

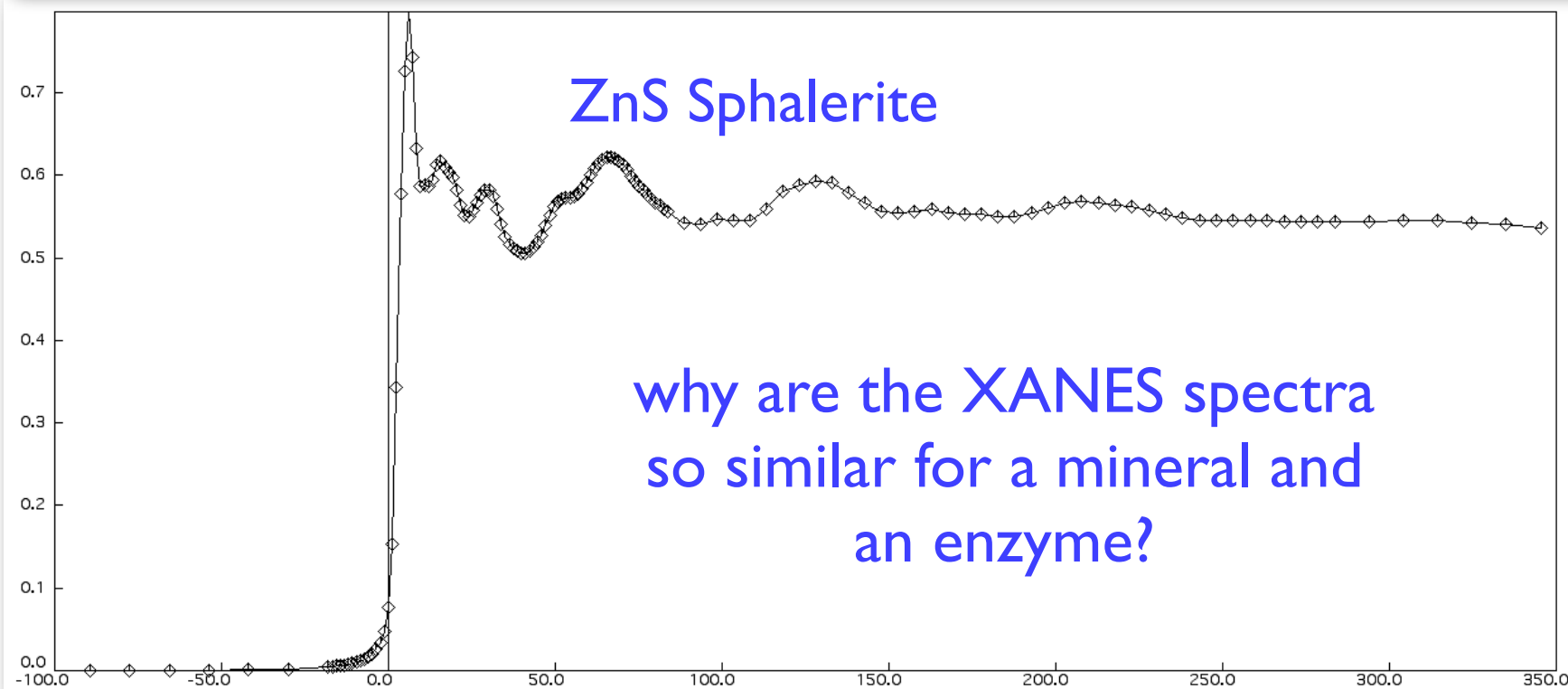
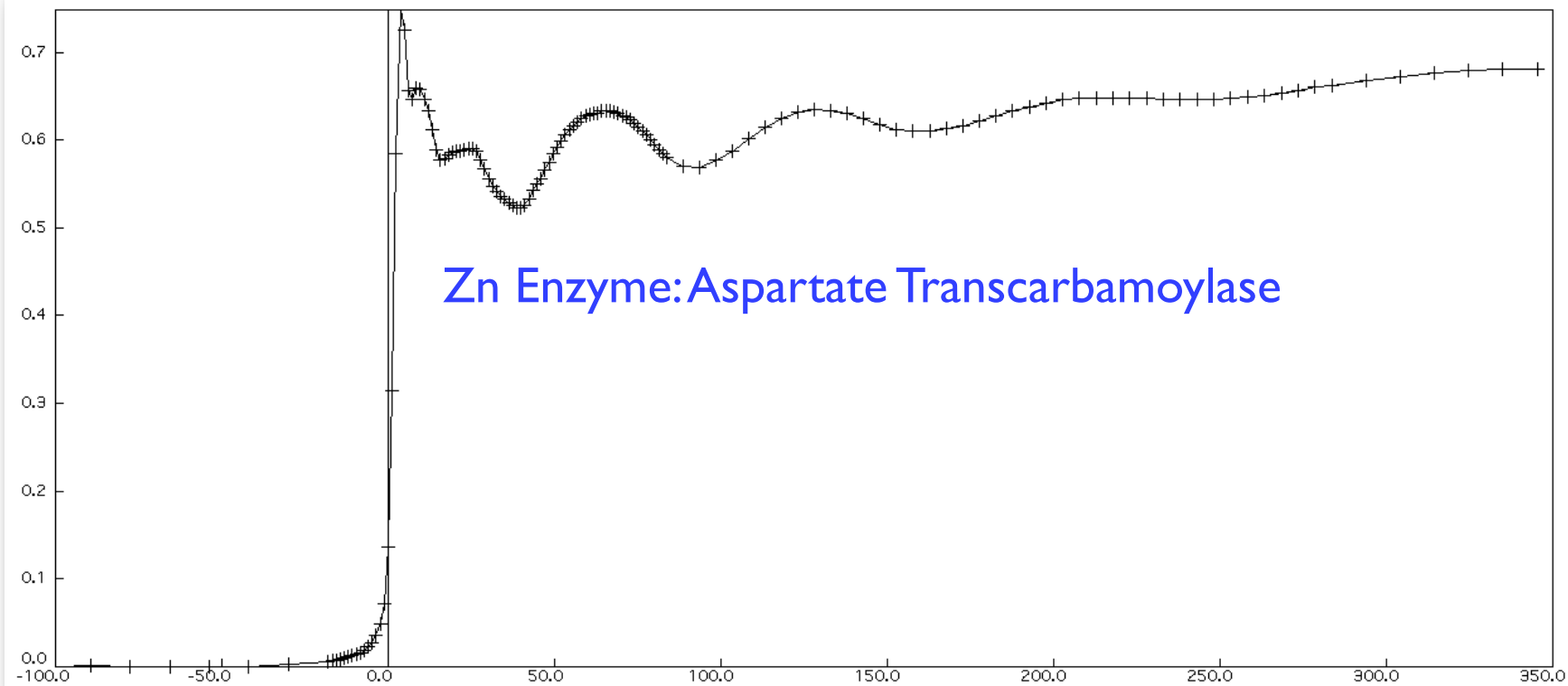
# Interpreting XANES

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# Scope of this talk

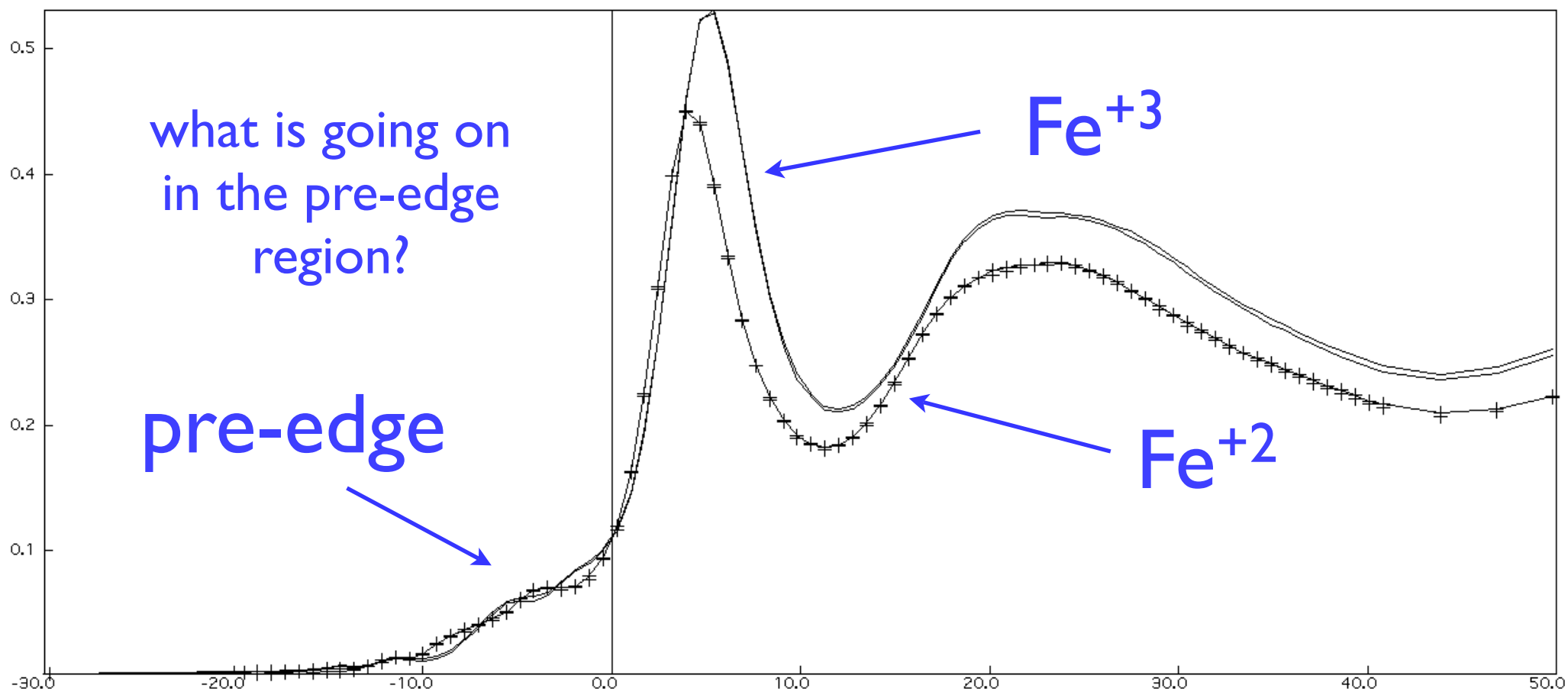
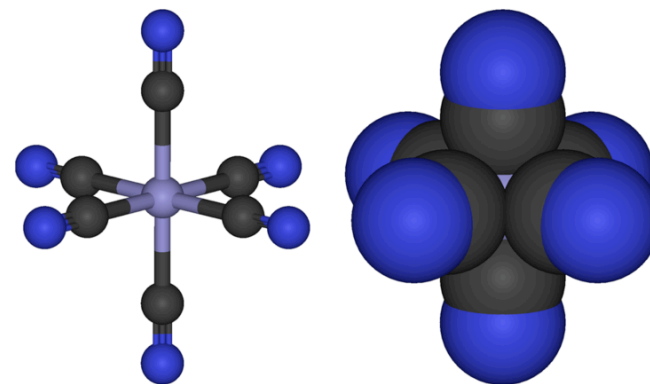
- The literature abounds with empirical correlations between edge shifts and formal charge state, and the relationships between pre-edge transitions and symmetry
- The purpose of this talk to try to dig below the surface of these correlations without getting buried in mathematics.
- I recommend Simon Bare's talk on XANES (2005 APS XAFS school) for a good overview of the applications and very interesting figures, and Bruce Ravel's APS XAFS school) talk on applying the FEFFx program to modeling data.

