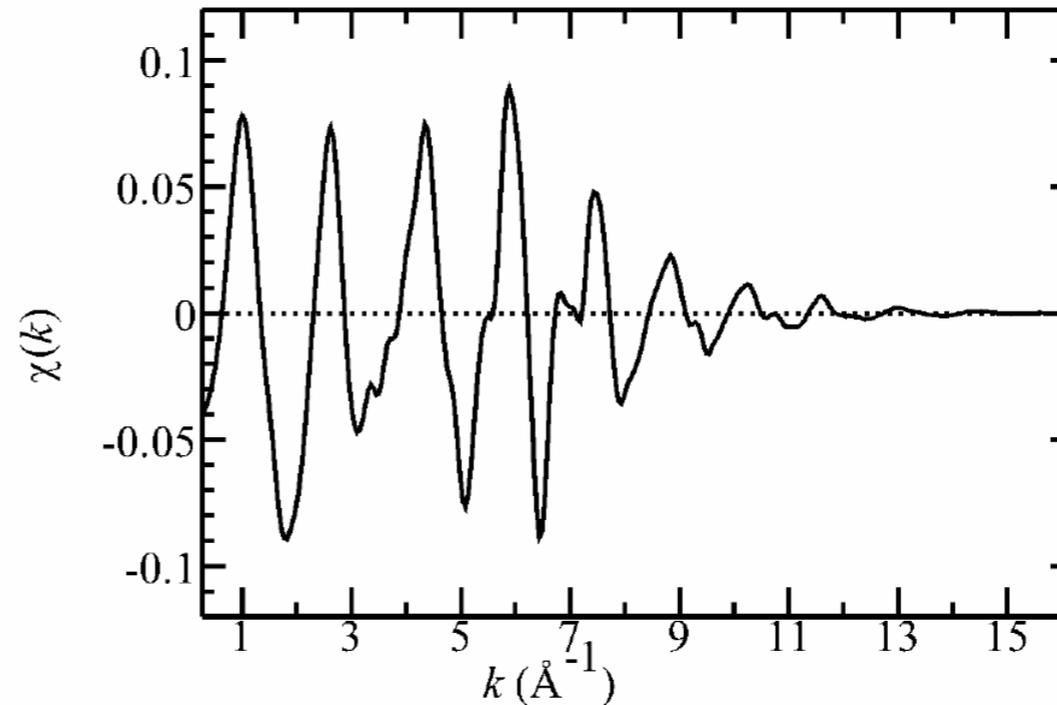
First convert to k-space

$$k = \sqrt{\frac{2m_e(E-E_0)}{\hbar^2}}$$

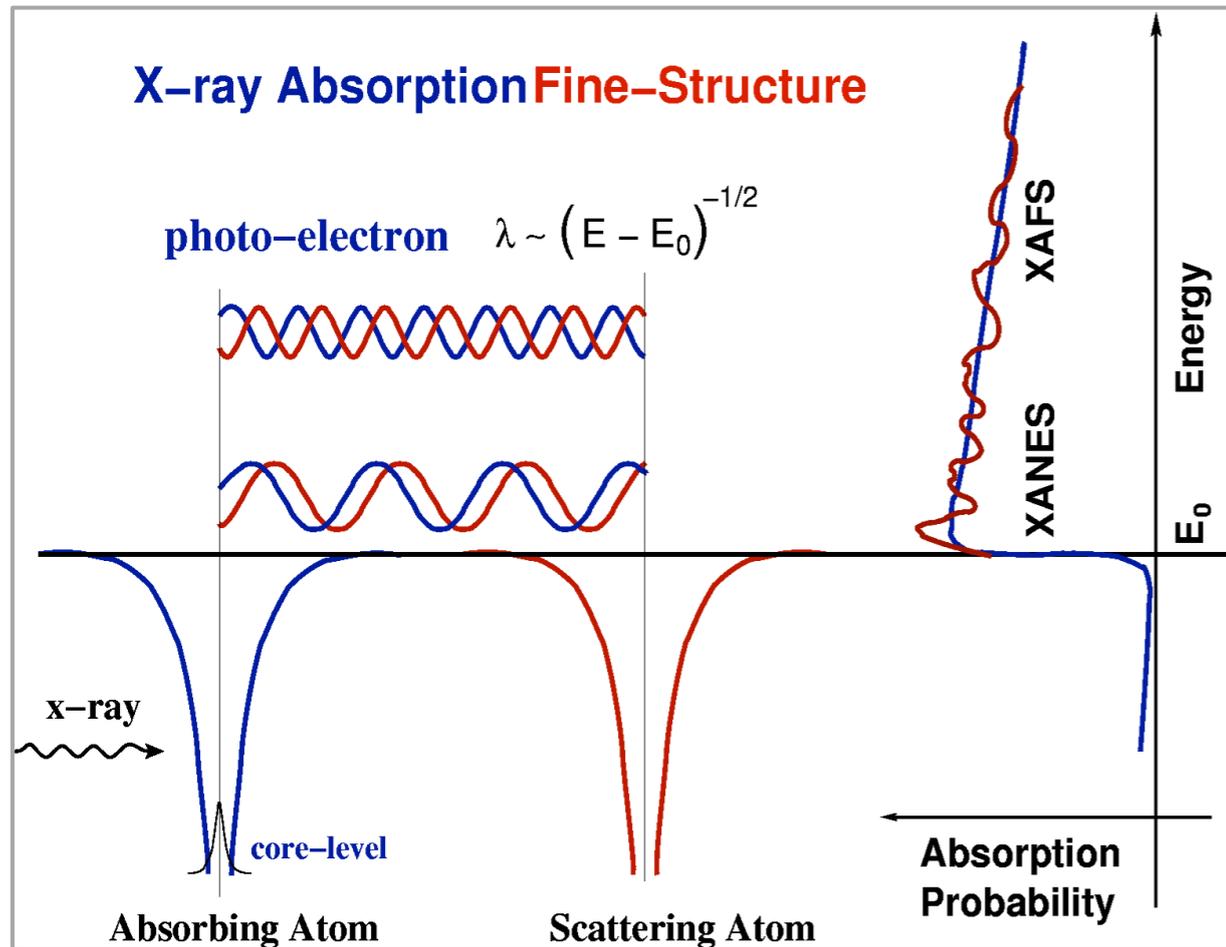
$$k = \sqrt{0.262(E - E_0)}$$

Then k³-weight to enhance oscillations at high k.

Note, getting high k data can be very challenging or impossible!



The EXAFS Equation



The EXAFS results from an outgoing photo-electron scattering from a neighbor atom, and returning to the core atom to interfere with the core level:

$$\chi(k) = \frac{e^{i2kR}}{kR} [kf(k)e^{i\delta(k)}] \frac{e^{i2kR}}{kR}$$

Outgoing photo-electron

Scattering from neighbor atom
(amplitude and phase depend on Z of neighbor atom)

Returning photo-electron

The EXAFS equation....

$$\chi(k) = \frac{e^{i2kR}}{kR} [kf(k)e^{i\delta(k)}] \frac{e^{i2kR}}{kR}$$

Photo-electron scattering

$$\chi(k) = \frac{Nf(k)}{kR^2} \sin [2kR + \delta(k)]$$

The EXAFS Equation for 1 atomic site (no disorder)

Averaging over all atoms in the sample, which has a distribution of distances (including structural and thermal disorder) the EXAFS Equation becomes:

$$\chi(k) = \frac{Nf(k)}{kR^2} e^{-2k^2\sigma^2} \sin [2kR + \delta(k)]$$

σ^2 = mean-square disorder in R

This fairly simple equation allows us to model near-neighbor species - through $f(k)$ and $\delta(k)$ - and distance R , and coordination number N .

Generalized expression for EXAFS....

$$\chi(\mathbf{k}) = \sum_j \frac{N_j f_j(\mathbf{k}) e^{-2R_j/\lambda(\mathbf{k})} e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(\mathbf{k})]$$

Where, N_j = number of atoms of type j

R_j = interatomic distance

σ_j^2 = mean-square deviation in R_j (Debye-Waller)

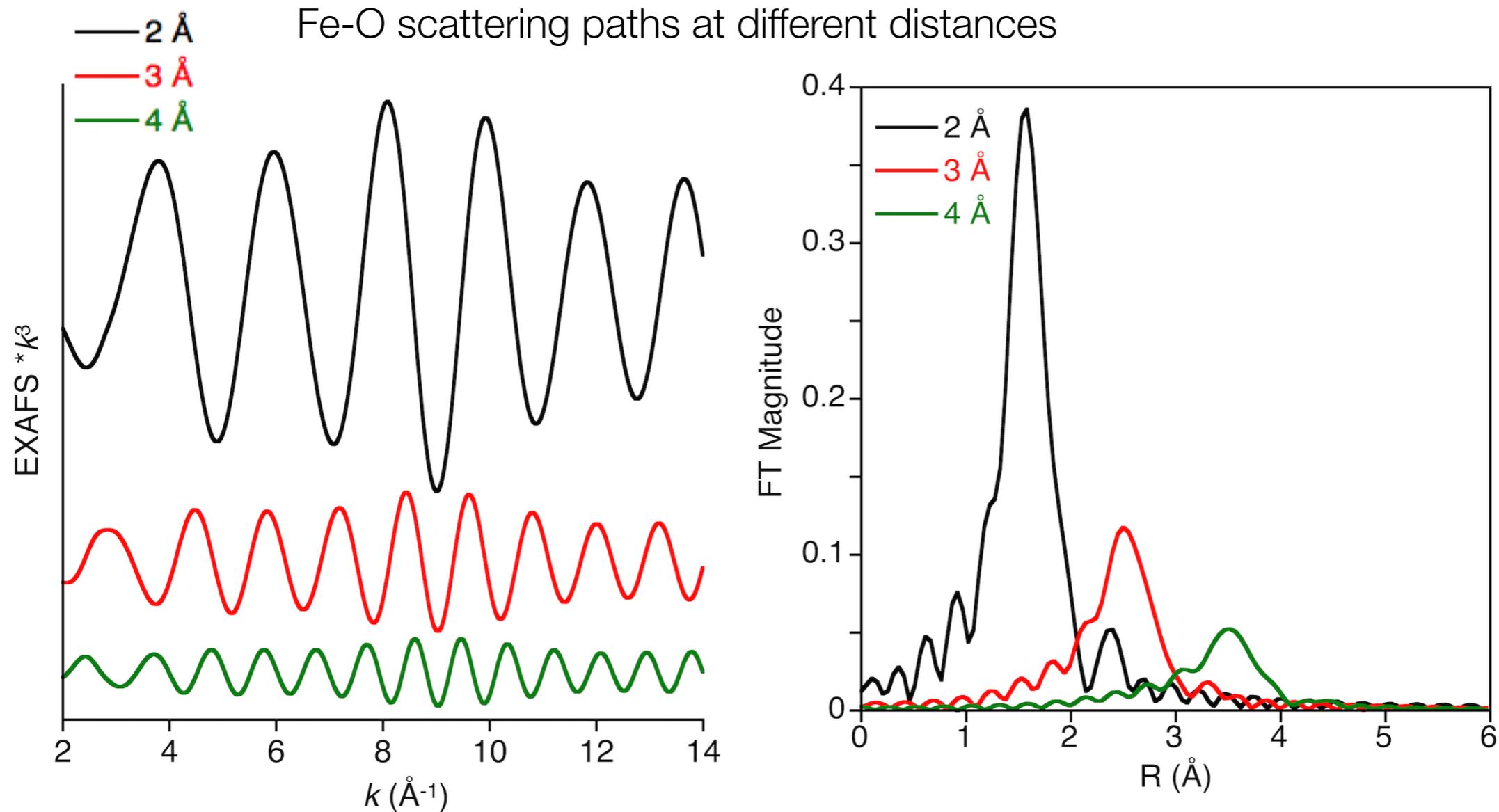
$\lambda(k, R_j)$ = photo-electron mean free path

$f_j(k)$ = amplitude function

$\delta_j(k)$ = phase function

Summation is over all sets of similar scatterers, j .

