Lecture 4.

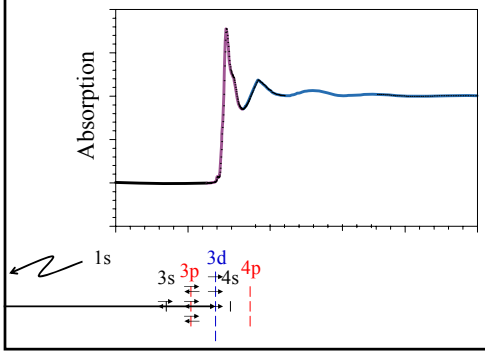
Near edge structure

Review

- Overview of XAS (EXAFS, XANES, XRF…)
- Interactions of x-rays with matter
- Measurement of x-rays and XAS
- Information content of EXAFS/XANES
- Some potential limitations in EXAFS

X-ray absorption spectroscopy

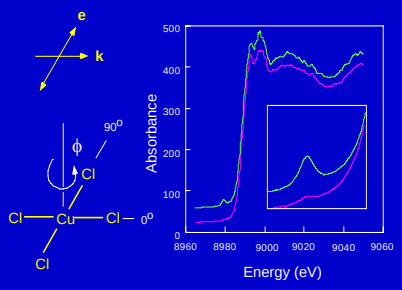
XANES EXAFS



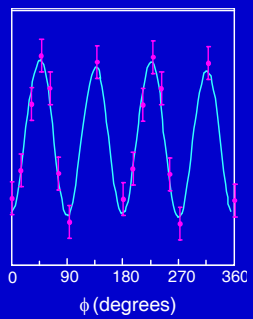
1s→3d transitions

- Dipole forbidden (Δ L = 2) for centrosymmetric complexes
- Weak, but not absent, for all first row transition metals
- Possible mechanisms
  - 3d+4p mixing (not possible for centrosymmetric complexes
  - vibronic coupling
  - direct quadrupole coupling

Orientation dependence of 1s→3d transition



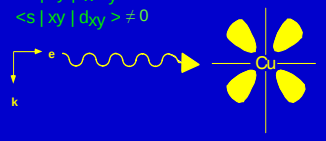
Four-fold periodicity to 1s→3d transition



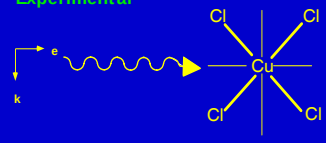
Quadrupole transitions – ΔL=2

Theoretical

<s | xy |dx2-y2> = 0
<s | xy | dxy > ≠ 0



Experimental



Selection rules for quadrupole transitions

$$\sigma_{z^2} = 6\sqrt{5}\sin^2\theta\cos^2\theta\sin^2\psi \bullet \zeta_{z^2}$$

$$\sigma_{x^2-y^2} = 2\sqrt{5}\sin^2\theta[\sin\psi\sin 2\phi - \cos\theta\cos\psi\cos 2\phi]^2 \bullet \zeta_{x^2-y^2}$$

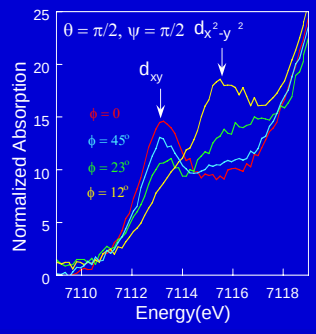
$$\sigma_{xy} = 2\sqrt{5}\sin^2\theta[\sin\psi cso 2\phi - \cos\theta\cos\psi\sin 2\phi]^2 \bullet \zeta_{xy}$$

$$\sigma_{yz} = 2\sqrt{5}[\cos\theta\sin\psi\cos\phi - \cos 2\theta\cos\psi\sin\phi]^2 \bullet \zeta_{yz}$$

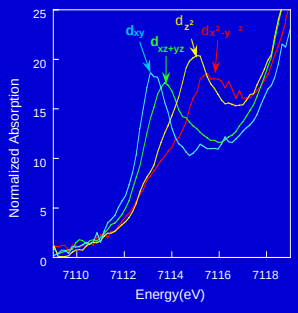
$$\sigma_{xz} = 2\sqrt{5}[\cos\theta\sin\psi\sin\phi - \cos 2\theta\cos\psi\cos\phi]^2 \bullet \zeta_{xz}$$