An  
early  
puzzle



Another early puzzle

# Fe hexacyanides



# XANES and EXAFS

- It has long been known that x-ray edge spectra are related to the structure around the absorbing atom. XAS was actively studied for more than four decades with some clarity and some confusion. Around 1970 Sayers, Stern, and Lytle put together the key elements that explained EXAFS as a short range order theory and how it could be used for structure determination.
- In the '70s near-edge structure (XANES) was still a puzzle. Over the next few decades it became clear that the basic phenomena in EXAFS and XANES are the same, but some complications in the theory such as large angle multiple scattering tend to be less pronounced in EXAFS than in XANES.
- Consolidation:  $XANES + EXAFS = XAFS$

# Qualitative Analysis of XANES

- Empirically valid, but needs theory to explain why
- There are several complementary ways to interpret XANES.
- What is the most useful approximation for the final state wavefunction? Molecular Orbital? Scattering? Band Structure? What?

## Basics

Absorption depends on  
transition matrix element

$$\mu \propto \left| \int \psi_f^* \hat{\epsilon} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} \psi_i d^3r \right|^2$$

dipole and quadrupole terms



$$\approx \left| \int \psi_f^* (\hat{\epsilon} \cdot \vec{r} + i(\hat{\epsilon} \cdot \vec{r})(\vec{k} \cdot \vec{r})) \psi_i d^3r \right|^2$$

Matrix element **projects out** the part of the  
final state that is of right symmetry (e.g  
p-symmetry for K-edge/dipole selection rules)

# basics

## Selection rules for discrete transitions

	Electric dipole (E1) ("allowed")	Magnetic dipole (M1) ("forbidden")	Electric quadrupole (E2) ("forbidden")
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Rigorous rules	1. $\Delta J = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ )	$\Delta J = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ )	$\Delta J = 0, \pm 1, \pm 2$ (except $0 \not\leftrightarrow 0,$ $1/2 \not\leftrightarrow 1/2, 0 \not\leftrightarrow 1$ )
	2. $\Delta M = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ when $\Delta J = 0$ )	$\Delta M = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ when $\Delta J = 0$ )	$\Delta M = 0, \pm 1, \pm 2$

	3. Parity change	No parity change	No parity change
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With negligible configuration interaction	4. One electron jumping, with $\Delta l = \pm 1,$ $\Delta n$ arbitrary	No change in electron configuration; i.e., for all electrons, $\Delta l = 0,$ $\Delta n = 0$	No change in electron configuration; <i>or</i> one electron jumping with $\Delta l = 0, \pm 2,$ $\Delta n$ arbitrary
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For *LS* coupling only

5. $\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
6. $\Delta L = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ )	$\Delta L = 0$ $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ (except $0 \not\leftrightarrow 0, 0 \not\leftrightarrow 1$ )



# radial wavefunctions

- electric dipole selection rules require p final states for K, L<sub>1</sub> edges, s and d for L<sub>2,3</sub>
- For a given n, as l increases, the average probability density moves to shorter radius.
- -> d orbitals are closer in than p or s.
- -> Interpretation of K, L<sub>1</sub> edges is a little different than L<sub>2</sub>, L<sub>3</sub> edges because their final state wavefunctions are less compact

# K and L<sub>I</sub> edges

- dipole selection rules are usually good to a few percent, but quadrupole terms cannot be totally neglected (quad/dipole matrix element ratio of order  $Z/(2*137)$ )
- near threshold p final states are spread out compared to d (e.g. peak in  $4\pi r^2 \psi^2$  of hydrogenic 3p wavefunction: 3p is  $12a_0/Z$  vs  $9a_0/Z$  for 3d)
- free atom  $\mu(E)$  may be sharply peaked (remnant of bound p state in free atom), which is broadened into a resonance when atom placed into condensed matter
- High barrier may be presented by negatively charged neighbors -> sharp white lines

# L<sub>2</sub> and L<sub>3</sub> edges

- d and s final states - transitions are much stronger to d. Final bound d states are relatively well localized -> narrow peaks (white lines)
- energies of edges L<sub>2</sub> and L<sub>3</sub> differ because of relativistic effects (spin-orbit). Edges may appear different because of selection rules on J.

# White lines

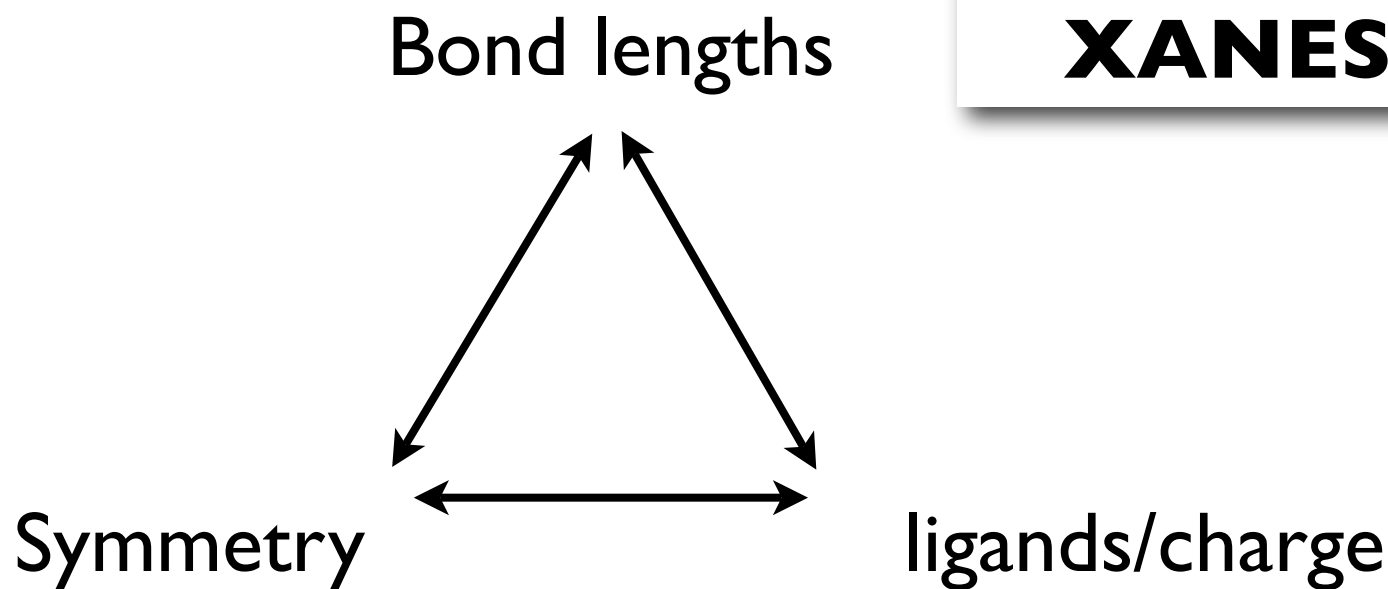
- intensities depend on matrix elements and occupancy of any bound final states
- matrix elements depend on overlap between the wavefunctions (-> distances)
- transitions are forbidden into filled orbitals (consequence of Pauli exclusion principle)
- filling of orbital suppresses white line

# Core Hole Lifetime

- The core hole (vacancy in the initial state following x-ray absorption) is unstable. It decays in a short time  $\sim 1$  femtosecond, typically by emitting a fluorescence photon or auger electron.
- By the uncertainty principle, the energy width of a state is inversely proportional to its lifetime.
- Higher atomic number elements have shorter lifetimes  $\rightarrow$  greater broadening. This gets to be a limitation for high  $Z$  edges although it can be deconvoluted out in favorable cases.
- Low atomic number ( $\sim Z=8$ ) spectra “NEXAFS” can be interpreted in great detail because of sharp spectral lines
- **X-ray Inelastic Scattering can be used to suppress core hole lifetime broadening and explore XANES in detail**

# Key factors influencing XANES

**The same factors  
that control  
structure also  
control the  
XANES Spectra**



In some systems the bond lengths depend smoothly on the formal charges.

For example, average bond lengths scale approximately as  $\sim 1/r^4$  in Mn oxides (MnO, MnO<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, KMnO<sub>4</sub>) despite differences in local site symmetry.

Empirical correlations between formal charge state and edge shifts are primarily mediated through changes in bond lengths. Direct influences exist but are smaller in magnitude.