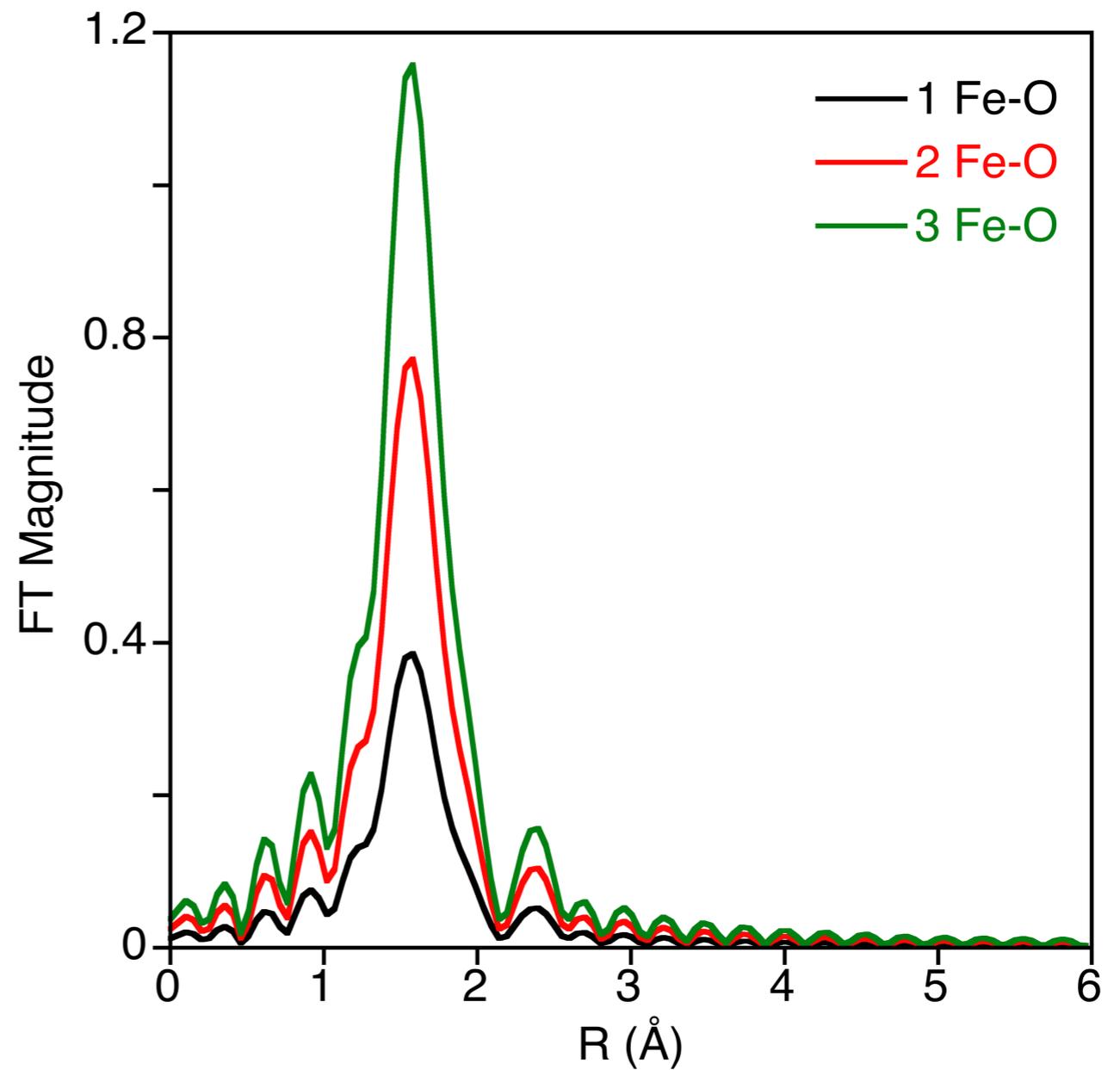
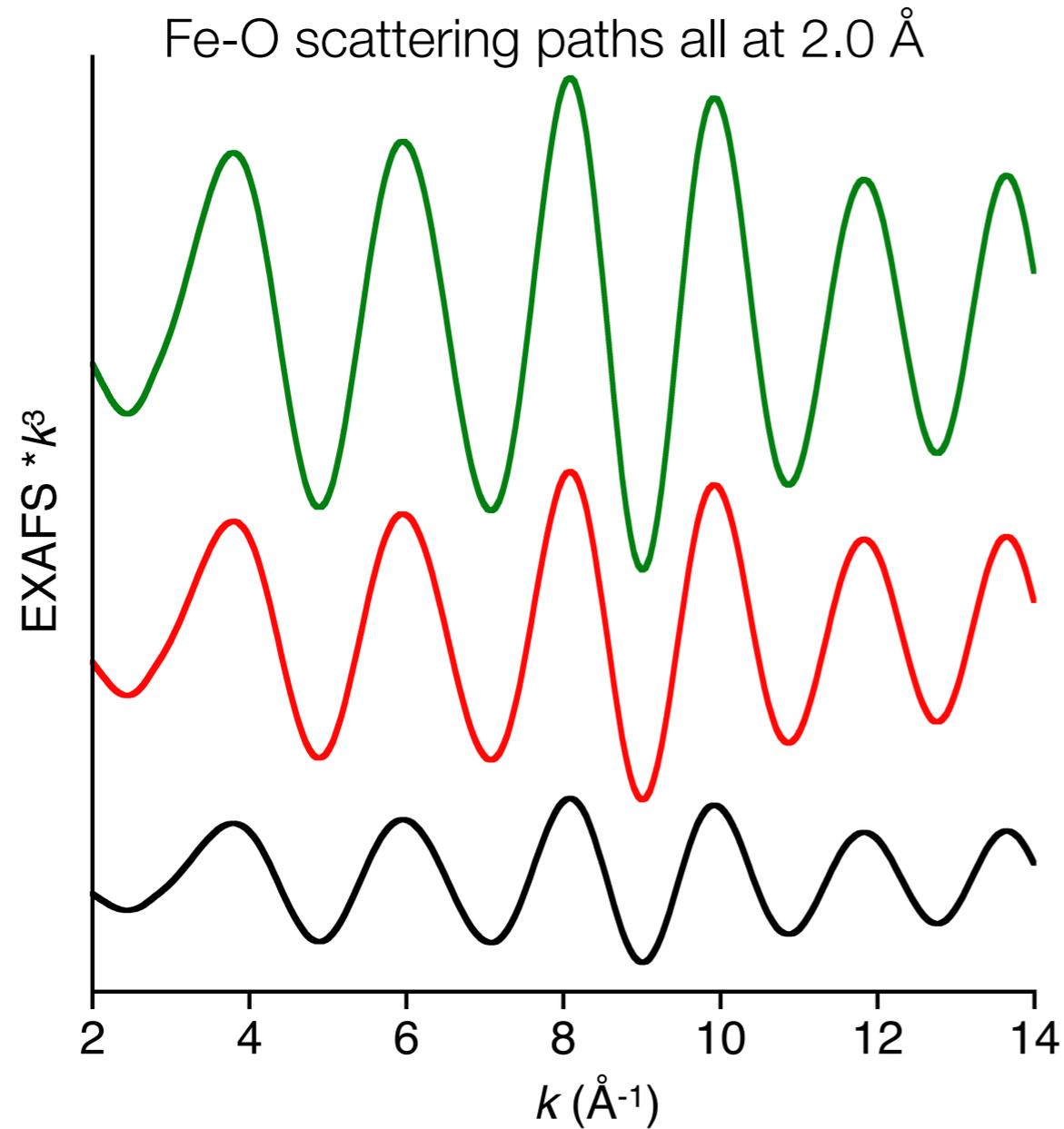
The Effect of Distance on the EXAFS Signal



The larger the distance R , the more rapid the oscillations will be (longer distance => higher frequency).

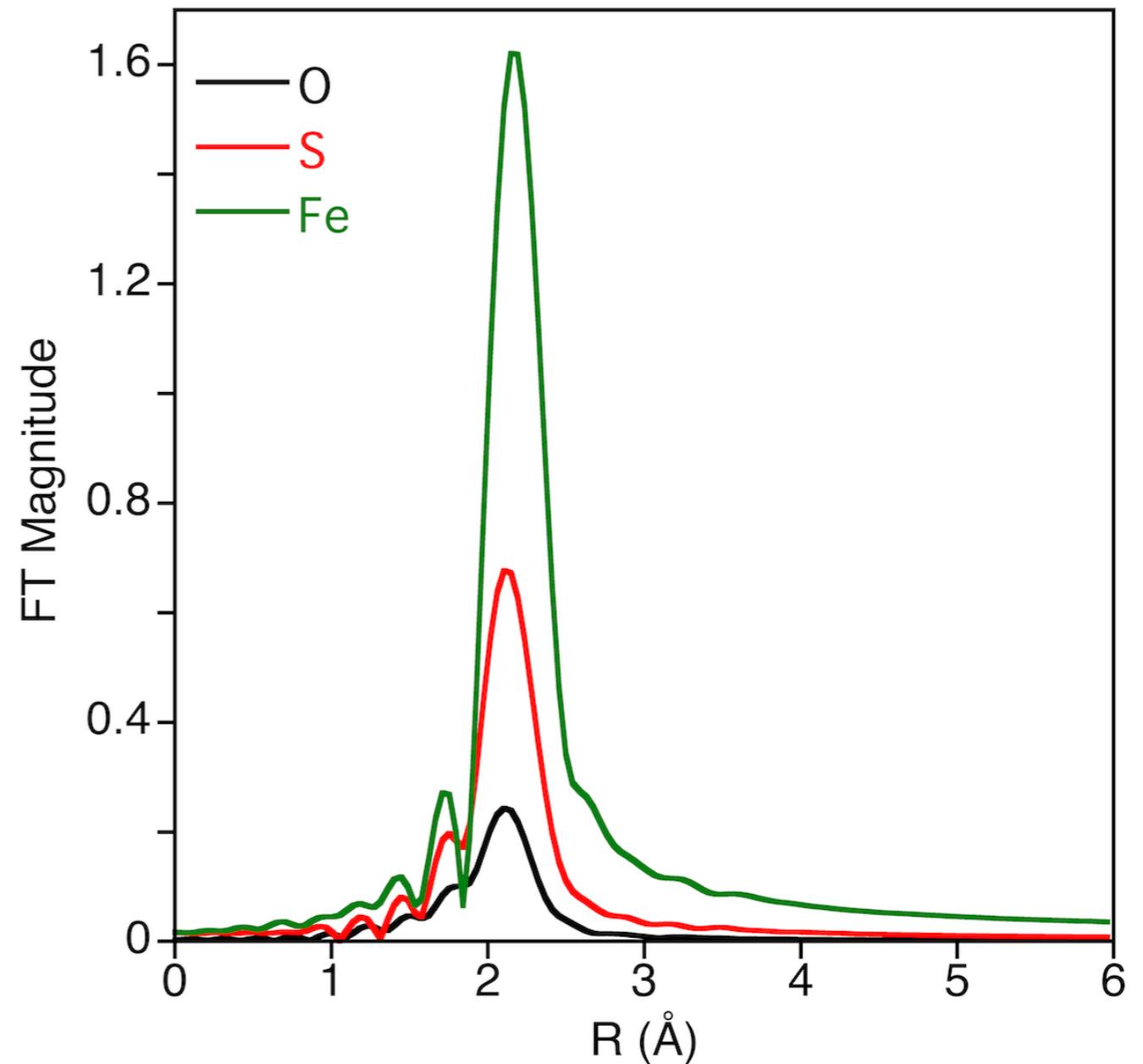
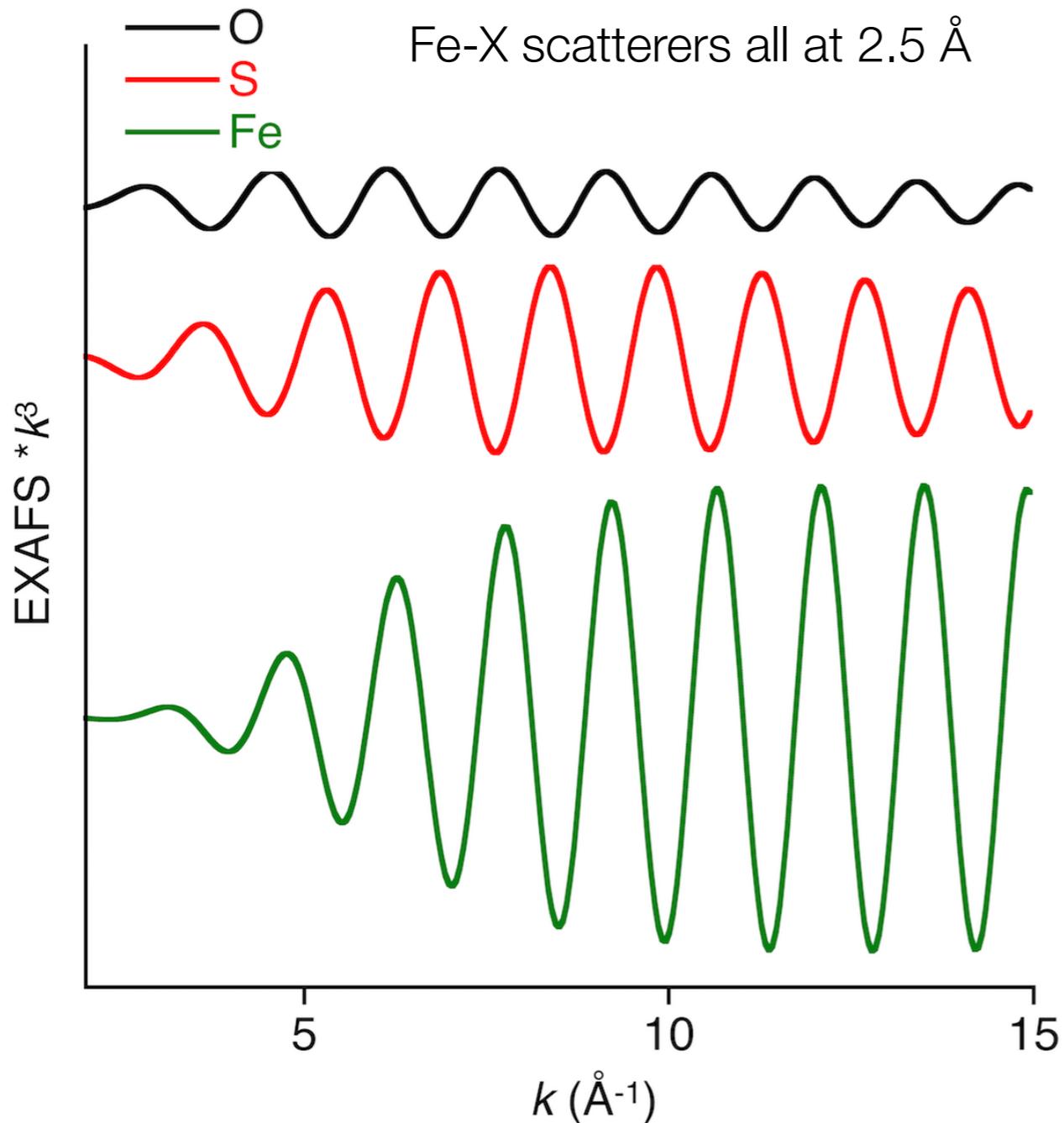
Distance (R) also reduces the EXAFS amplitude by $1/R^2$. Therefore, the longer the distance the weaker the EXAFS will be.

