XANES Measurements and Interpretation

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Acronyms

**XANES**

- X-ray Absorption Near Edge Structure

**NEXAFS**

- Near-Edge X-ray Absorption Fine Structure

The two acronyms should be interchangeable but over the years NEXAFS has become terminology for “low Z” elements - C, N, O...
What Is XANES?

- XANES is region of x-ray absorption spectrum within ~50eV of the absorption edge.
- Suggested that division is that at which wavelength of excited electron is equal to distance between absorbing atom and its nearest neighbor. \( \lambda (\text{Å}) \approx \frac{12}{[e(\text{eV})]}^{\frac{1}{2}} \).
What Is XANES?

XANES = Pre-edge + Edge + XANES

(X-ray absorption spectrum of Ti K-edge of Ba$_2$TiO$_4$)
Terminology

- Traditionally, set energy scale and calibrate energy by taking maximum of first derivative of edge as “E_0”.
- Then any peaks below this energy are “pre-edge” peaks.
“Pre-edge” Peaks

- True energy zero is the Fermi energy: there can be no transitions below this energy.
- If “edge” energy correctly defined as $E_F$ there are, by definition, no “pre-edge” features!
- Often difficult to distinguish between bound (localized) and unbound (delocalized) states.
Why Are We Interested In XANES?
Local Coordination Environment

• Ti K-edge XANES shows dramatic dependence on the local coordination chemistry.
Why Are We Interested In XANES? 
Oxidation State

- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
What Is XANES and Why Are We Interested?

XANES is strongly sensitive to the chemistry (formal oxidation state and geometry) of the absorbing atom.

<table>
<thead>
<tr>
<th>Region</th>
<th>Transitions</th>
<th>Information Content</th>
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<tbody>
<tr>
<td>Pre-edge</td>
<td>Features caused by electronic transitions to empty bound states. Transition probability controlled by dipolar selection rules.</td>
<td>Local geometry around absorbing atom. Dependence on oxidation state and bonding characteristics (chemical shift).</td>
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<tr>
<td>Edge</td>
<td>Defines ionization threshold to continuum states.</td>
<td>Dependence on oxidation state (chemical shift), main edge shifts to higher energy with increased oxidation state. (As much as 5 eV per one unit change).</td>
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<tr>
<td>XANES</td>
<td>Features dominated by multiple-scattering resonances of the photoelectrons ejected at low kinetic energy. Large scattering cross section.</td>
<td>Atomic position of neighbors: interatomic distances and bond angles. Multiple scattering dominates but <em>ab initio</em> calculations providing accessible insight (e.g. FEFF8).</td>
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XANES Transitions

• XANES directly probes the angular momentum of the unoccupied electronic states: these may be bound or unbound, discrete or broad, atomic or molecular.

• Dipole selection rules apply*: $\Delta l = \pm 1$, $\Delta j = \pm 1$, $\Delta s = 0$.

• Primary transition will be:
  • $s \rightarrow p$ for K ($1s$ core electron) and $L_1$ ($2s$ core electron initial state) edges
  • $p \rightarrow d$ for $L_2$ ($2p_{1/2}$) and $L_3$ ($2p_{3/2}$) edges

• But…..final state usually not atomic-like and may have mixing (hybridization) with other orbitals. This is often the interesting part of the XANES!

* Some transitions are true quadrupolar transitions. These are usually very weak.
**XANES Interpretation**

- The EXAFS equation breaks down at low-$k$, which complicates XANES interpretation.

- **We do not have a simple equation for XANES.**

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of:

- **coordination chemistry** regular, distorted octahedral, tetrahedral…
- **molecular orbitals** p-d hybridization, crystal field theory
- **band structure** the density of available occupied electronic states
- **multiple scattering** multiple bounces of the photoelectron

- These chemical and physical interpretations are all related:

  **What electronic states can the photoelectron fill?**
Advantages of XANES vs. EXAFS

- Spectra simpler to measure than EXAFS: features intense, concentrated in small energy region.

- Weak temperature dependence (Debye-Waller), so spectra can be recorded at reaction temperature \((\text{in situ})\).

- Faster to measure than full spectrum: <msec demonstrated.

- Sensitive to chemical information: valence, charge transfer.

- Probes unoccupied electronic states: important in chemistry.

- Often used as simple “fingerprint” to identify presence of a particular chemical species.