# Energy levels vs R

- the simplest picture of XANES is of the electron escaping through a cage of neighboring atoms
- If the electron is well confined, you get a narrow peak in the absorption (e.g. white line). If not, the absorption peak is broadened or absent altogether.
- generally, if you put a particle in a box you get bound states (or resonances) at low energies and continuum states at higher energies
- if the box is made smaller, the levels go up in energy (because of the uncertainty principle). This makes the edge shift to higher E, and usually principal maximum becomes less peaked.



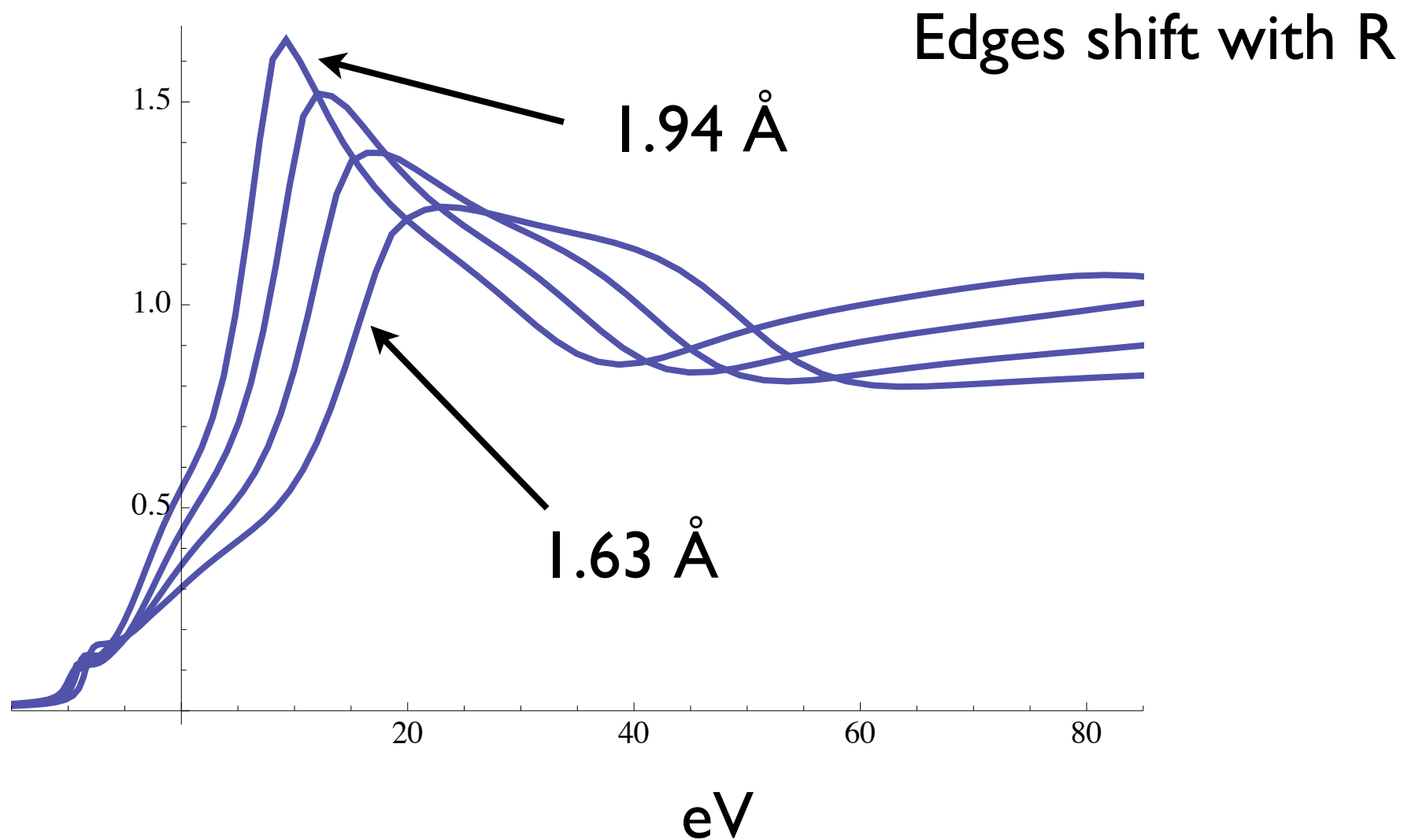
# E vs R Scaling

- Hartree et al. (1934) proposed that at the principal maximum (white line), the interatomic distance  $R$  is one wavelength
- In eV Å units,  $E \sim 150/R^2$
- Simple, but qualitatively correct
- $1/r^2$  scaling can be used to determine average nearest neighbor bond lengths from XANES alone.

