Basic Principles and Applications of XAFS

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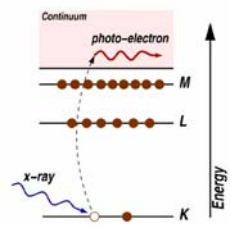
X-Ray Absorption Fine Structure (XAFS)



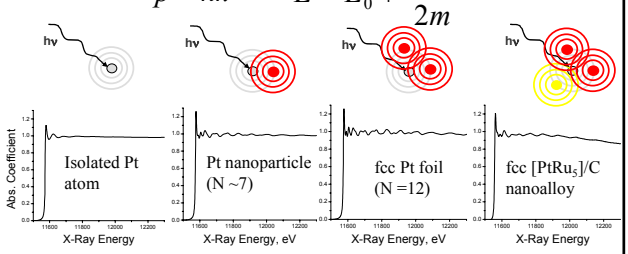
$$E = E_0 + E_k$$

$$E_k = \frac{p^2}{2m}$$

XANES:
X-ray absorption near edge structure

EXAFS:
Extended X-ray absorption fine structure

$$p = \hbar k \qquad E = E_0 + \frac{\hbar^2 k^2}{2m}$$



$$\mu(E) \propto \left|\langle f|\hat{H}|i\rangle\right|^2 \delta(E_f)$$

$$\chi(k) \sim N e^{-2k^2\sigma^2} f(k)\sin(2kr+\delta)$$

Parameter Space:

This parametrization is the same for SS and MS paths:

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)} \qquad E_0 = E_0^{bkg} + \Delta E_0$$

$$R = R_{model} + \Delta R$$

Amplitude

$$\chi_\Gamma(k) = \frac{N S_0^2}{kR^2}\left|f^{eff}(k)\right| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin\left[2kR - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

FEFF

Fitting EXAFS Theory to the Data:

$$f(R_i) = \tilde{\chi}(R_i) - \tilde{\chi}_{\mathrm{M}}(R_i)$$

$$\chi_\nu^2 = \frac{1}{\nu}\sum_{i=1}^{N_{\mathrm{idp}}}\left(\frac{f_i}{\varepsilon_i}\right)^2 = \frac{N_{\mathrm{idp}}}{N\nu}\sum_{i=1}^{N}\left(\frac{f_i}{\varepsilon_i}\right)^2$$

$\nu = N_{\mathrm{idp}} - P$ (Number of degrees of freedom)

$N_{\mathrm{idp}} = \dfrac{2\Delta k \Delta R}{\pi}$ (Number of relevant independent data points)

E. A. Stern
Phys. Rev. B **48**, 9825-9827 (1993)

$$\chi_\nu^2 = \frac{1}{\nu}\sum_{i=1}^{N_{\mathrm{idp}}}\left(\frac{f_i}{\varepsilon_i}\right)^2 = \frac{N_{\mathrm{idp}}}{N\nu\varepsilon^2}\sum_{i=1}^{N}\left[\mathrm{Re}(f_i)^2 + \mathrm{Im}(f_i)^2\right]$$

Analysis strategy

Implementation
- Find the best analysis software that can implement your strategy.
- IFEFFIT has convenient interface and allows for a large variety of strategies

Analysis Strategy
- -Plan on doing reality checks;
- -Reference compounds should be measured and analyzed first;
- -Try to maximize the number of degrees of freedom in the fits
- (use constraints, experimental/theoretical info etc.)

Conceptual Modeling
- -Start with the crude picture first, then refine it;
- -Homogeneous or heterogeneous environment? (bulk or nano, eq. or ineq. unit cell positions, solution or separate phases etc.)

FEFF Fitting and Error Analysis

Pre-process the data:
Remove background: $\mu(E) \rightarrow \chi(k)$.

AUTOBK algorithm: M. Newville, P. Livins, Y. Yacoby, E. A. Stern, and J. J. Rehr, Phys. Rev. **B**47, 14126-14131 (1993).