The Effect of Coordination Number



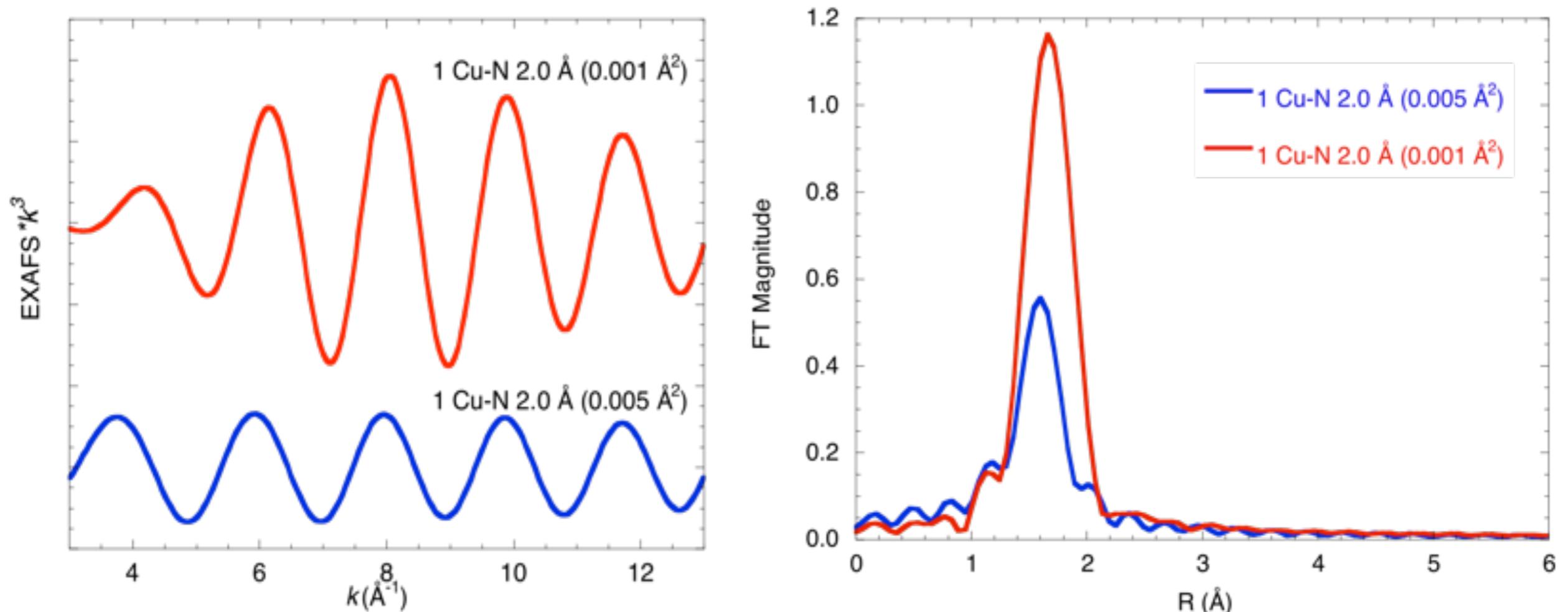
For a given backscatterer at distance R , amplitude increases linearly with N (the number of atoms).

The Effect of Backscatterer Identity



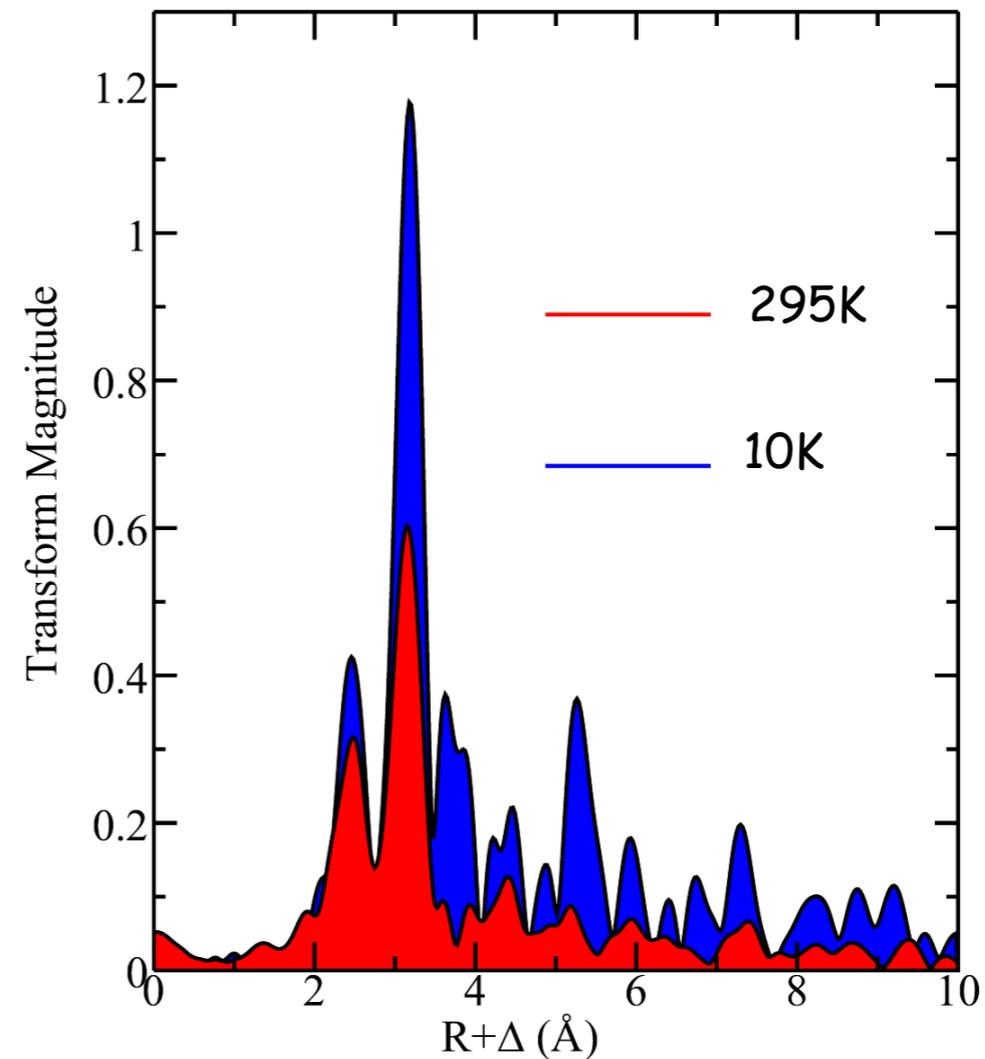
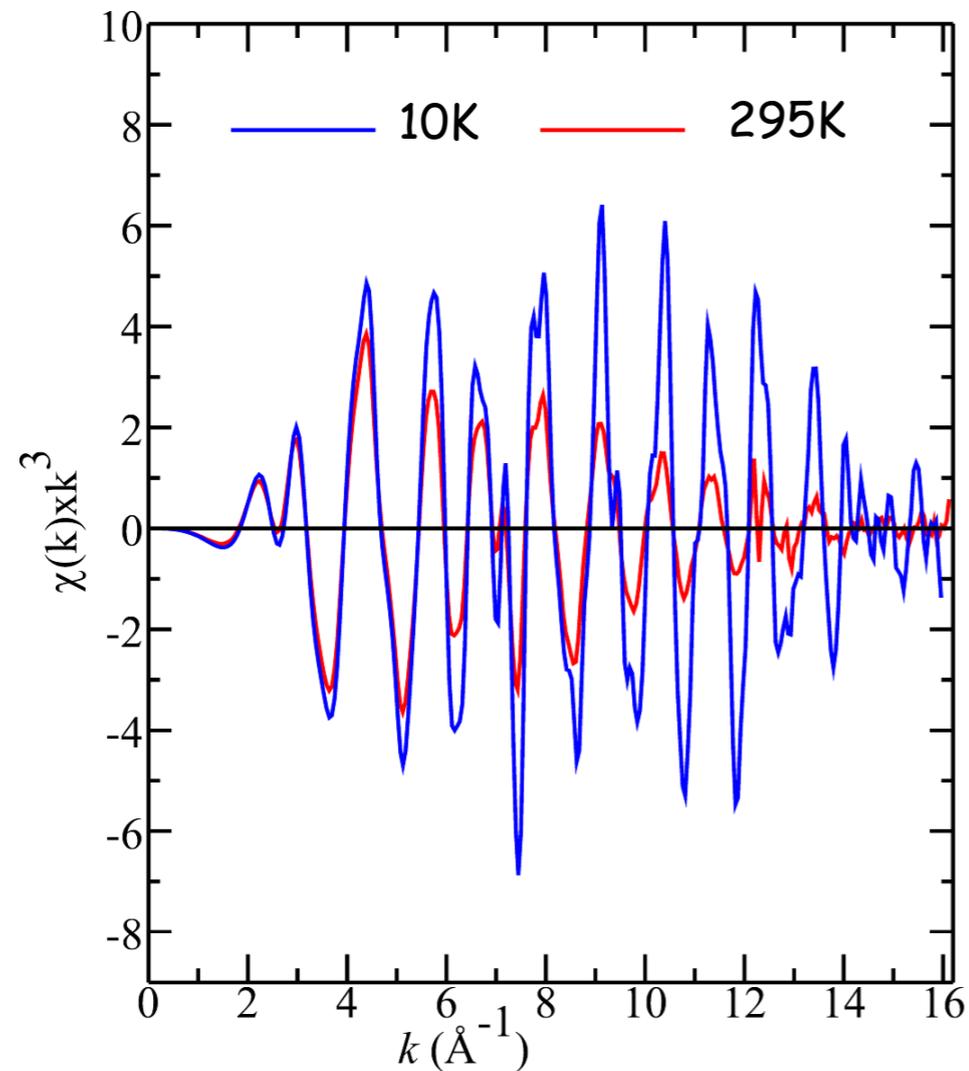
The heavier the atom the larger the modulation in the absorption coefficient and the stronger the contribution to the EXAFS

The Effect of The Debye-Waller Factor on the EXAFS Signal



The Debye-Waller factor accounts for thermal vibration and static disorder. At 10K, thermal vibration is minimized and static disorder dominates. More later...