theory

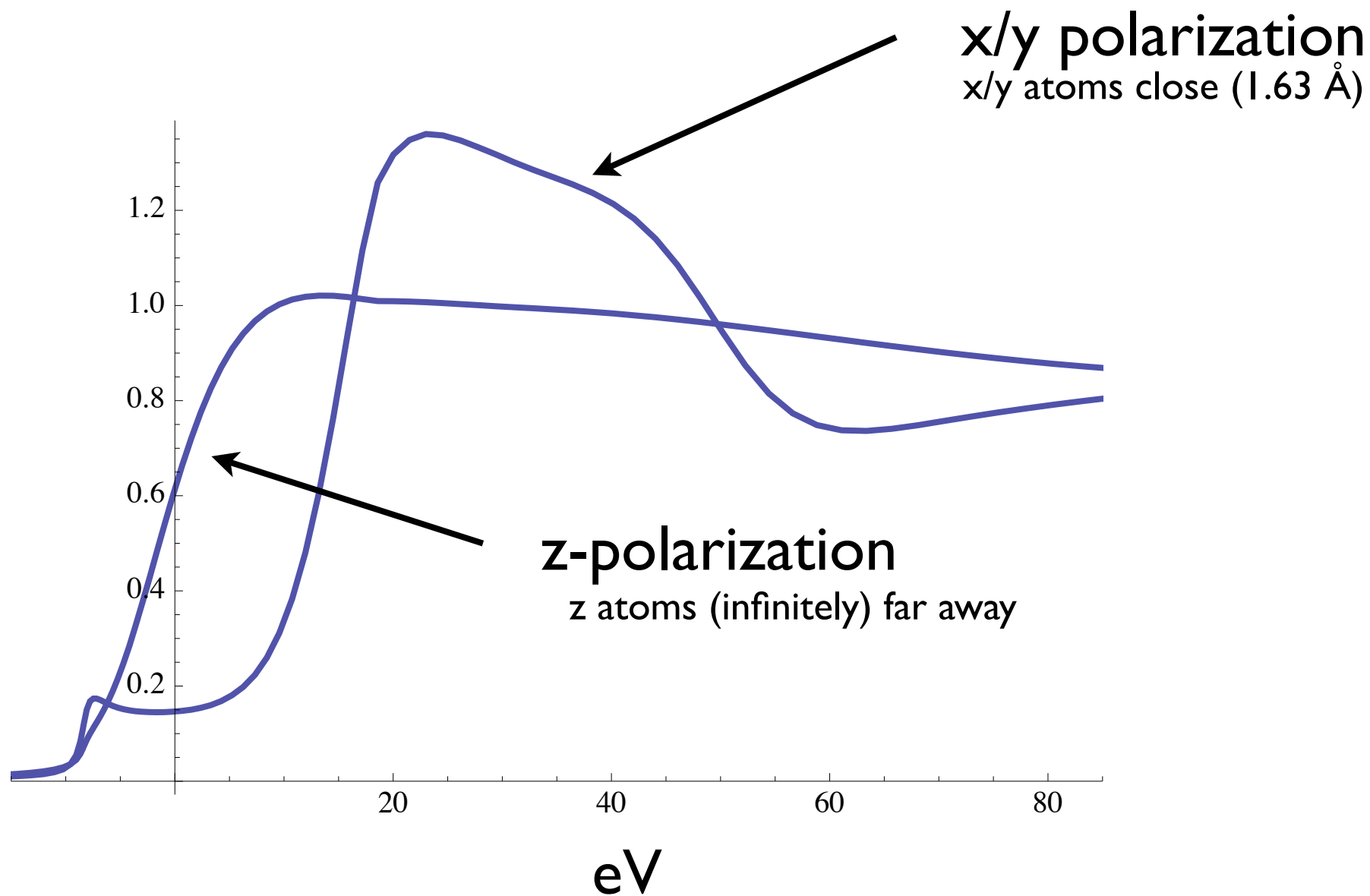
# MnO<sub>4</sub> planar cluster

$r=1.63, 1.73, 1.84, 1.94 \text{ \AA}$  feff8.2 SCF/FMS



# MnO<sub>4</sub> planar cluster

$r=1.63 \text{ \AA}$  feff8.2 SCF/FMS



# Pre-edge transitions

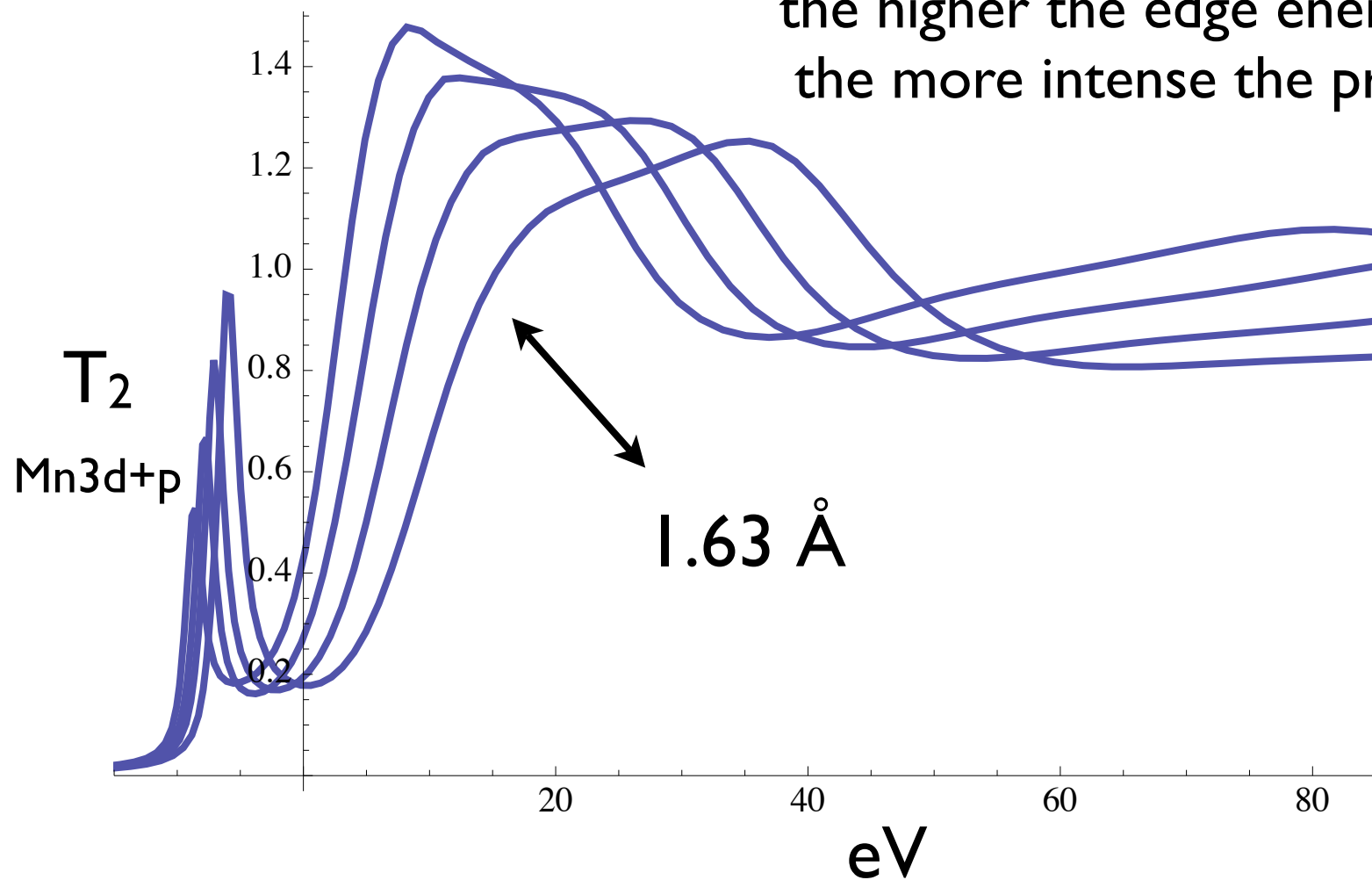
- Hamiltonian has the symmetry of local environment. In an inversion-symmetric site, orbitals of different parity don't mix in an eigenfunction.
- s states are even parity; p states are odd; d states are even. parity is  $(-1)^l$
- K-edge: Since only p states are dipole-allowed, if there are strong transitions to a MO with mostly d character, the environment **cannot** be inversion symmetric.
- Pre-edge peak intensities also are strongly influenced by bond lengths since wavefunctions are exponentially decaying

theory

# MnO<sub>4</sub> tetrahedral cluster

$r=1.63, 1.73, 1.84, 1.94 \text{ \AA}$   $f_{\text{eff}} 8.2$  SCF/FMS

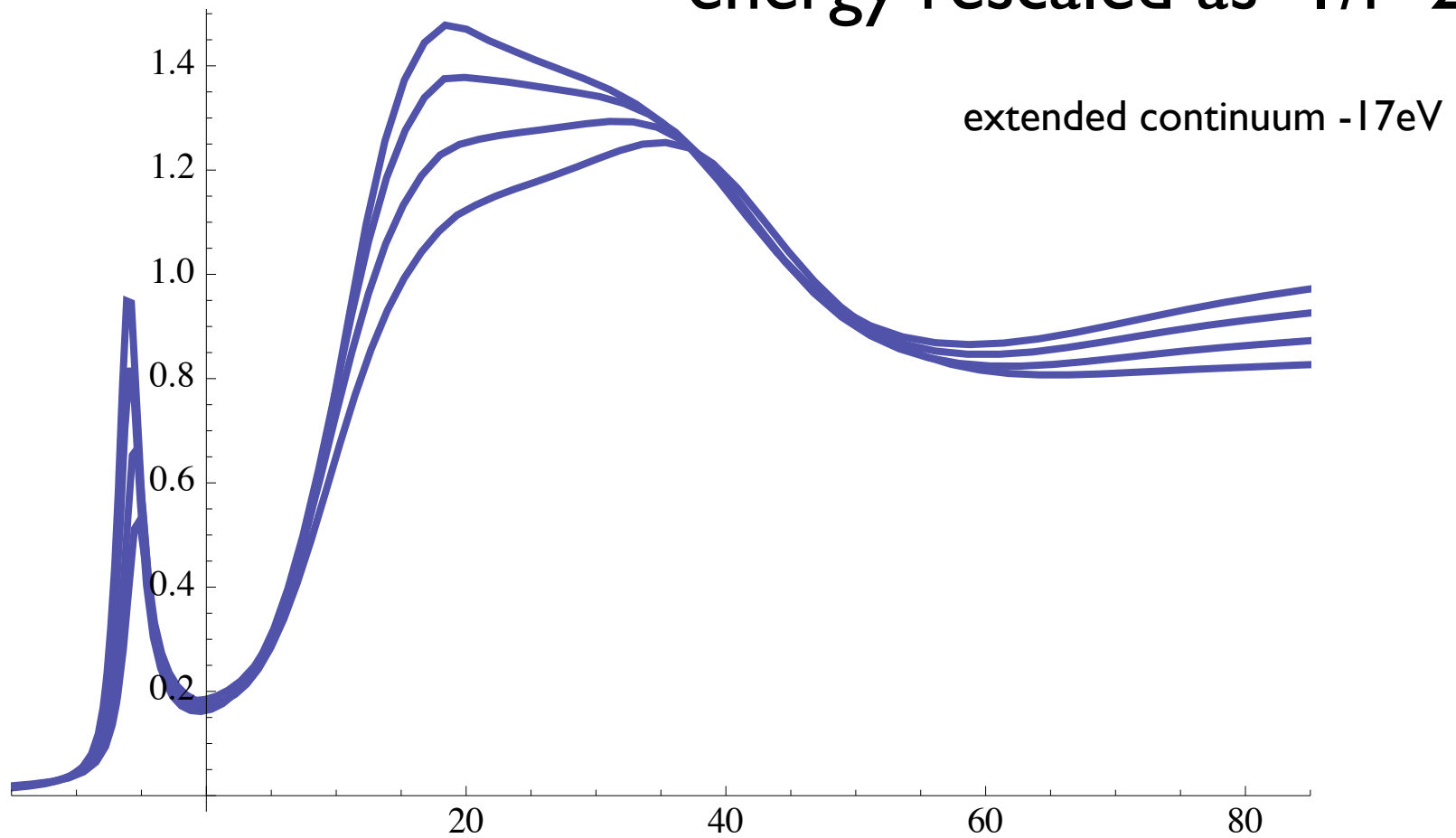
the shorter the distance,  
the higher the edge energy and  
the more intense the pre-edge



# MnO<sub>4</sub> tetrahedral cluster

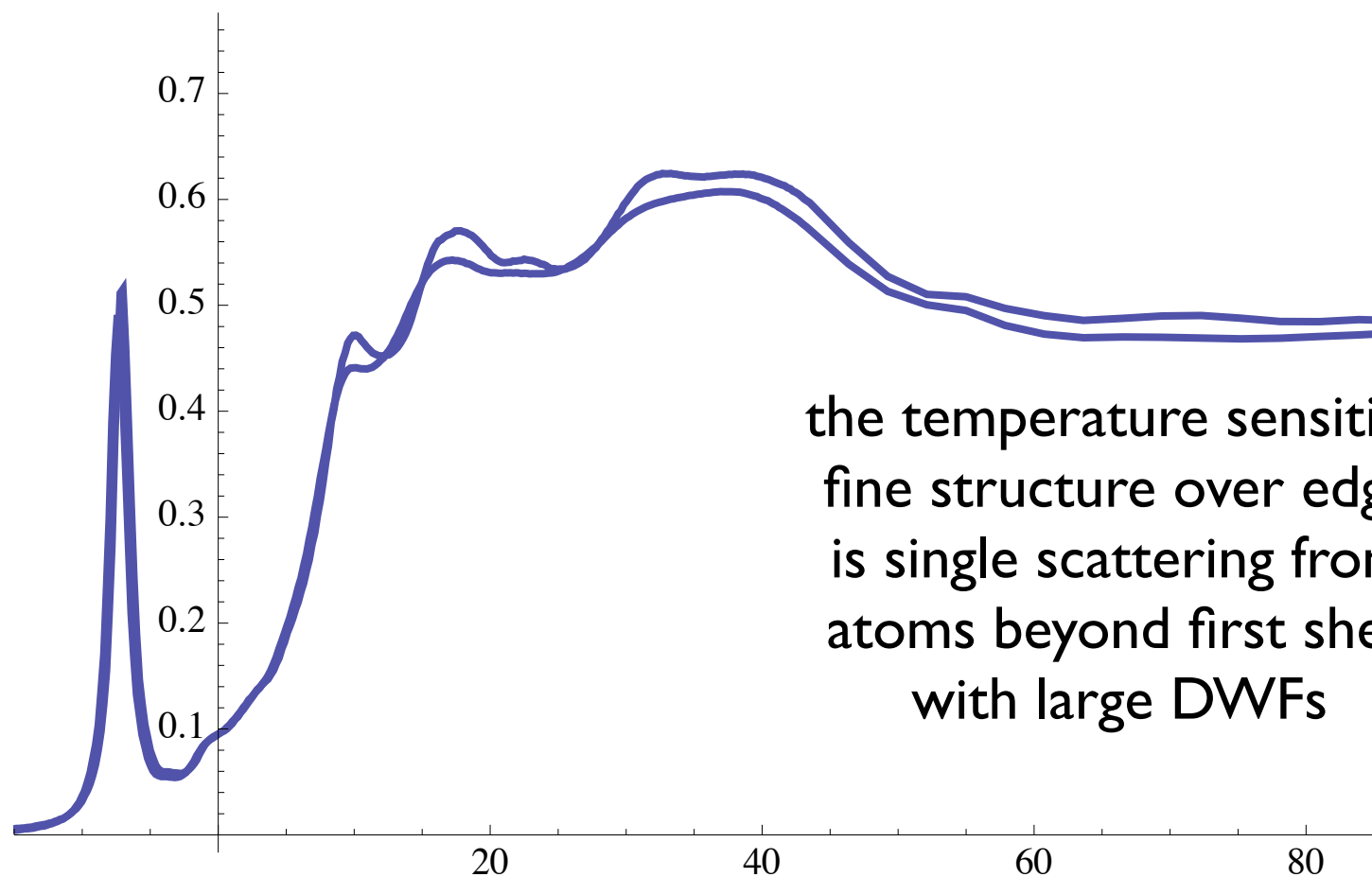
r=1.63, 1.73, 1.84, 1.94Å feff8.2 SCF/FMS