Fourier transform data: $\chi(k) \rightarrow \tilde{\chi}(r)$

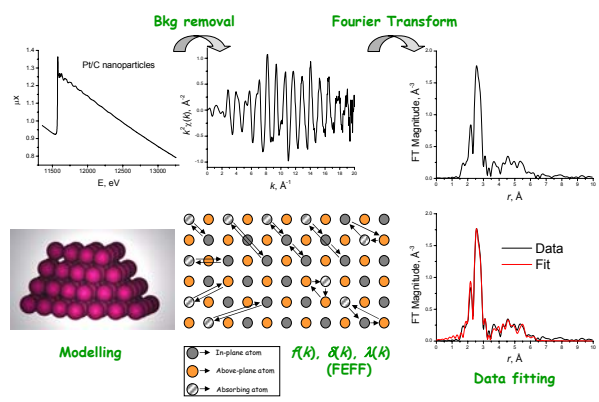
Pick a model

Calculate $f(k)$, $\delta(k)$ and $\lambda(k)$: FEFF

FEFF review: J.J. Rehr & R.C. Albers, *Rev. Mod. Phys.* (2000) 72, 621-654

Fit theory to data

Error analysis $\{x_i \pm \delta x_i\}$



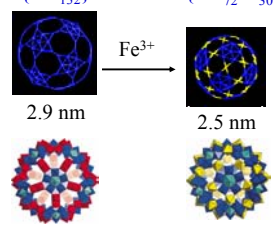
Applications of XANES and EXAFS
to basic and applied sciences

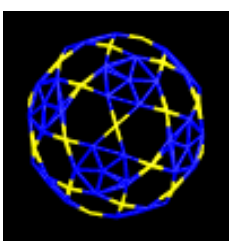
EXAFS in macromolecules

Giant inorganic molecules, Polyoxomolybdates (POMs):

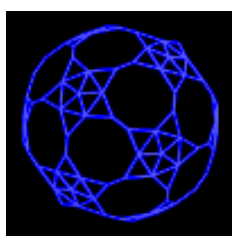
$[Mo_{132}O_{372}(HCOO)_{30}]$
$\{Mo_{132}\}$

$[Mo_{72}Fe_{30}O_{252}]$
$\{Mo_{72}Fe_{30}\}$





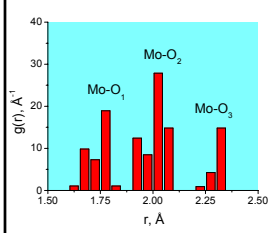
$\{Mo_{72}Fe_{30}\}$

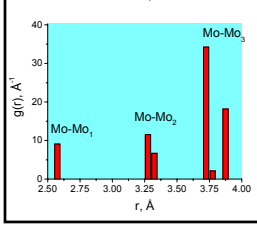


$\{Mo_{132}\}$

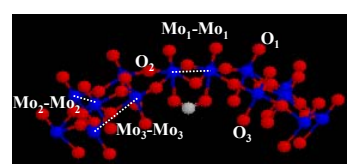
Modeling pair distribution functions using XRD results

$$g_{AB}(r) = \frac{dN_{AB}}{dr}$$

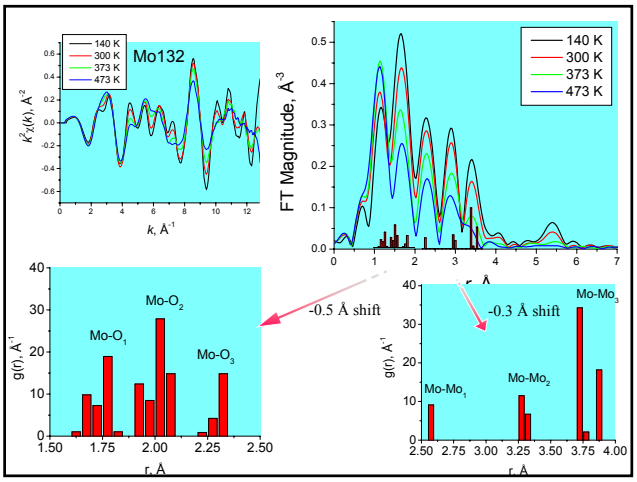




Mo_{132}



A. I. Frenkel, S. C. Frankel, T. Liu
Structural stability of giant polyoxomolybdate molecules as probed by EXAFS
Physica Scripta, **T115**, 721 (2005).