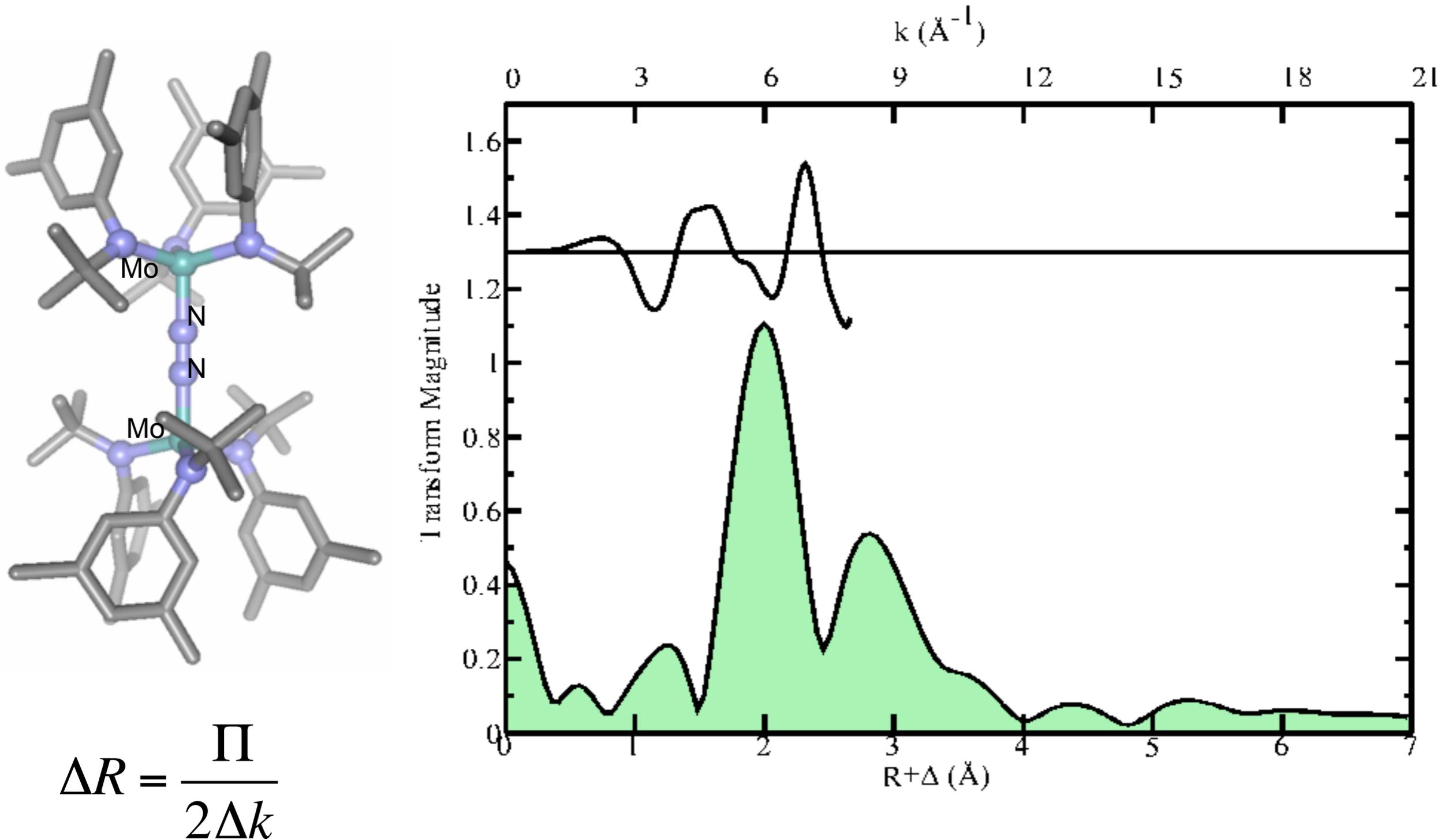
The effect of temperature...



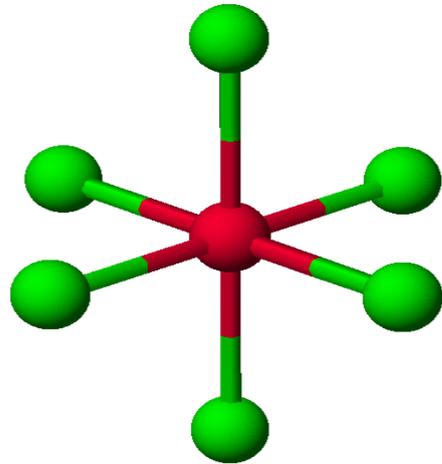
e.g. Sr K-edge EXAFS of a strontium model compound. At room temperature the EXAFS is weak, and outer shells not visible.

Modeling Debye-Waller factors can be much more complex at high temperatures (our simple Gaussian model often does not work).

The Effect of k-range on resolution



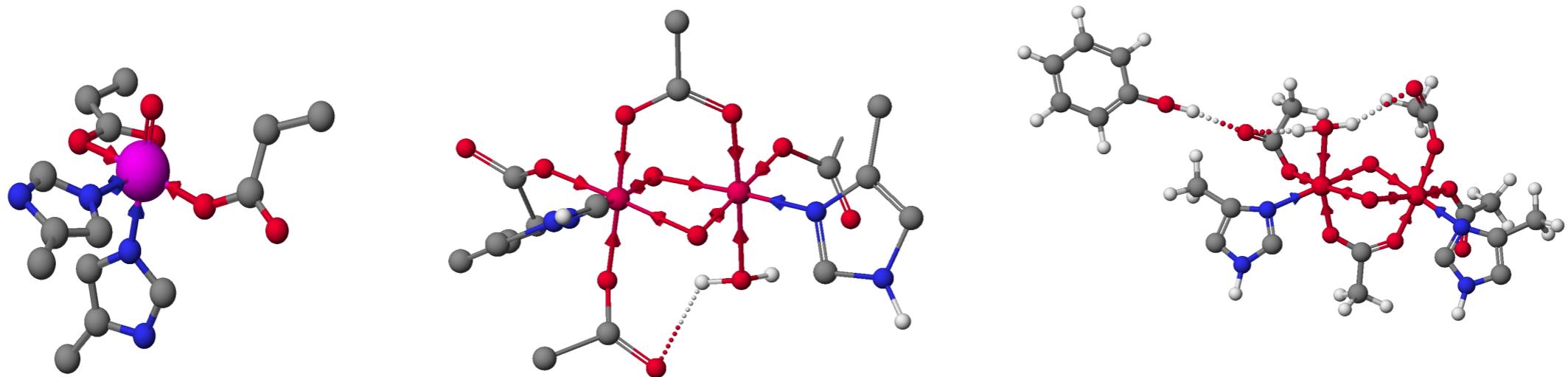
Resolution and Static Disorder....



A rigorously O_h site with all bonds exactly at 2.00 Å has no static disorder. The DW values will be small. On the order of $\sim 0.003 \text{ \AA}^2$.

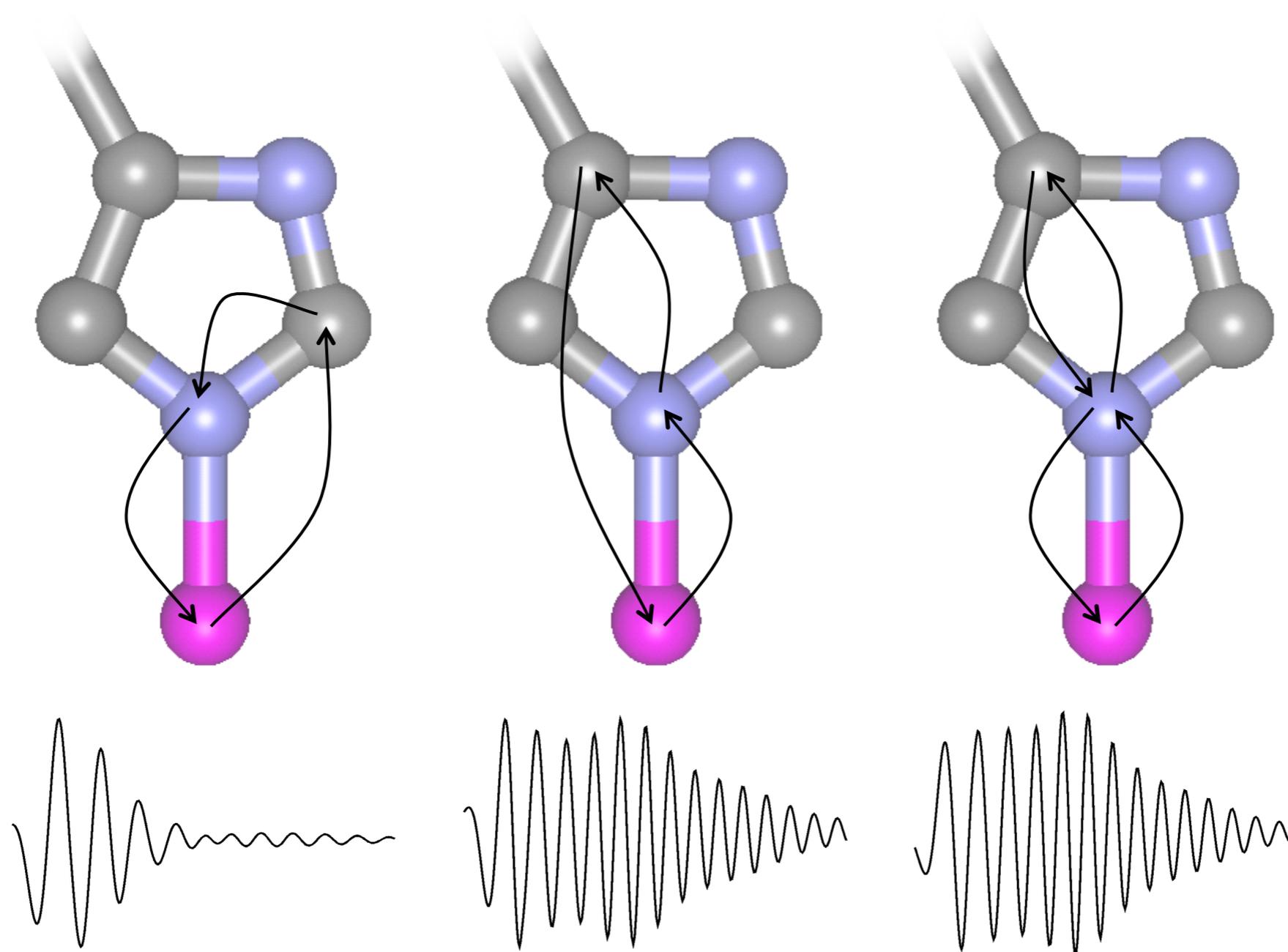
But biological active sites don't look like this!