energy rescaled as  $1/r^2$



expt.

# Solid $\text{KMnO}_4$ at 80K and 300K experimental data\*



the temperature sensitive  
fine structure over edge  
is single scattering from  
atoms beyond first shell  
with large DWFs

\* G Bunker thesis 1984

XANES landscape is from SS+MS  
among nearest neighbor tetrahedron  
SS from distant atoms adds  
temp dependent fine structure

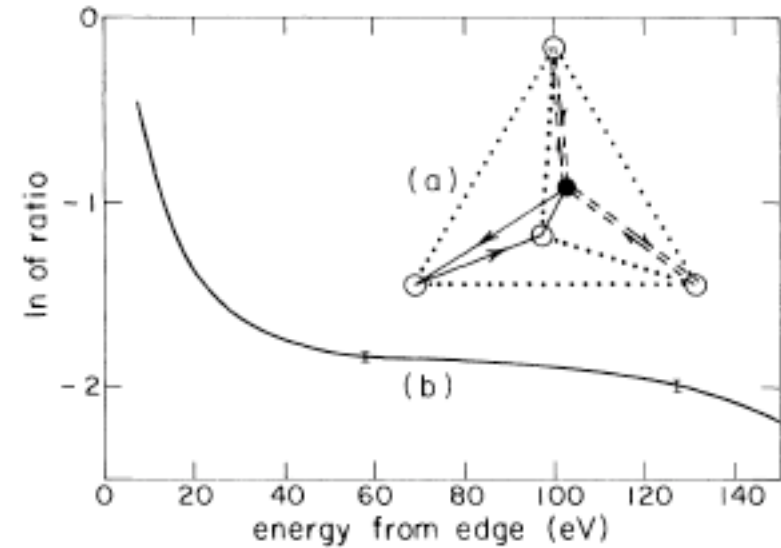
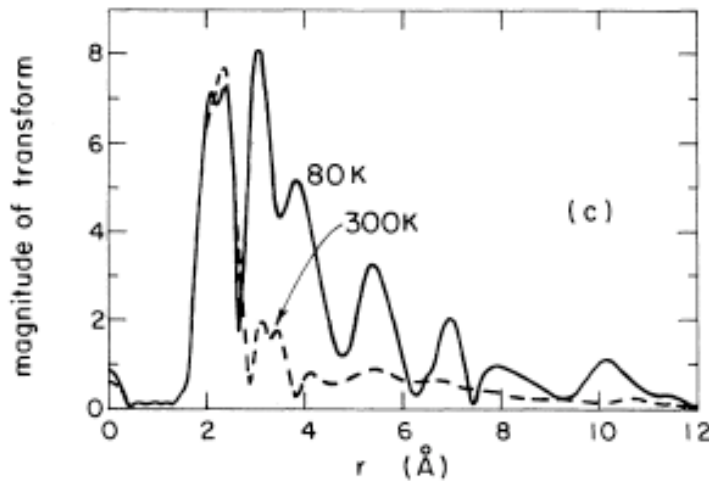
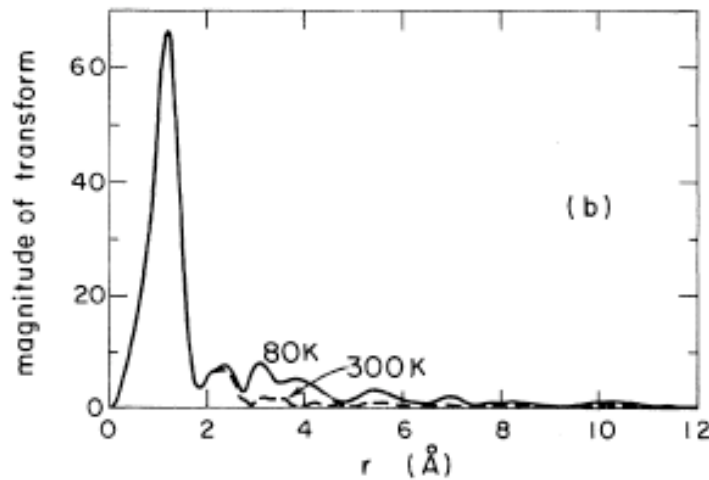
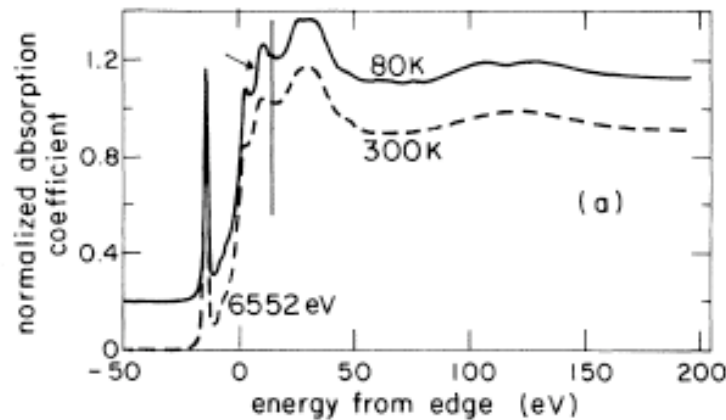
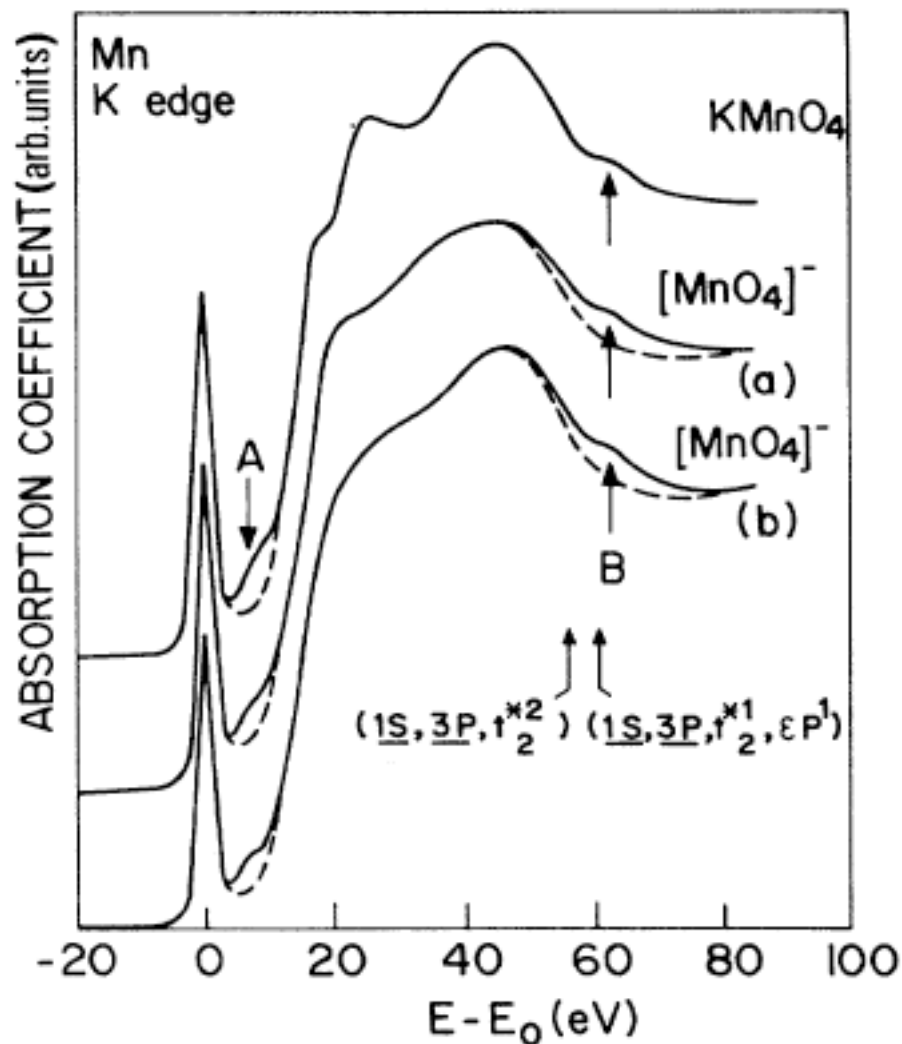