Applications of XANES

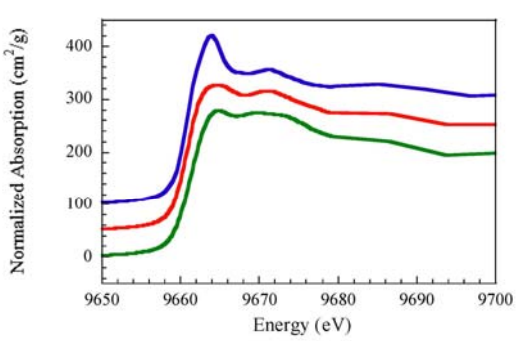
Contains information on:

-Average charge state of the absorber

-Local geometry

XANES spectra depend on Zn ligation

(J. Penner-Hahn, U. Michigan)



XANES spectra modeling by FEFF8

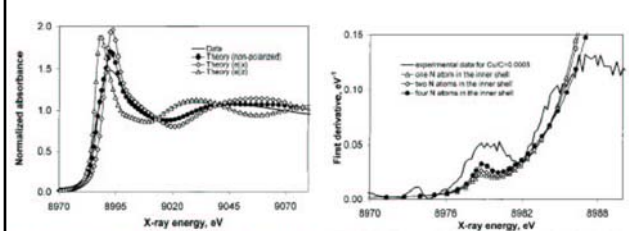
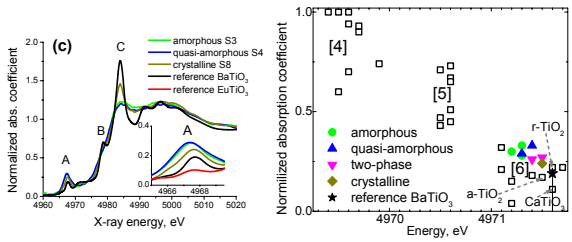


FIGURE 5. Comparison of the experimental and simulated Cu K-edge XANES spectra for $[Cu(H_2O)_6]^{2+}$. Equatorial and axial Cu−O distances used in the FEFF8 simulations were 1.97 and 2.24 Å, respectively. The theoretical XANES spectra calculated for two different polarizations are also shown.

FIGURE 6. Influence of the nitrogen incorporation in the first complexation shell of Cu^{2+}. Results of FEFF8 simulation. Axial and equatorial Cu−O distances fixed at 1.92 and 2.13 Å, respectively. Cu−N distance 2.00 Å.

A. I. Frenkel, G. V. Korshin, and A. Ankudinov,
XANES study of Cu 2+ - binding sites in aquatic humic substances,
Environ. Sci. Technol., **34** , 2138 (2000).