Biological active sites (and related models) have a lot of intrinsic disorder!



Static disorder is present in both the first shell and in the outer shell multiple scattering.

And Multiple scattering makes this even worse....



What does this mean for my EXAFS fitting?

EXAFS Calculations and Fitting...

$$\chi(k) = \text{const} \times \sum_{P(\text{pathways})} N_P \frac{|f_{\text{eff}}^{(P)}(k)|^2}{kR_P^2} \sin(2kR_P + \phi_k^{(P)}) e^{-2kR_P/\lambda_k} e^{-2\sigma_P^2 k^2}$$

FEFF calculates:

f_{eff} = scattering amplitude

ϕ = phase shift

λ = mean free photoelectron path

R_P : Length of the pathway

N_P : Number of equivalent scattering pathway

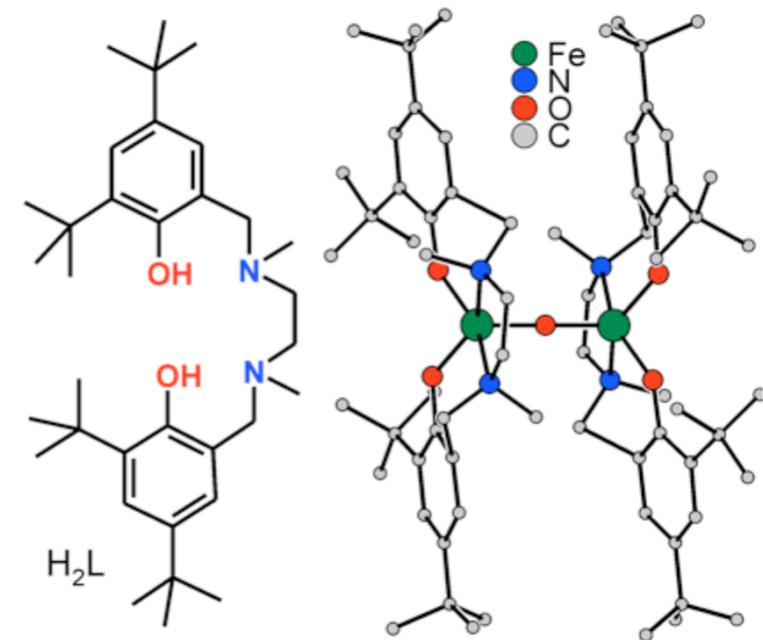
σ_P : Debye-Waller parameter for the pathway

For every single path in a given input model

Maximum Number of Independent Parameters is given approx by:

$$N_{\text{idp}} = \frac{2\Delta k \Delta R}{\pi} + 2.$$

Stern et al. Phys. Rev B, 48, 1993, 9825.



FEFF calculates 98 paths with >5% contribution (from just one iron!)

Paths *must* be grouped to avoid overfitting!

The Debye-Waller in More Detail....

Mathematically the fit DW is comprised of both thermal and static disorder.

$$\sigma_R^2 = \sigma_R^2(T) + \sigma_R^2(sd)$$

Programs such as FEFF calculate the thermal DW values for each scattering path separately.

$$\sigma_R^2(T) = \sum_i \frac{N_i}{N} \sigma_{R_i}^2(T)$$

Static disorder becomes significant when the resolution of your data do not allow you to separate similar paths

$$\sigma_R^2(sd) = \sum_i (R_i - \langle R \rangle)^2 \frac{N_i}{N}$$

Distance of path i

Average distance for a given set of paths

Assume 0.003 \AA^2 is a reasonable DW value for a single Fe-O/N scattering path at $\sim 2.00 \text{ \AA}$.

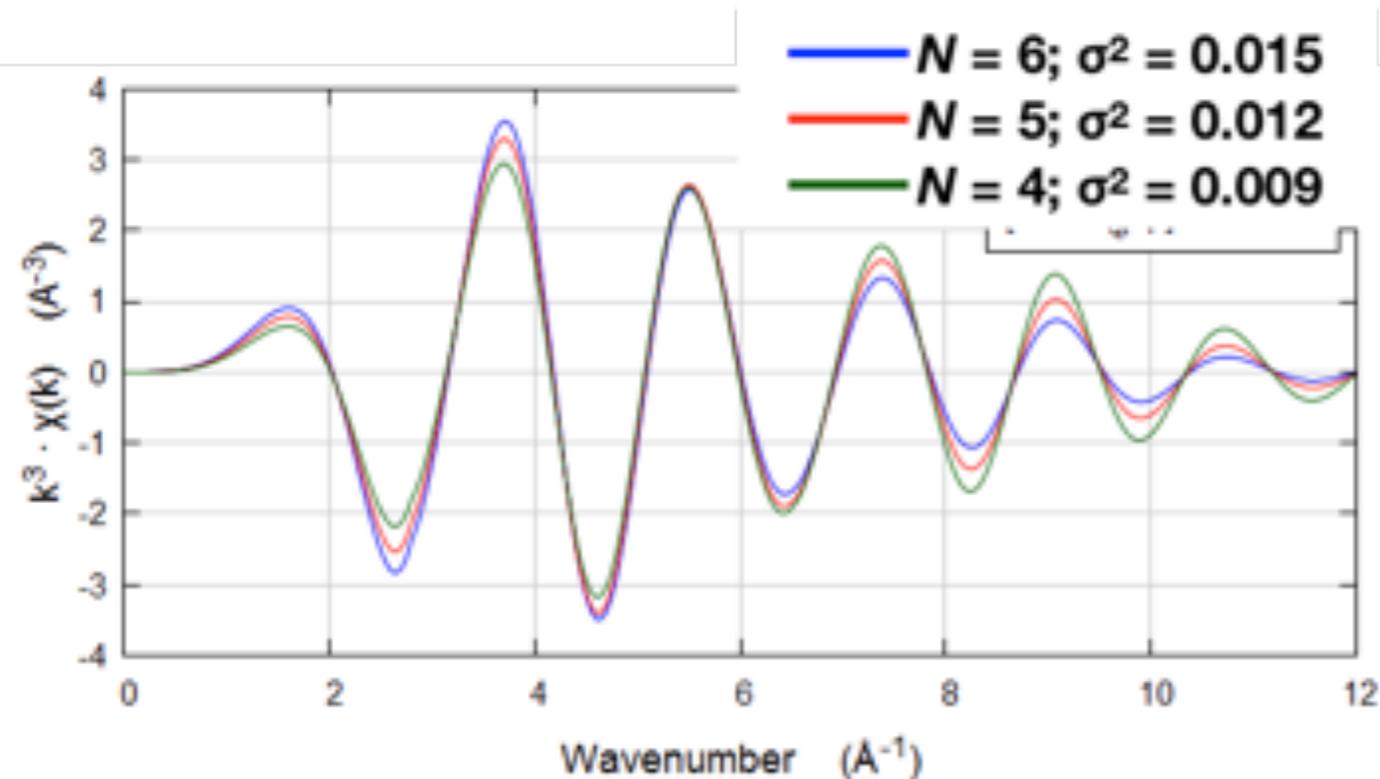
2 Fe-N/O at 2.00 \AA
2 Fe-N/O at 2.10 \AA
2 Fe-N/O at 2.16 \AA
avg Fe-N/O = 2.09 \AA

resolution for $k=2-11 \text{ \AA}$ data is 0.17 \AA

then the added static disorder component is 0.0043 \AA^2 or a $\sigma(T) + \sigma(sd) = 0.0073 \text{ \AA}^2$.

Outer shell MS can have *very* significant disorder!