- Beamlines with micro-probe capabilities can also scan energy and obtain XANES spectra with elemental distribution.
**XANES Analysis: Oxidation State Sulfur**

Sulfur K-edge XANES used to identify and quantify the form of sulfur in heavy petroleum, coals, soils etc.

11 eV edge shift from $S^{2-}$ to $S^{6+}$.

Spectra of S in similar environments similar: thiophene, benzothiophene.

Can be used as fingerprint.

XANES Analysis: Oxidation State Sulfur

Dodecyl sulfide, thiophene, tetramethylene sulfoxide, tetramethylene sulfone, sulfate(aq)
XANES Analysis: Oxidation State

Many, many examples in the literature……

Mo K-edge

V K-edge

Re L₃-edge

Ref: Cramer et al., JACS, 98 (1976) 1287


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Local Site Symmetry in Ti-containing Compounds

Symmetry around absorbing atom strongly affects pre-edge transition: ability to differentiate 4, 5, 6-fold coordination.
Local Site Symmetry in Ti-containing Compounds

- Correlation between absolute position and peak height of pre-edge peak: all 4-fold, 5-fold and 6-fold coordinated Ti compounds fall into separate domains.

- Ability to distinguish Ti coordination from pre-edge peak information.

XANES of 3d Transition Metals: Coordination

- For $T_d$ symmetry 1s to 3d pre-edge peak sharp and intense from Ti→Mn, decreases Fe→Cu, absent for Zn.
- Decrease in intensity due to progressive filling of the 3d band.
- $O_h$ symmetry shows only a small pre-edge peak throughout series.

“White line” Intensity of Group VIII Metals

- Peak historically called a “white line” as when it was detected by x-ray film it showed up as a white line due to the strong absorption.


- Transition from $2p_{3/2}$ to $5d$ states.
- Absence of peak for Au: $5d$ states almost completely occupied.
- For others Pt<Ir<Os<Re, corresponding to increase in number of unoccupied $5d$ states on the atoms.

L$_3$ edge XANES for 5$d$ metals
Quantification of “White Line”

- Fit to combination of Lorentzian and arctangent functions.
- Determine: area, fwhm, position.


- Linear correlation between white line area and number of 5d-holes for Au-Re
“White Line” Intensity: Oxides

Re L₃-edge - Transition from 2p3/2 to 5d states.

Re metal (Re⁰) - 5d⁵
ReO₂ (Re⁴⁺) - 5d¹
NH₄ReO₄ (Re⁷⁺) - 5d⁰

• Intensity of Re L₃ white line probes Re LDOS
“White Lines”: large change in absorption coefficient

- Step height linear with concentration from 100-10,000 ppm S - but relative white line intensity constant only for <2000 ppm.
- Important if using a “reference” spectrum for fitting or fingerprinting.
Pt $L_3$ and $L_2$ Edge XANES

- Significant difference in $L_3$ and $L_2$ edge XANES: 2p to 5d transitions.

- Pt 5$^d$3/2 filled, so no white line.

- $L_2$ shifted to align with $L_3$ edge.

- Same $l=2$ final density of states but because of selection rule, $\Delta j = \pm 1$, different total quantum number probed.

- $j=3/2$ probed by $L_2$-edge, $j=5/2$ probed by $L_3$-edge.
- Transition is $2p$ to $5d$: Pt $d$-band full, so “no” intensity at edge.
- PtGe intermetallics: charge transfer from $d$-band of Pt to Ge, resulting in significant intensity at edge.
- Use as signature of Pt-Ge intermetallic formation.
Effect of Adsorbed Hydrogen on Pt L\textsubscript{3} XANES

10-15Å Pt clusters supported on Al\textsubscript{2}O\textsubscript{3}

- White-line intensity decreases and spectra broaden to higher energies as H is added.
- Difference signal typically leads to broad structure \(\sim 8\) eV above absorption edge.
- Several different interpretations in the literature.
Which Edge to Choose: Energy Resolution

Mo K-edge XANES of Na$_2$MoO$_4$

![Graph showing XANES spectrum with Mo K-edge at 20.00 keV and effective resolution of 10 eV dominated by core-hole lifetime.]

- Mo K-edge at 20.00 keV, effective resolution of 10 eV dominated by core-hole lifetime.
Which Edge to Choose: Energy Resolution

• Comparison of normalized Mo L\textsubscript{3}-edge (2.5 keV) XANES of Na\textsubscript{2}MoO\textsubscript{4} with that of Mo K-edge (20.0 keV).