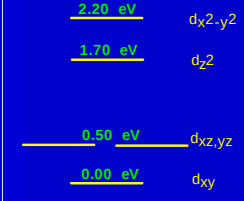
Brouder, C. *J. Phys. Condens. Matter*, **2** (1990) 701-738

1s→3d transitions for Fe porphyrins

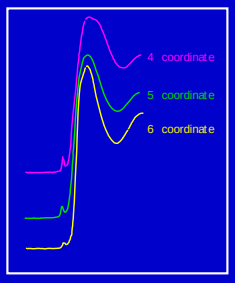


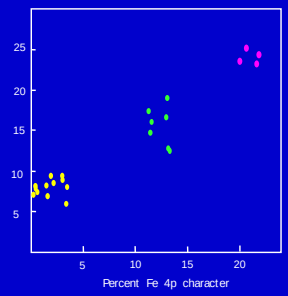
Isolated 1s→3d for Fe(OEP)(2-MeIm)





XANES for Fe(III) complexes





Roe et al., *J. Am. Chem. Soc.*, **106**, 1676

1s→3d intensity

- Weak for square–planar complexes
- Strong for tetrahedral complexes
- Correlates with coordination number

Multiplet effects

$Ti^{4+} = (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6 = {}^1S_0$

$Ti^{3+} = (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^1 = {}^2D_{3/2,5/2}$

$Ti^{2+} = (1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2 = {}^3F_{4,3,2} + {}^3P_{2,1,0} + {}^1D_{3,2,1} + {}^1G_{5,4,3} + {}^1S_0$

L edge of Ti^{4+}

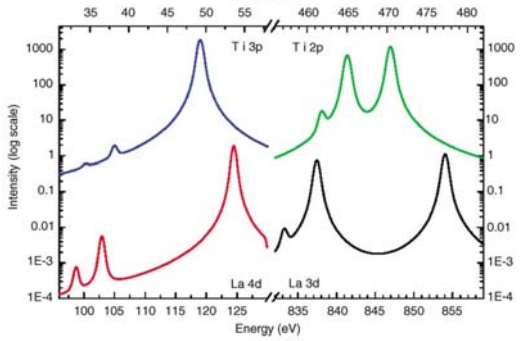
$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6 \rightarrow (1s)^2(2s)^2(2p)^5(3s)^2(3p)^6(3d)^1$

$(3d)^0 \rightarrow (2p)^5(3d)^1$

${}^1S_0 \rightarrow {}^1P_1, {}^1D_2, {}^1F_3, {}^3P_1, {}^3P_2 {}^3P_3, {}^3D_1, {}^3D_2, {}^3D_3, {}^3F_2, {}^3F_3, {}^3F_4$

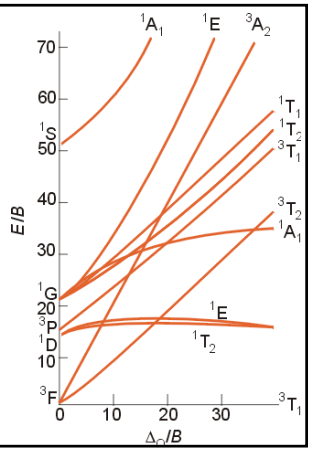
Allowed transitions: $\Delta J = \pm 1$ ${}^1S_0 \rightarrow {}^1P_1, {}^3P_1, {}^3D_1$