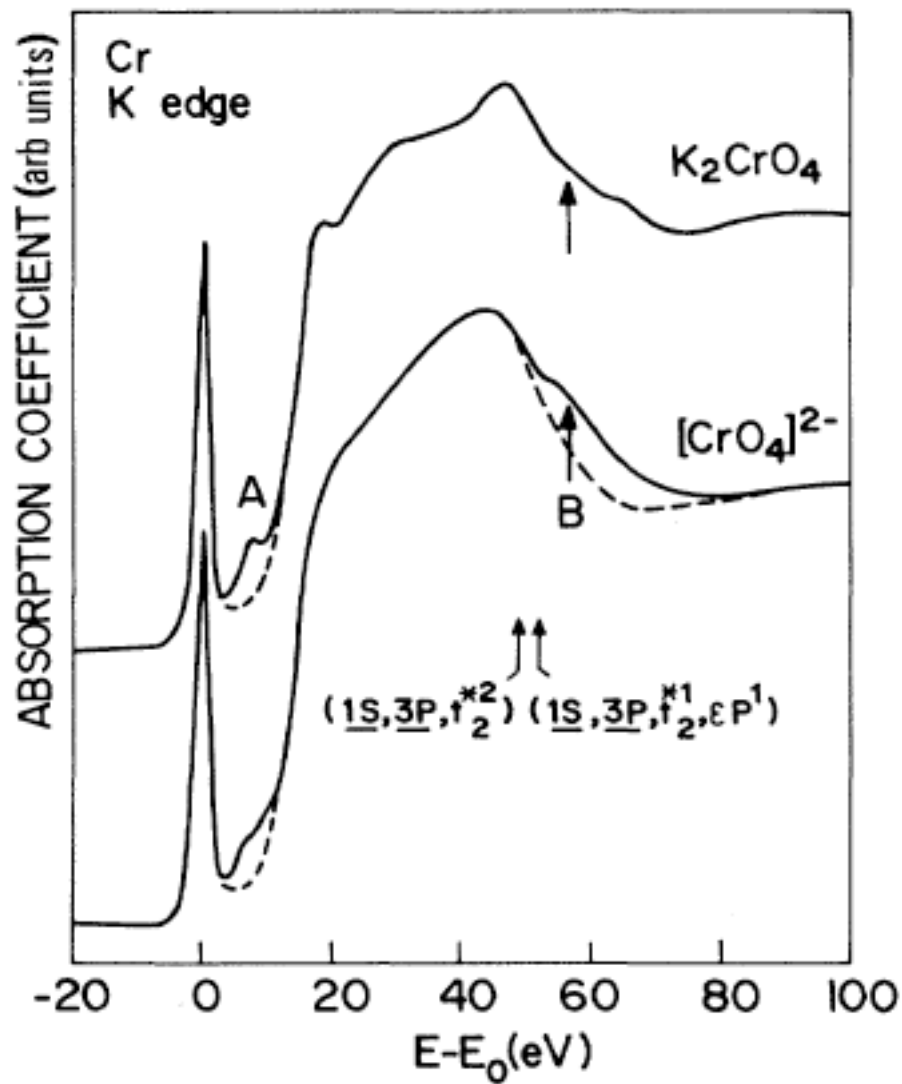
FIG. 2. (a) The two multiple-scattering paths that contribute to the second peak in the Fourier transform of  $\text{KMnO}_4$ , denoted by solid and dashed lines. The black dot is Mn, and the open dots are O atoms. (b) The logarithm of the ratio of the  $k$  dependence of the amplitudes of the first (SS) peak to the second (MS) peak of Fig. 1(b), plotted vs energy from the edge.





In addition to  
SS + MS +  
quadrupole  
transitions,  
there is good  
evidence for  
two-electron  
“shake-up”  
excitations

From Bianconi et al.  
Phys. Rev. B. **43**, 9 (1991)



Note the strong family resemblance between CrO<sub>4</sub>, MnO<sub>4</sub>, TiO<sub>4</sub>, MoO<sub>4</sub>

Tetrahedral  
Short bonds  
-> triangle path MS

Structure counts!

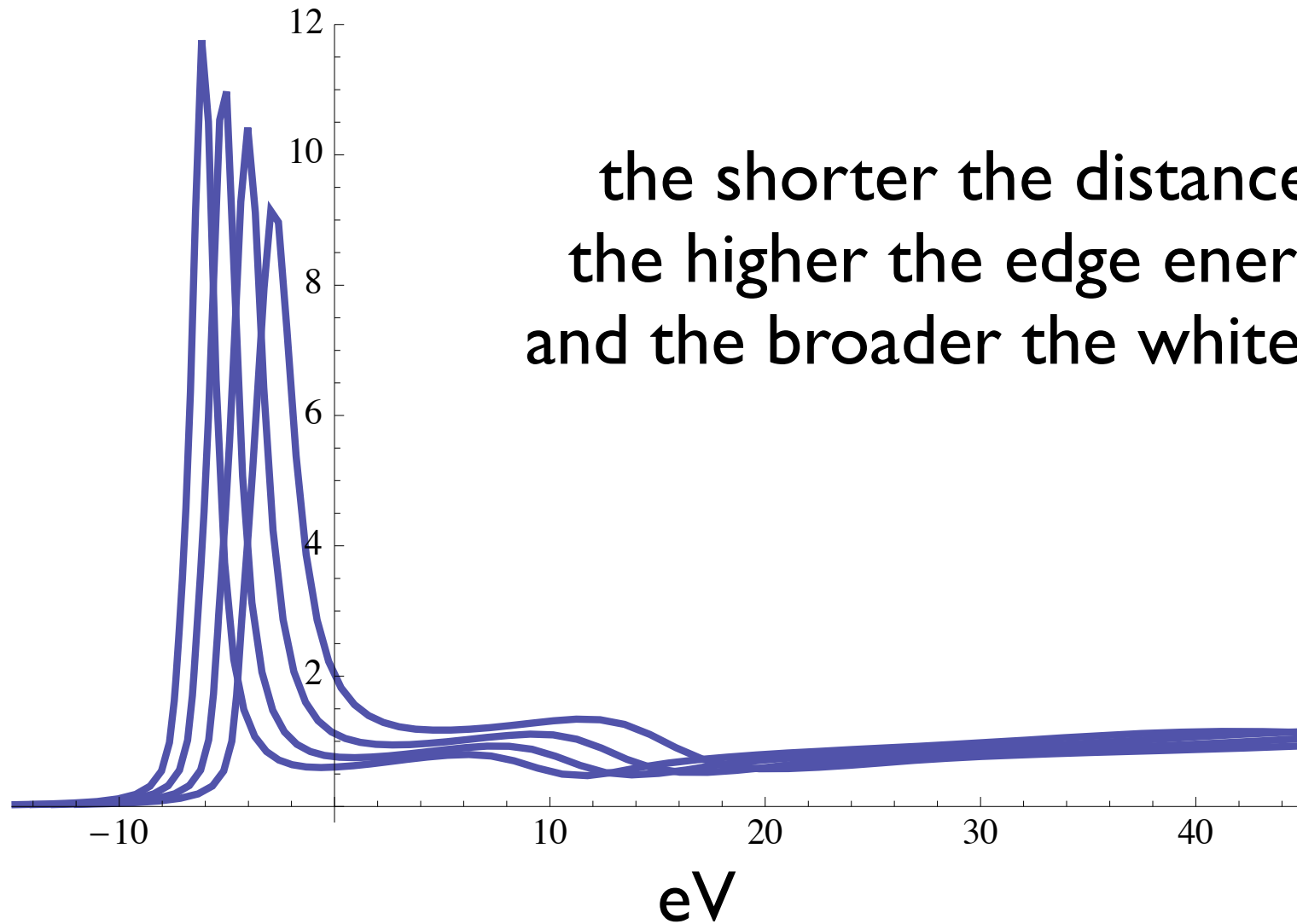
figure from Bianconi et al.  
Phys. Rev. B. **43**, 9 (1991)

# “Hexavalent Chromium”

- Environmental problem - mobile, reactive
- tetrahedral  $\text{CrO}_4^{2-}$  ion; similar to  $\text{MnO}_4^-$
- Easy to identify because of large pre-edge peak and characteristic edge shape
- short bonds, empty  $t_2^*$  MO
- $\text{Cr}^{6+}$  formal charge is **not** the important thing