- Mo L\textsubscript{3}-edge at 2.5 keV, 0.5 eV spectral resolution!
Which Edge to Choose: Energy Resolution

Sodium Molybdate, NaMoO₄
Mo atom tetrahedral coordination

Cobalt Molybdate, CoMoO₆
Mo atom octahedral coordination

Mo L₃-edge XANES

\[ \Delta E \text{ tetrahedral} = 2.2-2.5 \text{ eV}; \Delta E \text{ octahedral} = 3.25-4.2 \text{ eV} \]
**Time Evolution of XANES: Kinetics**

In situ temperature programmed reduction of Re$_2$O$_7$/Al$_2$O$_3$

- **Reduction in H$_2$**
- **RT**
- **500ºC**

Normalized Absorption

Photon Energy, keV

Normalized Absorption

Percent Re$_2$O$_7$ remaining

Temperature, ºC

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**Time Evolution of XANES: Kinetics**

TPR-XANES showing reduction of vanadium as catalyst is heated in H₂ to 500ºC

Recorded at X19A, 80 sec/scan
**Q-XANES & D-XANES**

**Quick XANES**

- Slew monochromator continuously to obtain a XANES spectrum in few seconds.
- All modes of detection.

**Dispersive XANES**

- Polychromatic beam dispersed onto linear detector.
- XANES spectrum in msec.
- Transmission only.
- Need extremely uniform samples.
**Micro-XANES**

- Use special optics to focus x-ray beam to 10µm diameter (X26A) or <1µm diameter at APS.

- Combined with x-ray microprobe: elemental composition maps and oxidation state/local coordination.

- Applications:
  - Speciation of metals in soils, sediments and organisms
  - Grazing incidence studies of cations and anions on surfaces
  - Time-resolved studies of reactions on surfaces and interfaces
  - High temperature studies (trace elements in melts)
  - Oxidation states of planetary material
  - High pressure phases (diamond anvil cell)

Analysis of Mixtures

• XANES useful technique to quantitatively determine composition of a mixture of species.

• Useful for following time evolution of species during a chemical reaction.

• Two most common methods:
  – Least squares linear combination fitting
  – Principal component analysis
Least Squares Linear Combination Fitting

- Use a linear combination of spectra of various reference samples.

- Allows quantification of species in multiple-component mixture from their fingerprint in the XANES region.

- Use a least-squares algorithm to refine the sum of a given number of reference spectra to an experimental spectrum.

- Simple method, easy to implement.

- **Must have good quality spectra of the reference compounds recorded under similar conditions.**
Linear Combination Fitting

Fit experimental data to linear combination of known reference compounds

TPR-XANES of *in situ* reduction of Ce$_{0.7}$Zr$_{0.3}$ oxide

LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature
**Principal Component Analysis**

- Used since 1970’s in other chemical spectroscopy†. First published reference in XANES 1992*.  
- Traditional approach: choose pure model standard, fit edges to these standards, but…  
- How many standards are needed?  
- How do we know models are reasonable?  
- If you have wrong group of standards…there is no way to get the correct answer…

**Principal Component Analysis**

- PCA estimates number of distinct species in a series of spectra.
- Used as a first stage of analysis.
- Based on linear algebra - each spectrum represented as a vector.
- Goal is to find number of components that can reproduce the experimental spectra to within experimental (statistical) error.
- No *a priori* assumptions on number/type of components.
- Growing popularity in XANES spectroscopy*.


Feff8.1 and XANES

• Dramatic progress in past decade both in theory and *ab initio* calculations.

• Significant progress has been made in understanding XANES.

• Quantitative theory central to quantitative interpretation of XAFS spectra in terms of local geometric and electronic structure.

• Will hear more about Feff tomorrow!
Feff8.1 and XANES: Pt L-edges

Feff reproduces differences in white line at Pt L$_{3,2}$-edges

Pt L$_3$-edge XANES as function of Pt cluster size

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**Summary**

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<tr>
<th>XANES is a much larger signal than EXAFS</th>
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<td>XANES can be done at lower concentrations, and less-than-perfect sample conditions.</td>
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<th>XANES is easier to crudely interpret than EXAFS</th>
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<td>For many systems, the XANES analysis based on linear combinations of known spectra from “model compounds” is sufficient.</td>
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<td>More sophisticated linear-algebra techniques, such as principal component analysis can be applied to XANES spectra.</td>
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<th>XANES is harder to fully interpret than EXAFS</th>
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<td>The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.</td>
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<td>This situation is improving…..</td>
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