Simulations of L edges

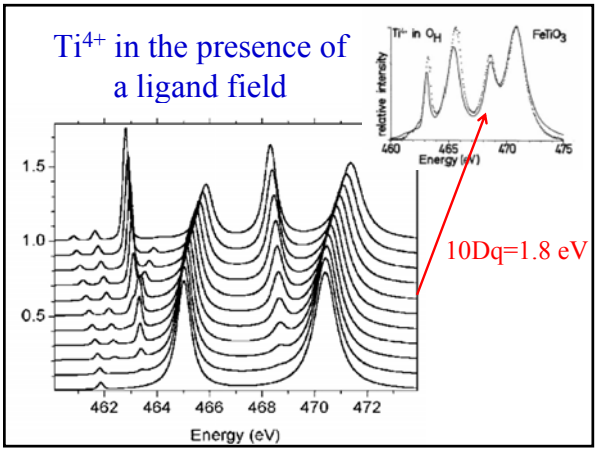


DeGroot, *Coord. Chem. Rev.* **2005**, *249*, 31–63

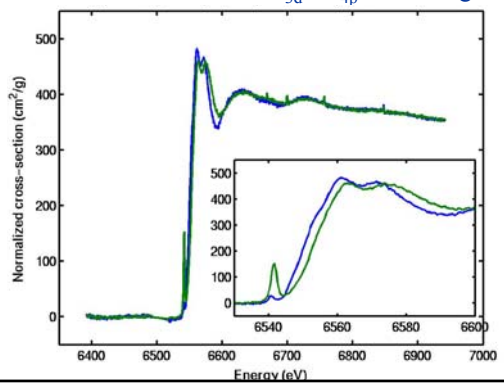
But – life is not really this simple – need to consider ligand field: d^2 terms vs ligand field



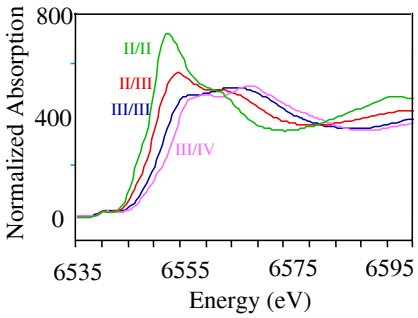
Ti^{4+} in the presence of a ligand field



M=O, M=N, etc. have intense pre-edge transitions due to M_{3d}+M_{4p}+O mixing

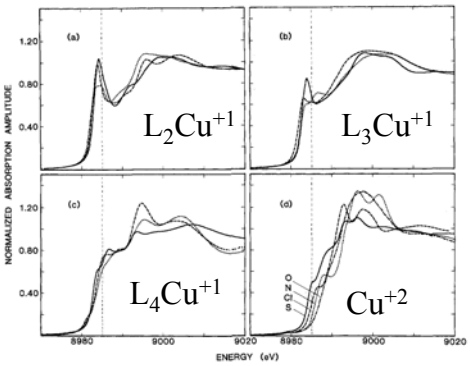


Dependence of XANES on Oxidation State



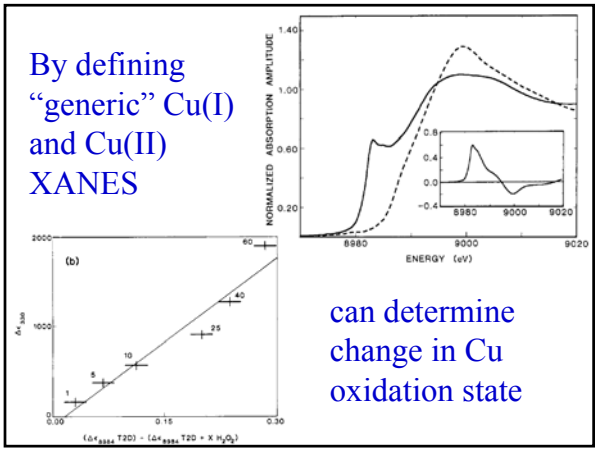
Why does edge shift with oxidation state?

- Electrostatics – harder to remove bound electron
- "Continuum resonance" – higher oxidation states have shorter bonds (in general).