# SO4 tetrahedral cluster

$r=1.63, 1.73, 1.84, 1.94\text{\AA}$   $f_{\text{eff}}8.2$  SCF/FMS

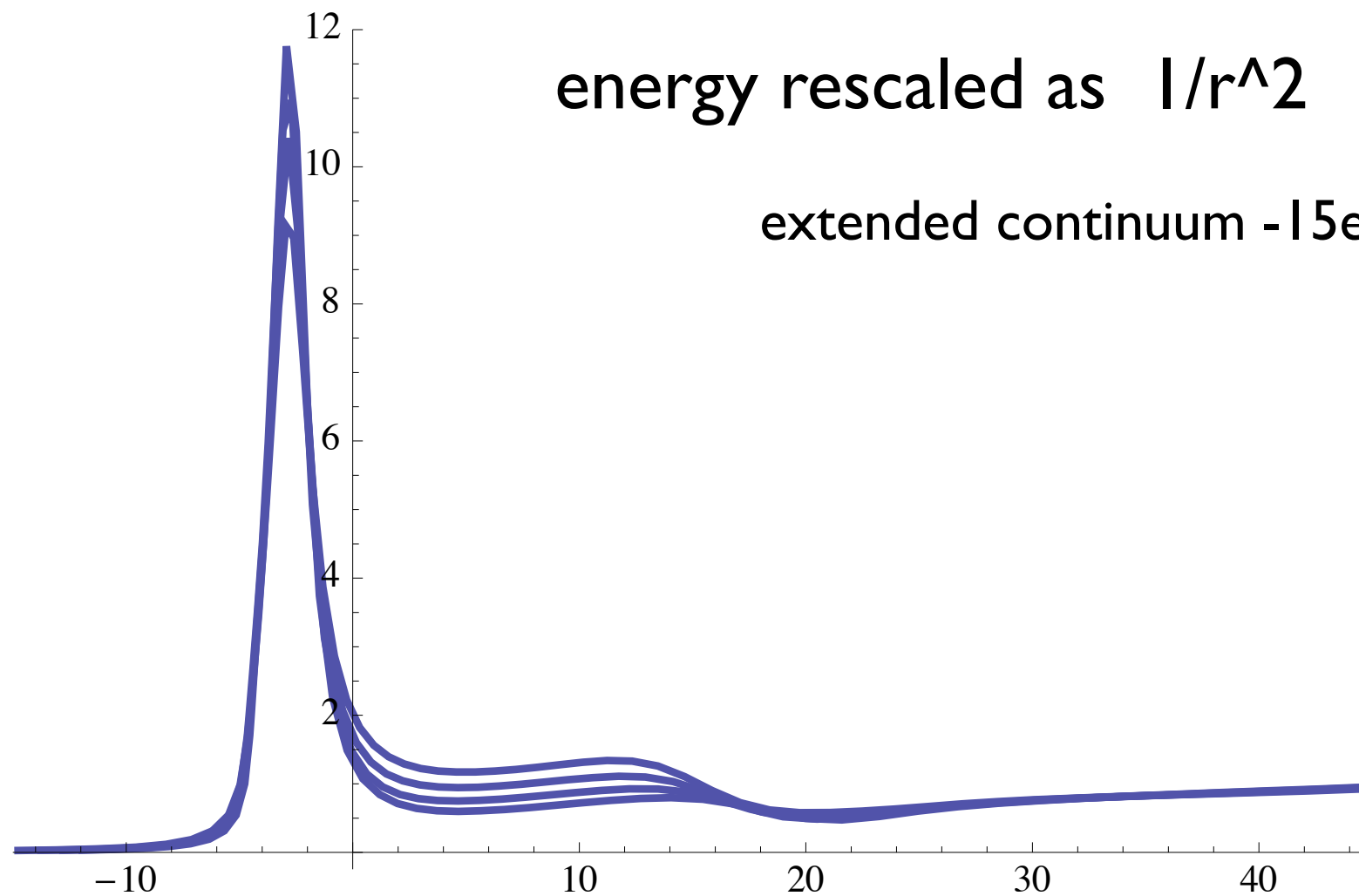


# SO4 tetrahedral cluster

$r=1.63, 1.73, 1.84, 1.94\text{\AA}$   $f_{\text{eff}}8.2$  SCF/FMS

energy rescaled as  $1/r^2$

extended continuum -15eV



cautionary

In the previous cases the XANES was not strongly sensitive to the chemistry. It's mostly driven by the physics of electron scattering.

For example, the model  $\text{MnO}_4$  calculations were for a **neutral** cluster (charge transfer happens during SCF process).

But if orbitals are partially filled, transitions can turn on or off depending on orbital occupancy.

For example Cu(I) vs Cu(II).

Cu(II) has a 3d hole  $\rightarrow$  3d peak.

Cu(I): no 3d hole  $\rightarrow$  no 3d peak.

# Back to an old puzzle

- Aspartate transcarbamoylase tetrahedral ZnS
- Zn sulfide (sphalerite and wurtzite)
- why are the edge structures so similar, but the EXAFS is so different?
- $\text{GeCl}_4$  XANES also quite similar
- Ge is next to Zn, Cl is next to S in periodic table
- This suggests that XANES depends primarily on structure and secondarily on charge transfer

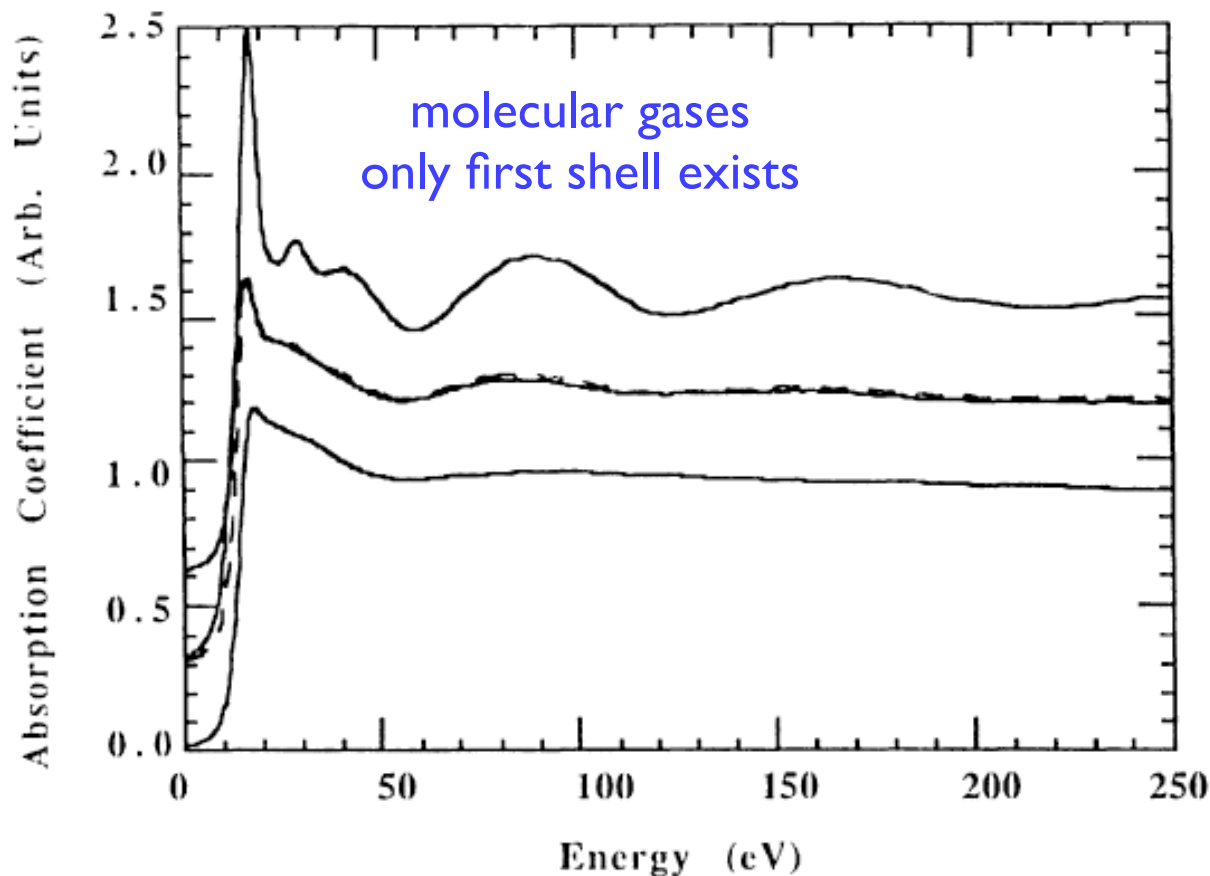
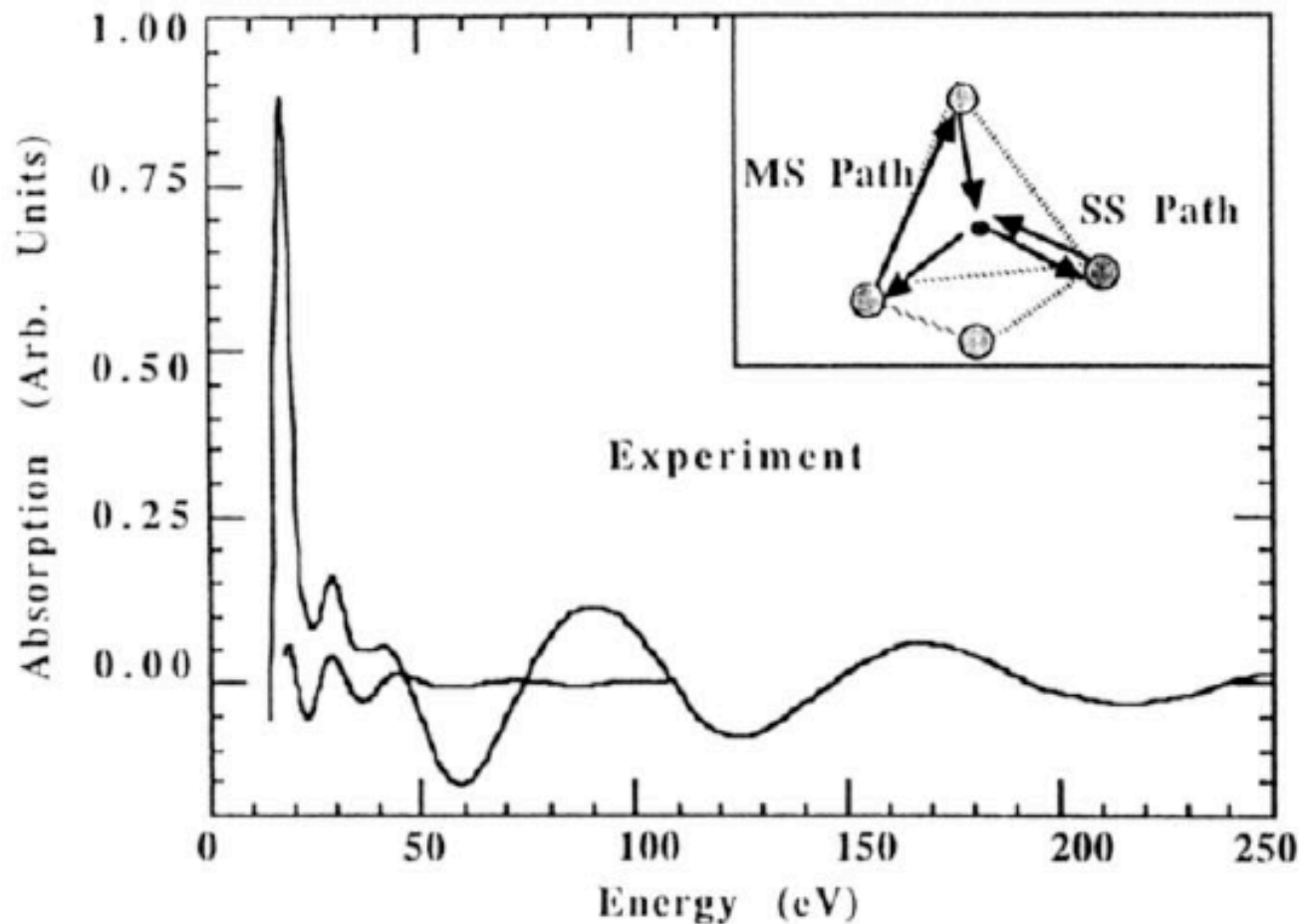


FIG. 1. Measured x-ray absorption spectra of, from top to bottom, GeCl<sub>4</sub>, GeH<sub>3</sub>Cl, and GeH<sub>4</sub>. Data have been normalized and have had a linear pre-edge background removed. The dashed curve is an approximation of GeH<sub>3</sub>Cl made by a linear superposition of GeCl<sub>4</sub> and GeH<sub>4</sub> as described in the text. Deviation between the solid and dashed lines for GeH<sub>3</sub>Cl is due to multiple scattering.