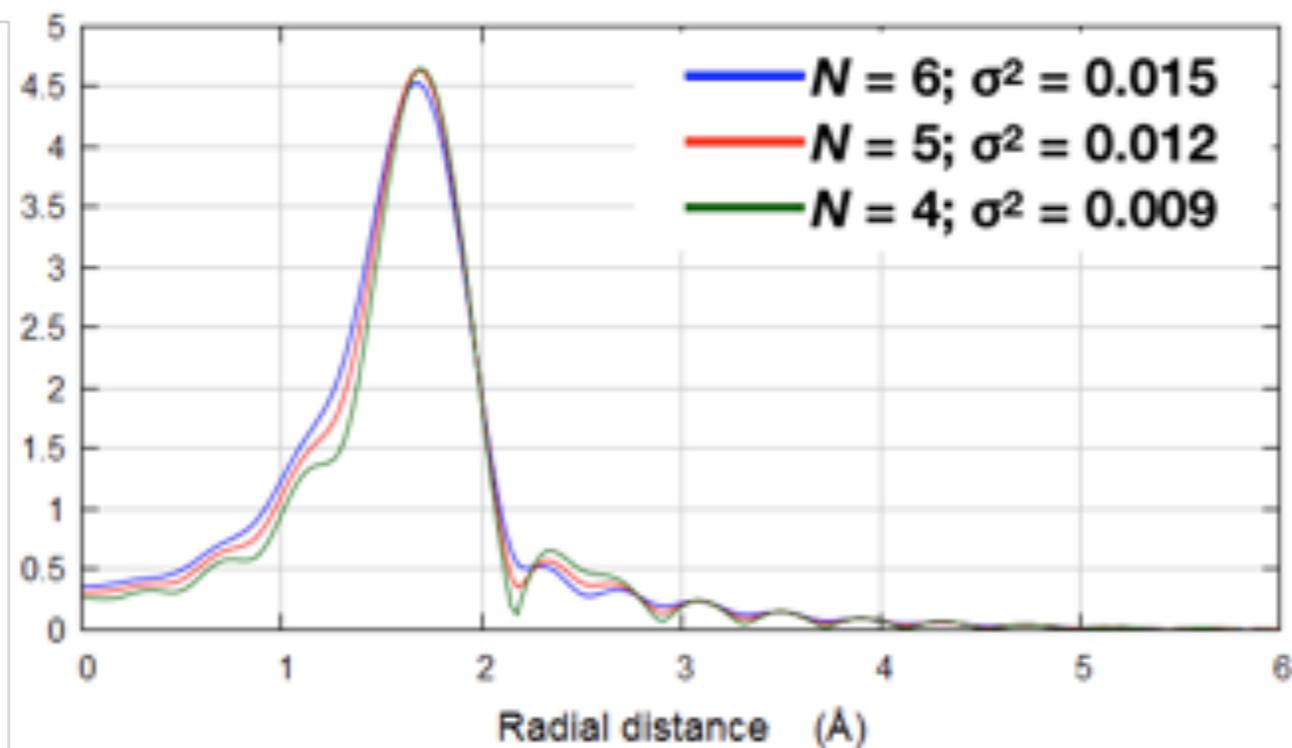
Uncertainty in Coordination Number



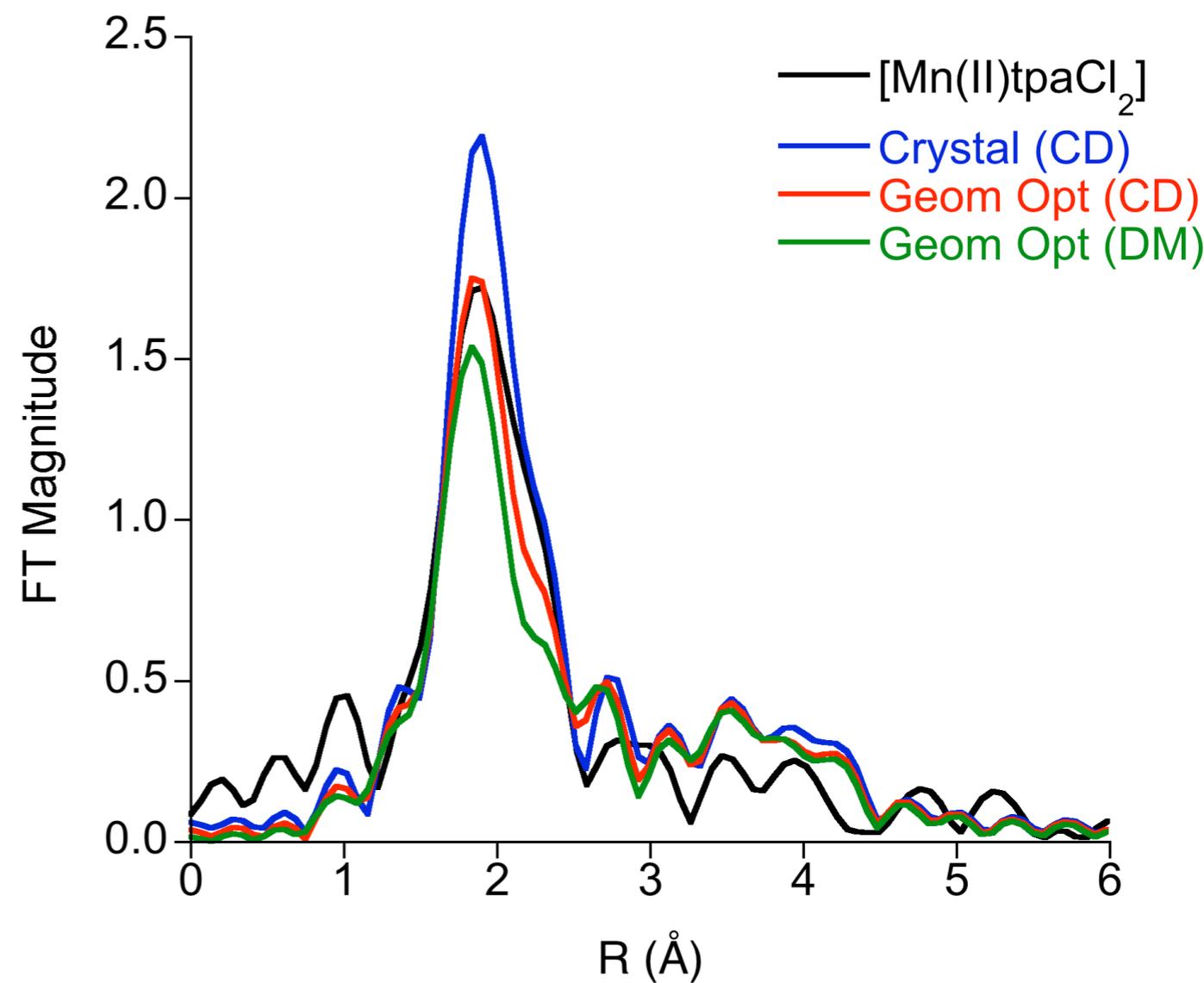
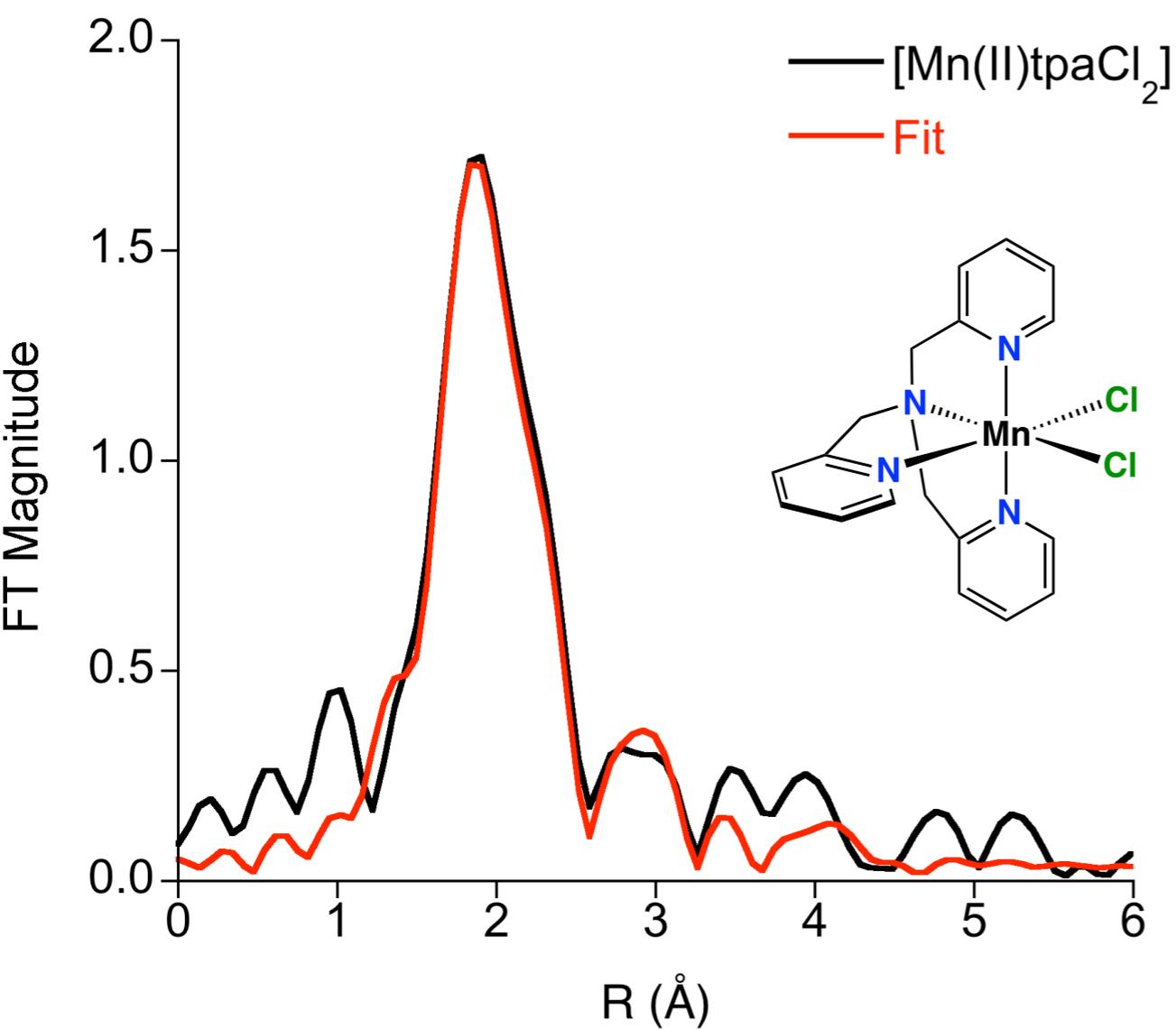
The impact of disorder results in greater uncertainties in coordination number

Correlated pre-edge analysis can help (in some cases) - we can calculate these well!

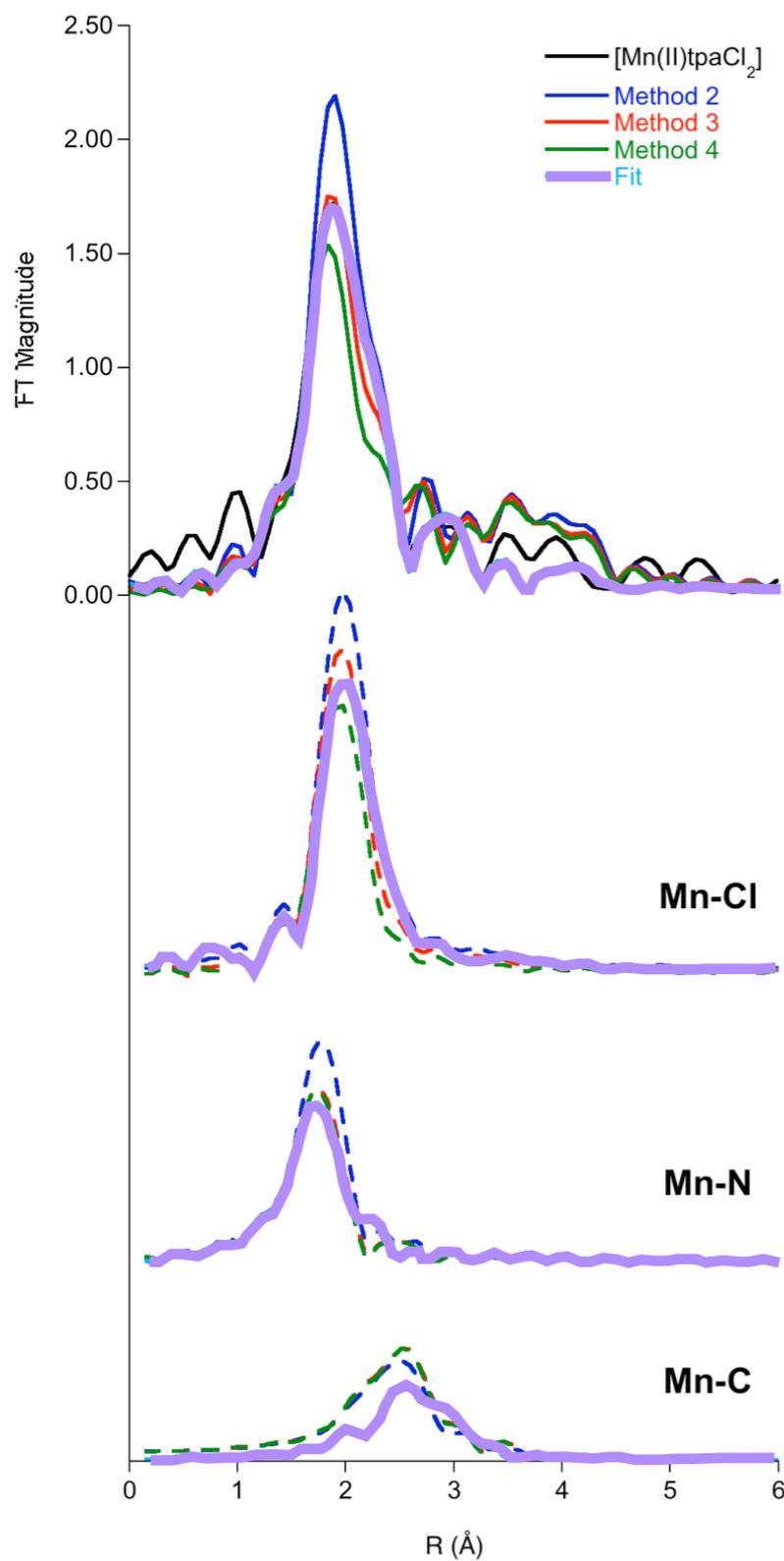
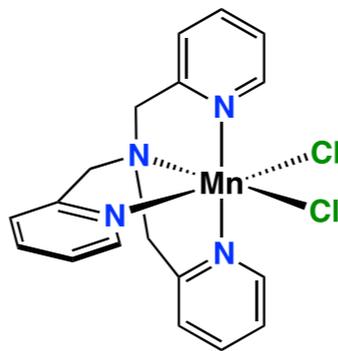
But how well can we calculate EXAFS? Can it be used in a predictive fashion?