XANES spectra depend on the local geometry



A. I. Frenkel, Y. Feldman, V. Lyahovitskaya, E. Wachtel, I. Lubomirsky, Physical Review B **71**, 024116 (2005).

XANES spectra depend on the local oxidation state

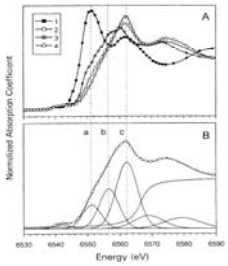
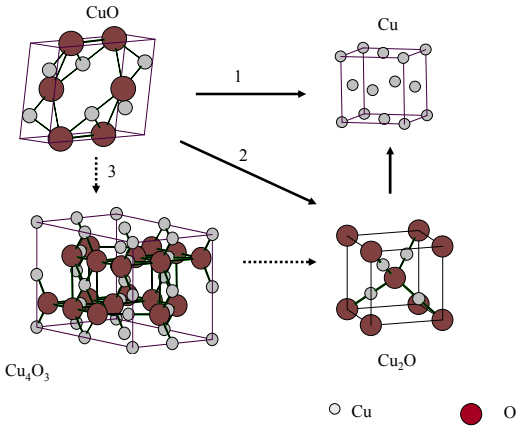
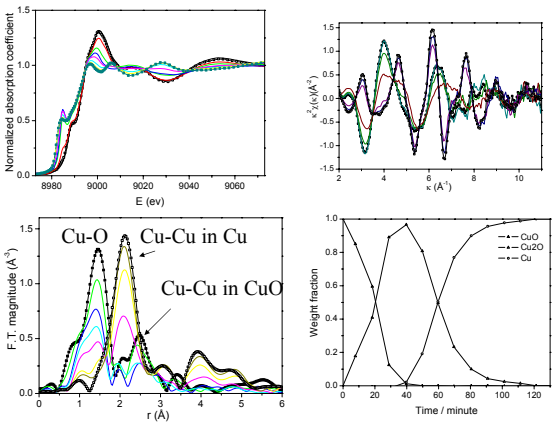


Figure 2. (A) Manganese K-edge XANES spectra of the solid phase products of birnessite reaction with glucose and/or glycine in the Maillard reaction. 1: glucose-glycine-birnessite, 2: glucose-birnessite, 3: glycine-birnessite, all at an initial pH 7.00, following reaction at 45°C for 15 d, and 4: pure birnessite. (B) Typical deconvolution of an XANES spectrum (sample 2) into several gaussian peak functions and an arctangent step function which reflects continuum transition of the photoelectron. As described earlier, the three major peaks were taken to represent different oxidation states of manganese (2+ (a), 3+ (b) and 4+ (c)). The two minor peaks at the end were required to obtain a complete fitting of the spectrum, and probably represent unspecified transitions. The relative percent contributions of the +2, +3, and +4 states are for 1: Mn(II) 50%, Mn(III) 10%, Mn(IV) 40%; 2: Mn(II) 20%, Mn(III) 30%, Mn(IV) 50%; 3: Mn(II) 20%, Mn(III) 45%, Mn(IV) 35%; and 4: Mn(II) 10%, Mn(III) 30%, Mn(IV) 60%.

A. Jokic, A. I. Frenkel, M. Vairavamurthy, and P. M. Huang, Geophys. Res. Lett., **28,** 3899 (2001).

How to analyze a mixture of species (environmental, biological, chemical sciences)





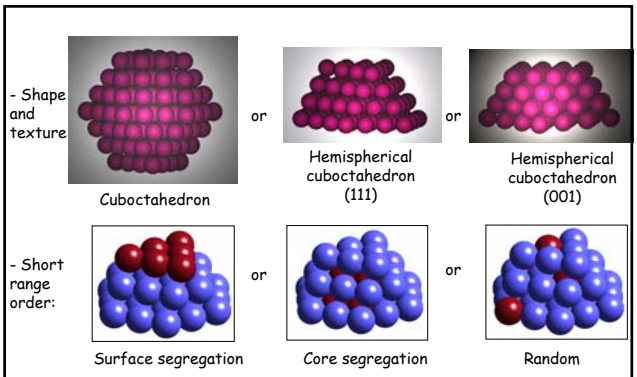
X. Wang, J. C. Hanson, A. I. Frenkel, J.-J. Kim, J. A. Rodriguez
J. Phys. Chem. B **108**, 13667 (2004).

EXAFS and nanoscience

- structure, disorder in a nanoscale object,

-dynamics and kinetics during in situ transformations

-investigation of catalysts



A. I. Frenkel
Solving the 3D structure of metal nanoparticles
Zeitschrift fur Krystallographie, **222**, 605-611 (2007).