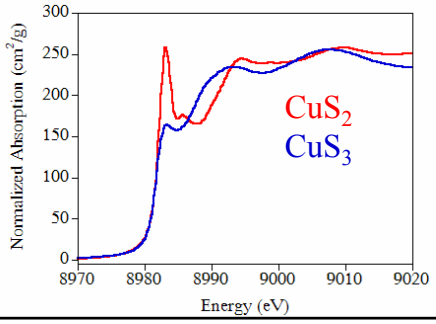
Kau et al., J. Am. Chem. Soc., 1987, 109, 6433

By defining "generic" Cu(I) and Cu(II) XANES



can determine change in Cu oxidation state

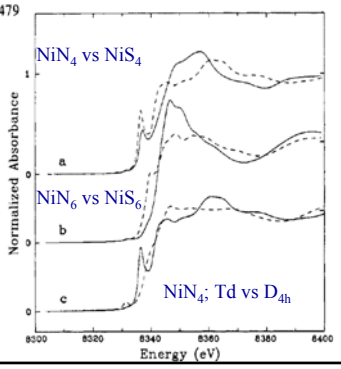
Sensitivity of XANES to geometry is consistent with expected density of unoccupied Cu 4p orbitals



X-ray Absorption Spectroscopic Evidence for a Unique Nickel Site in *Clostridium thermoaceticum* Carbon Monoxide Dehydrogenase

Stephen P. Cramer,*[1a,b] Marly K. Eidsness,[1c,d] W.-H. Pan,[1a] Thomas A. Morton,[1e] Steve W. Ragsdale,[1e,f] Daniel V. DerVartanian,[1e] Lars G. Ljungdahl,[1e] and Robert A. Scott*[1g]

Inorg. Chem. **1987**, *26*, 2477–2479



Theoretical calculations of XANES

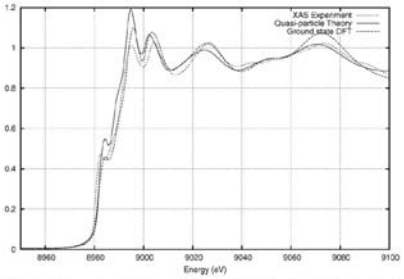
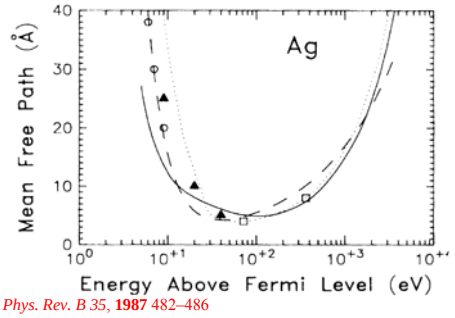


Fig. 1. XANES for K-shell Cu from XAS experiment (dots); from calculations with the FEFF8 code using the standard quasi-particle theory including a plasmon-pole self-energy and a screened core-hole (solid line); and from ground state density functional theory without a core-hole (dashes). Note that ground state theory (without a core-hole) is in reasonable agreement with experiment at the edge, but has too large an amplitude at high energies, where the standard theory is in reasonable agreement.

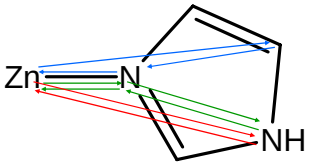
Rehr and Ankudinov, *Coord. Chem. Rev.* **2005**, *249* 131–140

Mean-free path increases dramatically for energies near the edge – accounts for some of the difficult with XANES caculations