Fitting vs. Predicting



A Closer Look

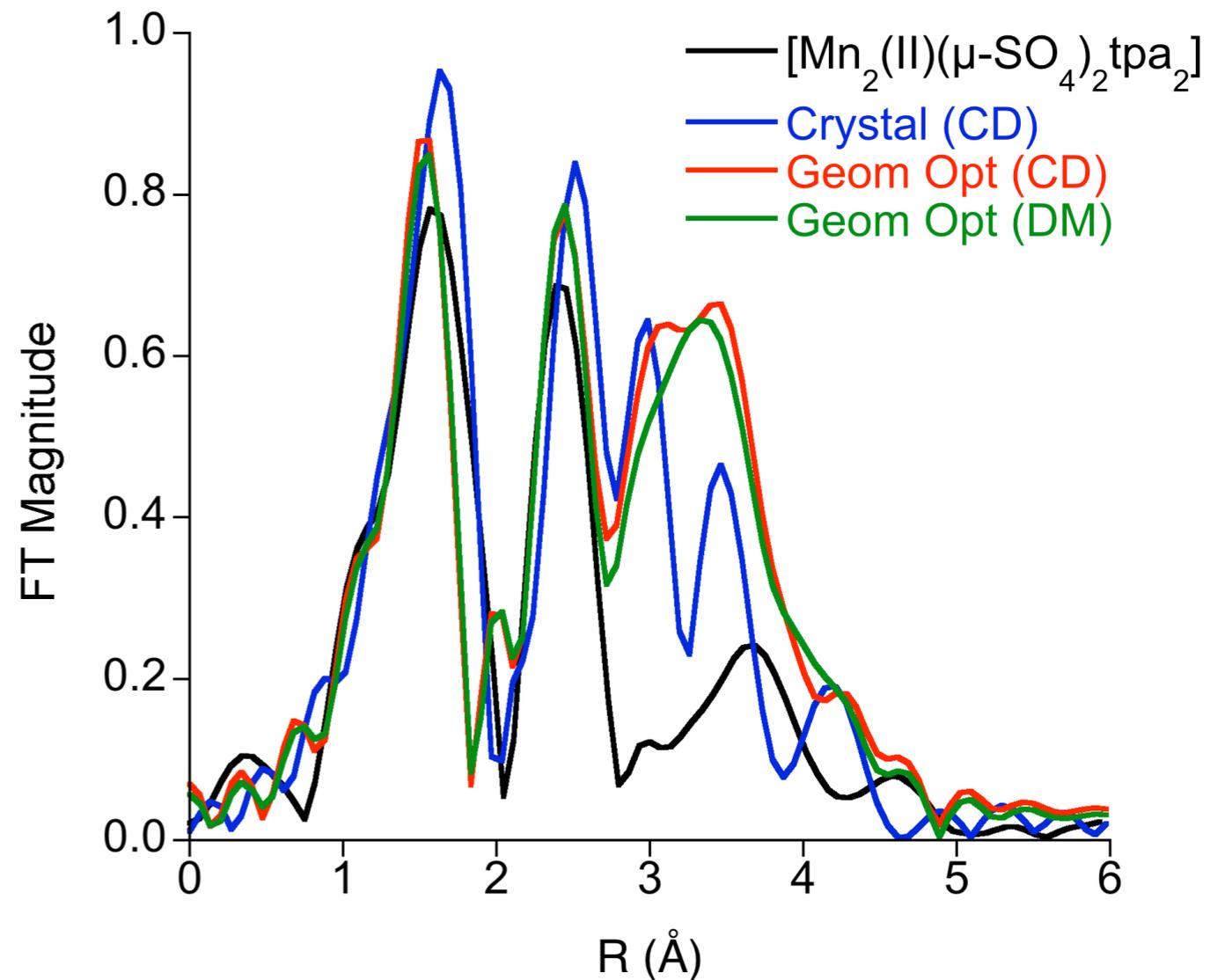
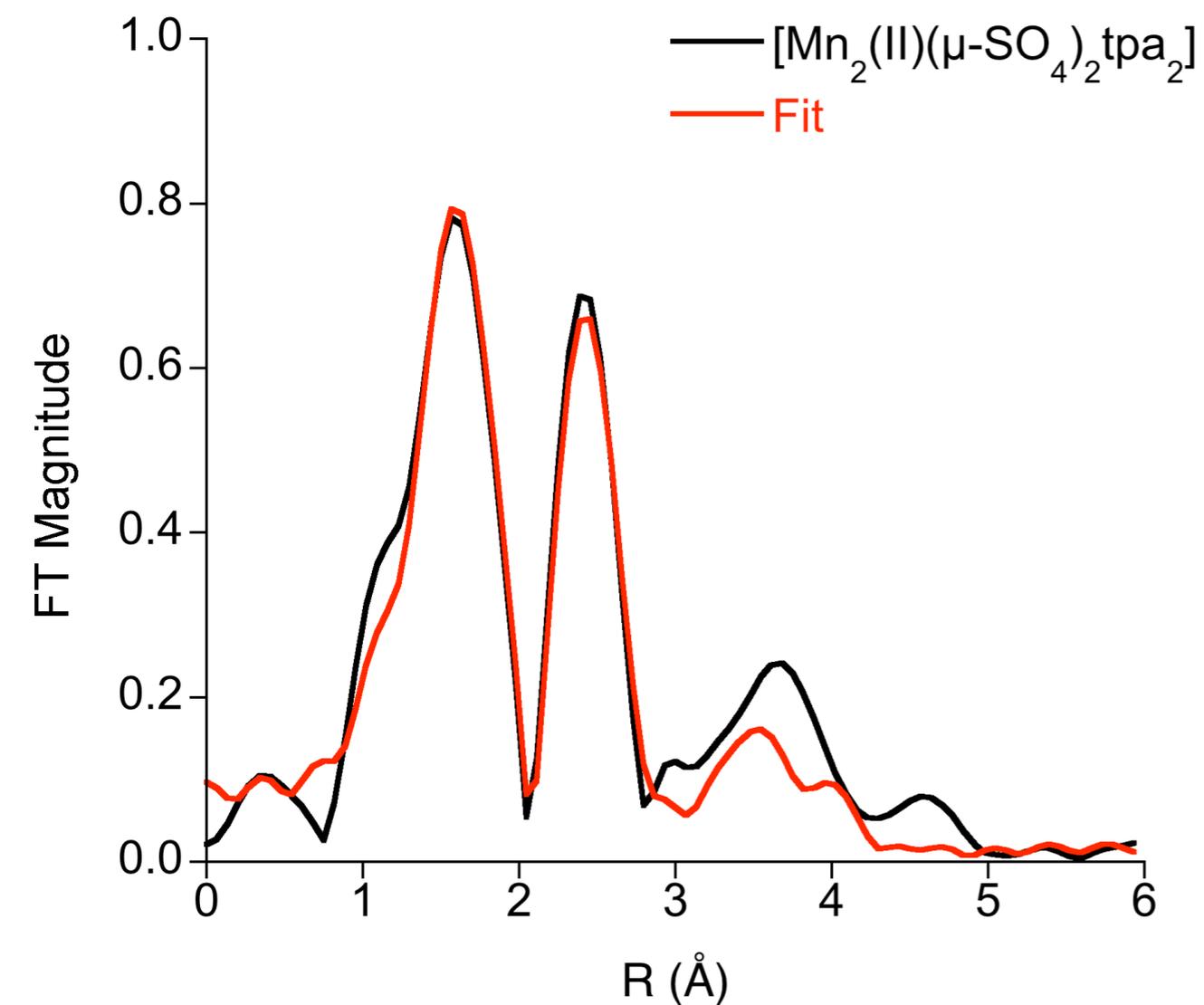
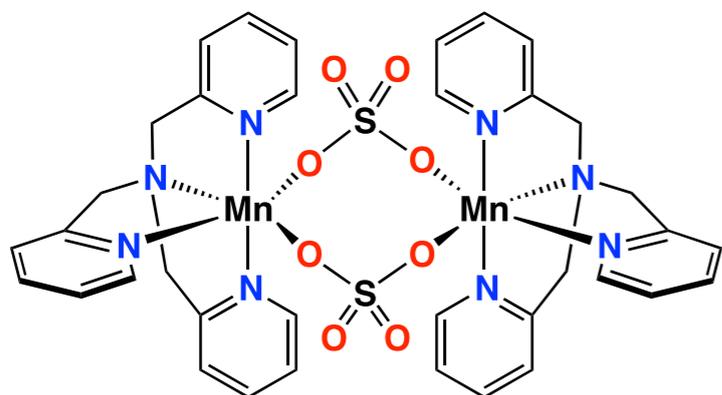


Path		Fit (Data)	Crystal (CD)	Geom Opt (CD)	Geom Opt (DM)
Mn-Cl	R (Å)	2.44	2.44 (± 0.02)	2.43 (± 0.04)	2.43 (± 0.04)
	σ^2 (Å ²)	0.0025	0.0017 (± 0)	0.0017 ($\pm 0.1e-4$)	0.0035 ($\pm 4e-4$)

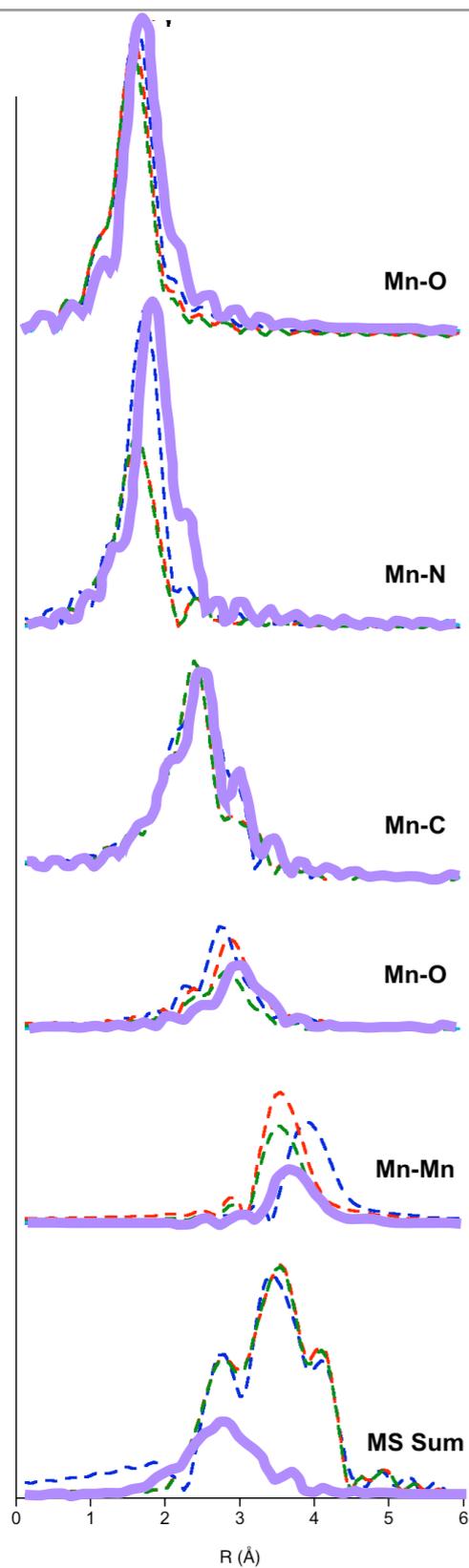
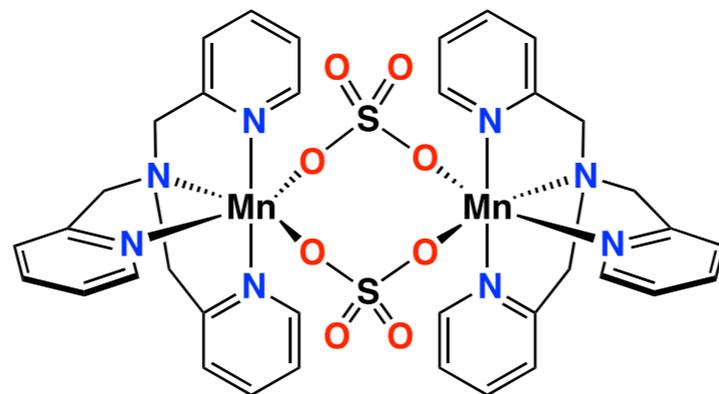
- ▶ Distances predicted well
 - ✓ $\Delta R = 0-3\%$
- ▶ DW factors predicted poorly
 - ✓ $\Delta \sigma^2 = 32-147\%$
 - ✓ Possibly better predictions using DM method

Similar trends for Mn dimers?