Multiple scattering signal extracted by taking linear combinations of spectra of the molecular gases GeCl<sub>4</sub>, GeH<sub>3</sub>Cl, and GeH<sub>4</sub>

from Bouldin et al  
Phys Rev B 38, 15 (1988)





Fine structure  
over edge is  
from multiple  
scattering

from Bouldin et al  
Phys Rev B 38, 15 (1988)

FIG. 2. The measured, normalized x-ray absorption of  $\text{GeCl}_4$  and the multiple-scattering contribution to the x-ray absorption isolated by subtracting the single-scattering terms determined experimentally from  $\text{GeH}_3\text{Cl}$  and  $\text{GeH}_4$ . The MS contribution is given (per 4 Cl) by:  $[\text{GeCl}_4] + 3[\text{GeH}_4] - 4[\text{GeH}_3\text{Cl}]$ . Inset shows the single- and multiple-scattering paths in the  $\text{GeCl}_4$  molecule.

# Dichroism & polarization

- Always present, but often isotropically averaged out in polycrystals or solutions, or by using magic angle spinning
- Absorption coefficient transforms under rotations like a second rank tensor (not simply as  $\text{Cos}^2q$ )
- In dipole approximation,  $\mu$  depends on relative orientation of polarization vector and sample axes
- Quadrupole terms additionally introduce weak dependence on  $k$  vector of incident x-ray beam

# Effect of core-hole

- The inner-shell vacancy (“core hole”) effectively increases the nuclear charge by 1 compared to the neutral atom
- The dynamics of this can affect the XANES (e.g. by introducing “shake-down” transitions, which involve ligand to metal charge transfer)
- see Bair and Goddard, 1983, configuration interaction calculation of Cu and CuCl<sub>2</sub>

# a common error

- Angular momenta always refer to a center
- A wave function of particular angular momentum wrt on center is a mixture of angular momenta about another center!
- A p orbital on an oxygen neighbor is not a p orbital with respect to central atom
- For example a linear combination of s orbitals on ligands could possess some p-character with respect to center atom

# Fitting L-edges

- L-edges are sometimes modeled as sums of Lorentzian peaks plus an arctangent background
- a single bound state has lorentzian profile (it's the Fourier transform of a state that is exponentially decaying over its lifetime)
- The arctangent comes from adding up equal lorentzians with a step-function density of states
- There is no deep theoretical significance to it, but it can be useful

# Quantitative Theories

- Scattering/MO/CIDHF/Band Structure
- Approaches quantitative accuracy
  - black box; virtual experiment
  - can deconstruct spectra -> WFs, pDOS, etc.
- Simplified models
  - more accessible, but more approximate
- Best approximation depends on system, but scattering theory provides best unified picture of XANES and XAFS

# Multiple Scattering Approach (example: FEFF8)

- ⦿ rewrite squared matrix element in terms of real-space Green's function and scattering operators
- ⦿ expand GF in terms of multiple scattering even from different atoms
- ⦿ initial atomic potentials generated by integration of Dirac or Schrödinger equation
- ⦿ modified atomic potentials generated by overlap and optional self-consistent field (use for XANES)
- ⦿ complex exchange correlation potential computed
- ⦿ effects of atomic potentials are expressed through k-dependent partial wave phase shifts for different L
- ⦿ radial wave function vs E obtained by integration
- ⦿ Scattering paths calculated (e.g. Rehr Albers)
- ⦿ unimportant scattering paths are filtered out (except FMS)
- ⦿ final spectrum generated by summing finite number of paths, or, over restricted energy range, FMS (use for XANES)
- ⦿ **The use of projected densities of states can be very useful for XANES**

FEFFx: see papers of Rehr, Ankudinov, Zabinsky et al  
see also DLXANES, GNXAS, and EXCURV programs

# LCAO MO approach

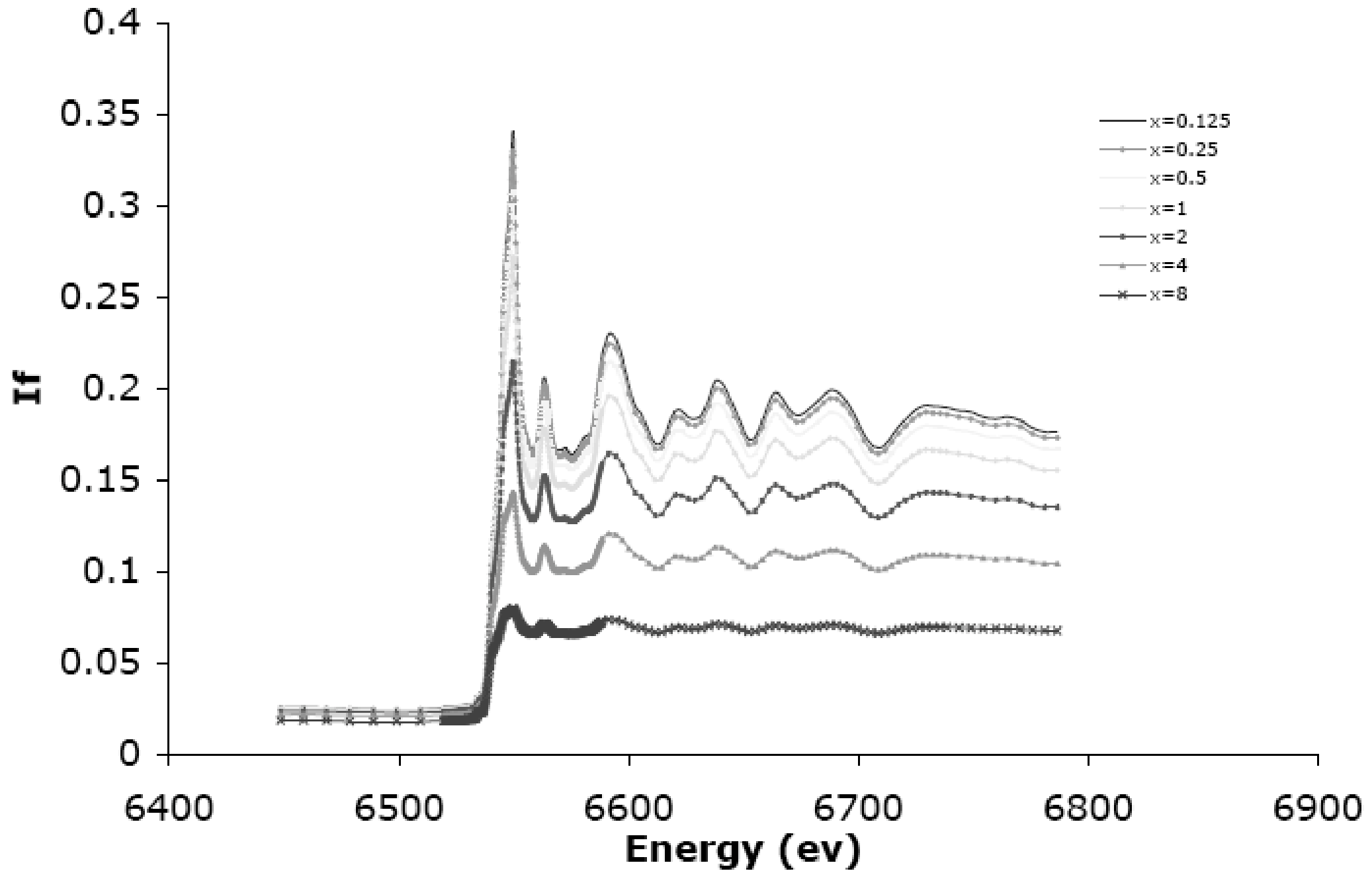
- Final state wavefunction is a linear combination of atomic orbitals contributed by the central atom and neighbors. Use  $Z+1$  approximation.
- Variational Method used to approximate eigenstates. Described in terms of local point group symmetry.
- Useful for understanding effects of bound states, symmetry, and polarization, but becomes less useful for delocalized states because of localized basis set
- there is a vast literature on these methods



## Thickness/particle size effects

- Many XANES spectra have prominent structure such as white lines
- The edge spectra can be distorted if particle sizes are not considerably less than one absorption length, in transmission and fluorescence
- It's difficult to draw correct conclusions from incorrect data

# Fluorescence vs Particle Size



see tutorial on sample prep 2006 APS XAFS school  
<http://gbxafs.iit.edu/training/tutorials.html>

# Conclusion

- Interpretation of XANES can be very informative. Empirical correlations between structure and spectra often can be readily observed.
- Simple relationships exist between symmetry, bond length, edge position, and intensities, but such qualitative analyses should be backed up by theoretical understanding. It's not always difficult.
- Care must be taken to avoid thickness and particle size effects or spectra will be distorted and conclusions will be wrong.
- Modern theoretical tools can be a great resource for deciphering XANES spectra, as can modern experimental techniques such as IXS.