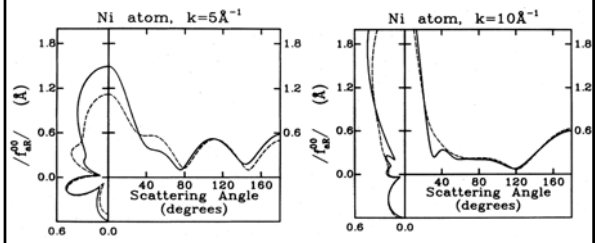


Penn, *Phys. Rev. B* 35, **1987** 482–486

The difficulty of simulating XANES is aalso due (in part) to multiple scattering

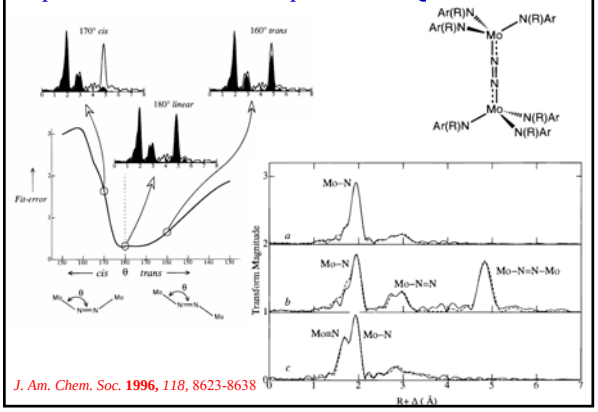


Scattering probability as a function of scattering angle



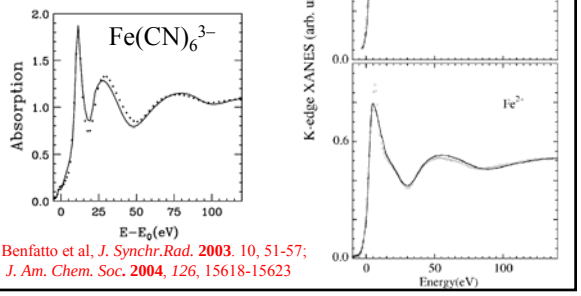
Barton and Shirley, *Phys. Rev. B* **1985**, *32*, 1892

Importance of linear multiple scattering

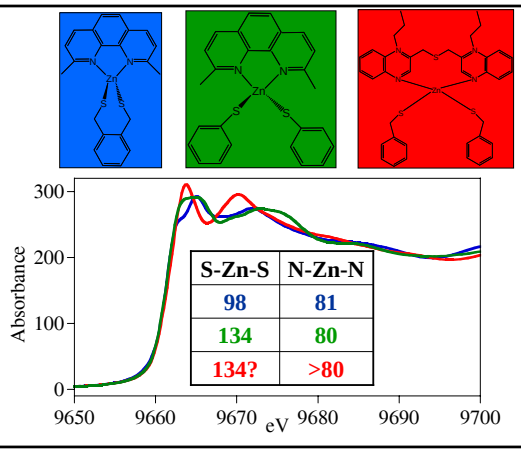


J. Am. Chem. Soc. **1996,** *118*, 8623-8638

MXAN can simulate XANES spectra (at least for some compounds under some conditions)



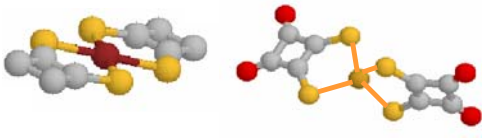
Benfatto et al, *J. Synchr.Rad.* **2003**. 10, 51-57;
J. Am. Chem. Soc. **2004**, *126*, 15618-15623



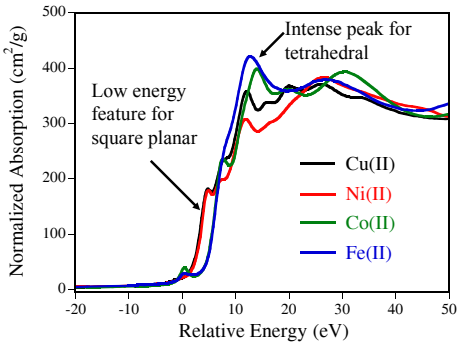
M(II)(dithiosquarate)$_2^{2-}$ provides a framework for testing effect of geometry

Square planar
Ni, Cu

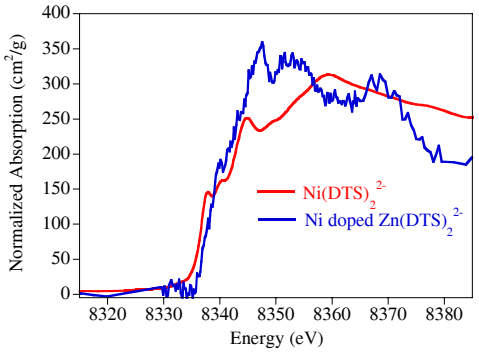
Tetrahedral
Fe, Co, Zn



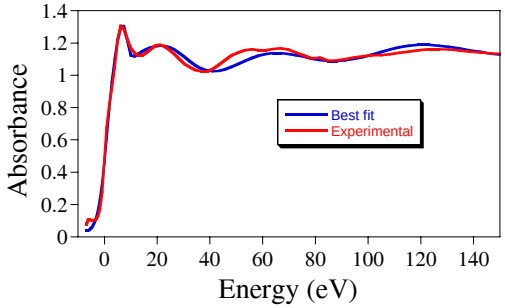
XANES changes appear to correlate with changes in geometry