Ab initio EXAFS of Dimers



A Closer Look

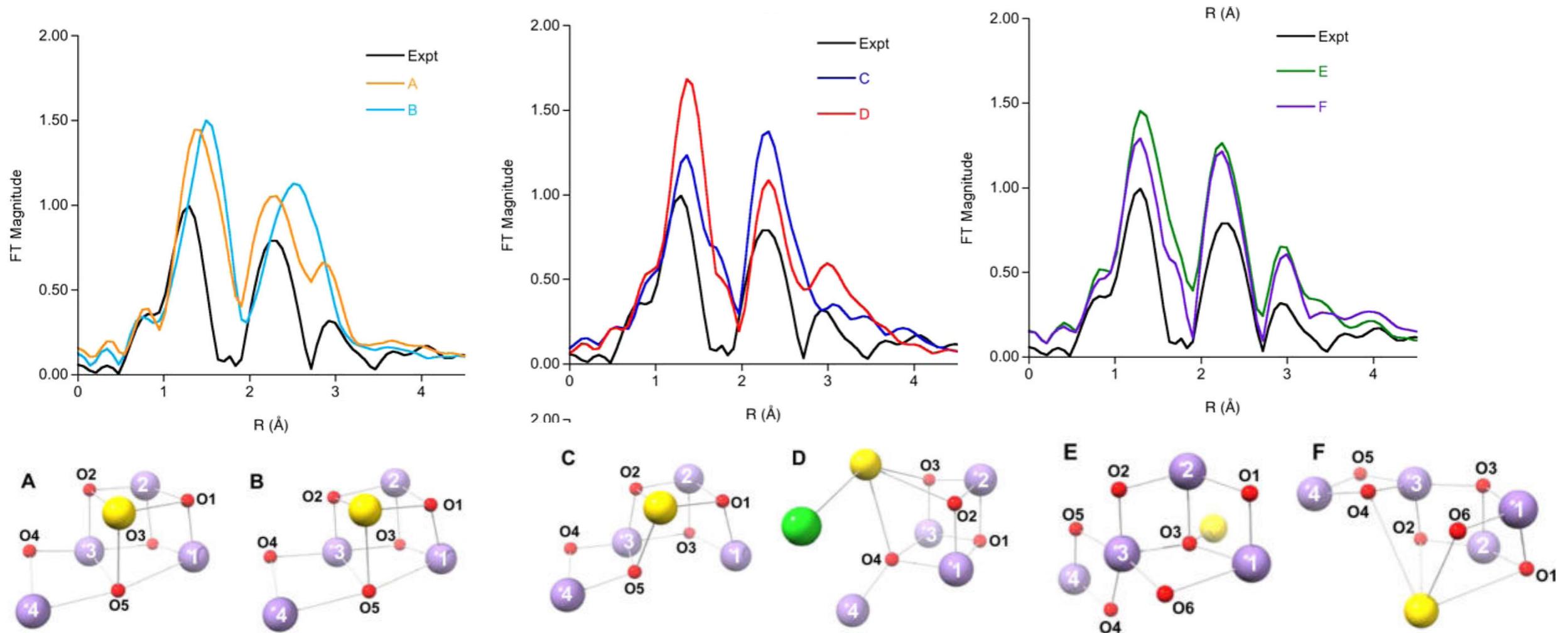


Path		Fit (Data)	Crystal (CD)	Geom Opt (CD)	Geom Opt (DM)
Mn-O	R	2.14	2.10 (± 0.03)	2.09 (± 0.04)	2.09 (± 0.04)
	σ^2	0.0016	0.0028 ($\pm 0.2e-4$)	0.0028 ($\pm 0.3e-4$)	0.0035 ($\pm 3e-4$)
Mn-Mn	R	4.23	4.42	4.06	4.06
	σ^2	0.0058	0.0013	0.0013	0.0035

- ▶ Distances predicted well
 - ✓ $\Delta R = 0.3-4\%$
- ▶ DW factors predicted poorly
 - ✓ $\Delta \sigma^2 = 10-119\%$
 - ✓ Possibly better predictions using DM method

How is this relevant to important questions in bioinorganic chemistry?

Application to the S1 state of the OEC



XFEL, Suga

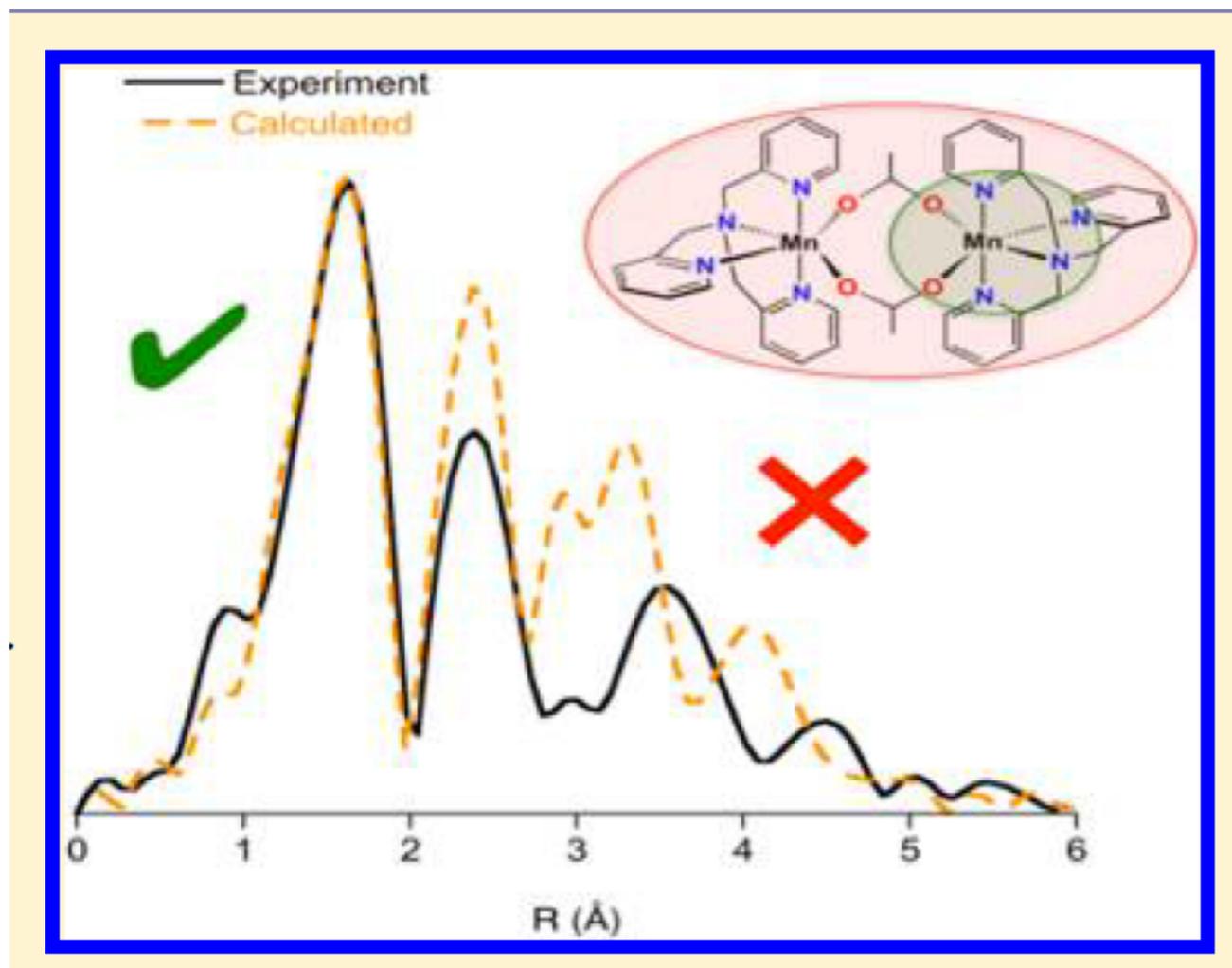
XRD, Umena

Structures proposed by various prominent experimental and theoretical research groups

The strength of EXAFS is in distance determination. Esp. M-M distances.
The ability to determine topology is *very* limited.

How Accurately Can Extended X-ray Absorption Spectra Be Predicted from First Principles? Implications for Modeling the Oxygen-Evolving Complex in Photosystem II

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DOI: 10.1021/jacs.5b00783
J. Am. Chem. Soc. 2015, 137, 12815–12834

At present state of the art EXAFS calculations cannot be used in a predictive fashion.

EXAFS must be fit....

Summary

XAS edges - provide electronic and geometric structural information
In the last decade significant progress has been made in calculations of both pre-edge and rising edge features. Enhancing predictive capability.

EXAFS - provides accurate local metrical information about a photoabsorber.
Requires modeling and fitting.

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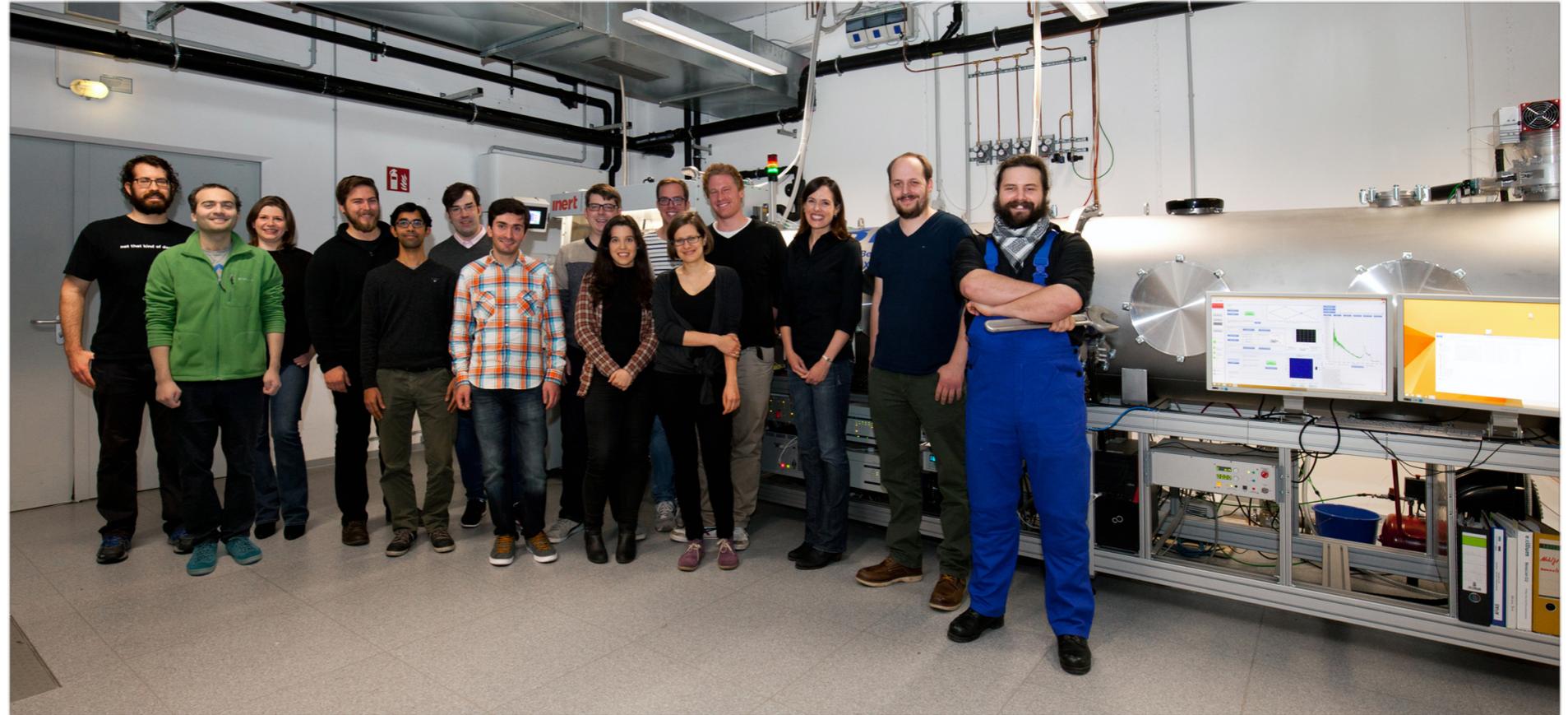
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