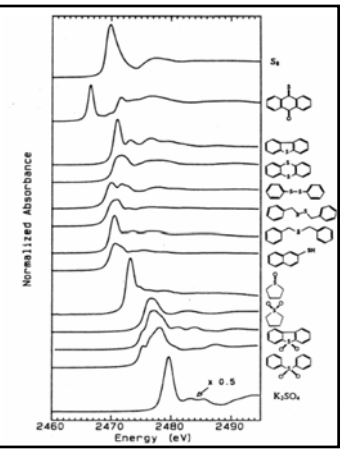
Doped samples support this assignment



Multiple-scattering simulations can reproduce main features of spectrum

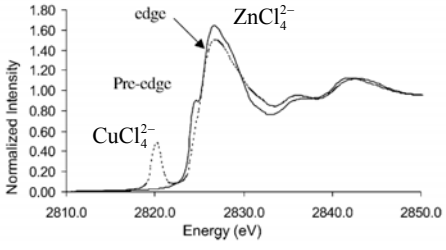


XANES studies are not limited to metals



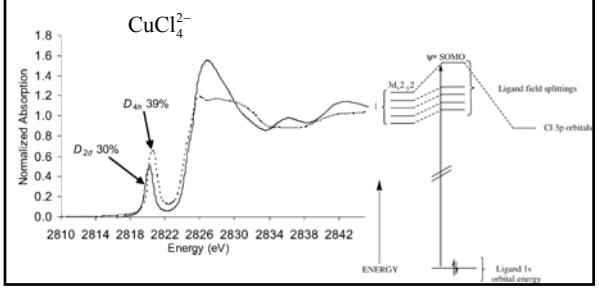
George and Gorbaty, *J. Am. Chem. Soc.* **1979** *101*, 3182

Ligand edges show pronounced dependence on metal identity

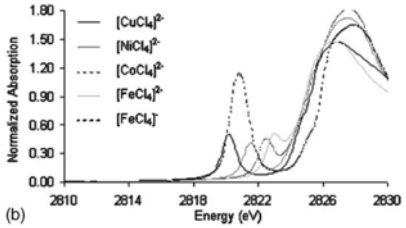


Hedman, et al., *J. Am. Chem. Soc.* **1990**, *112*, 1643

Pre-edge transition due to M_{3d}+L_{3p} mixing



Changes in pre-edge intensity correlate with changes in covalency



Equilibria for $Zn(SPh)_4^{2-}$ in DMSO

$$Zn(SR)_4^{2-} + TMA^+ \rightleftharpoons [Zn(SR)_4 \bullet TMA]^-$$

K_{IP} = 13 ±4 M^{-1}

$$[Zn(SR)_4 \bullet TMA]^- \rightleftharpoons Zn(DMSO)(SR)_3^- + SR^- + TMA^+$$

$K_{D,IP}$ = 0.01±0.009 M^2

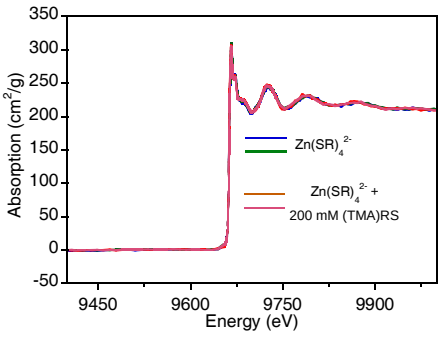
$$Zn(SR)_4^{2-} \rightleftharpoons Zn(DMSO)(SR)_3^- + SR^-$$

K_D= 0.13±0.12 M

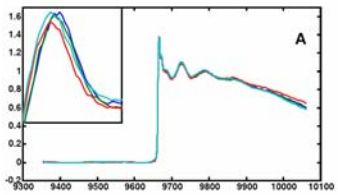
For 5 mM Zn, >75% dissociation

Wilker and Lippard, *Inorg. Chem.* (1997) **36**, 969.

XANES spectra show only very small changes with added thiolate



Conventional normalization misses changes in XANES



MBACK reveals subtle changes when thiolate is added