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.
**What Is XANES?**

XANES = **Pre-edge** + **Edge** + **XANES**

(X-ray absorption spectrum of Ti K-edge of Ba₂TiO₄)
**“White line”**

- In years past x-ray absorption spectra were taken with use of photographic plates.
- Absorption edges appeared as unexposed bands on the plate (developed in negative), or “white lines”.
- Very prominent for L-edges of transition metals in high oxidation states.
**Number of “XANES” Publications**

- On average ~500 publications per year in SciFinder!
Representative Publications (2005)


• Crystal-Quasicrystal Local Structural Transition in Al-Cu-Fe. JETP Letters (2005), 81(9), 479-483.

Why Are We Interested In XANES?
Local Coordination Environment

- Ti K-edge XANES shows dramatic dependence on the local coordination chemistry.

Both Ti$^{4+}$

Ba$_2$TiO$_4$

K$_2$TiSi$_3$O$_9$
Why Are We Interested In XANES? Oxidation State

- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
- First observation was by Berengren for phosphorus in 1920*!

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>
</tr>
</thead>
<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>
</tr>
<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>
</tr>
<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 ab initio calculations providing accessible insight (e.g. FEFF8).</td>
</tr>
</tbody>
</table>
**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 L₁ (2s core electron initial state) edges
  - $p \rightarrow d$ for L₂ (2p½) and L₃ (2p₃/₂) 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 (in situ):
  \[ \text{Exp}(-2k^2\sigma^2) = \exp(-2(0.5)^2 \times 0.005) \approx 1 \]
- 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)

<table>
<thead>
<tr>
<th>Sulfur type</th>
<th>Formal oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide</td>
<td>2-</td>
</tr>
<tr>
<td>Thiophene</td>
<td>1+</td>
</tr>
<tr>
<td>Sulfoxide</td>
<td>2+</td>
</tr>
<tr>
<td>Sulfone</td>
<td>4+</td>
</tr>
<tr>
<td>Sulfate</td>
<td>6+</td>
</tr>
</tbody>
</table>
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

**XANES Analysis: Oxidation State**

Mo K-edge XANES of Mo oxides

- Linear fit of Mo valence with K-edge position only obtained using a feature above the absorption edge!

Metal K-edge XANES

- Intense edge absorption due to dipole allowed $s \to p$ transition ($\Delta l = \pm 1$).
- Weaker pre-edge feature results from mixing of 3d-4p orbitals of suitable symmetry (or from quadrupolar allowed transition – ~2 orders magnitude weaker).
Molybdenum Oxides

Mo K-edge XANES

- Both nominally +6 oxidation state, but different XANES spectra.
- Edge shift – different degree of covalency of the Mo.
- Pre-edge peak much larger for tetrahedral coordination.
Transition Metal K-edge Pre-edge Peaks

Pure octahedral case

Centro-symmetric: no p-d mixing allowed; only quadrupolar transitions – very low intensity

Distortion from octahedral

p-d mixing allowed: dipole transition in pre-edge – increasingly larger intensity.

Pure tetrahedral

Largest pre-edge intensity.
**Local Site Symmetry in Ti-containing Compounds**

![Graph showing XANES spectra of Ti K-edge for different compounds](Ti_K-edge_XANES_RefCompounds.png)

- **Anatase**
  - 3d split by mixing with O2p into t2g and eg like orbitals.
  - 3rd peak is quadrupolar in nature.

- **Fresnoite**
  - 5 coordinate
  - 3rd peak is quadrupolar in nature.

- **Barium orthotitanate**
  - 4 coordinate

- **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.

Ligand-Metal Binding from Ligand K-edge XANES

- Provides direct experimental measurement of the ligand 3p character in the highest occupied molecular orbital (HOMO).
- Allows study of “spectator” ligand effects.
Ligand-Metal Binding: Cl K-edge XANES

- Position of the ligand pre-edge peak depends primarily on the d manifold energy (M oxidation state). Those compounds with d-band closest to the Cl 3p energy have strongest M-Cl bonding, and highest covalency.

- In Pt(NH₃)₃Cl₂ there is no direct M-Cl bonding: Cl is a “spectator” ligand – so no pre-edge peak.
**“White line” Intensity of 4d Metals**

- Transition from $2p^{3/2}$ to $4d$ states.
- Absence of peak for Ag: $4d$ states almost completely occupied ($d^{10}$).
- For others Pd ($d^9$)<Rh ($d^7$)<Ru ($d^6$)<Mo ($d^5$), corresponding to increase in number of unoccupied $4d$ states on the atoms.

**L$_3$ edge XANES for 4d metals**

- Linear correlation between white line area and number of 4d-holes for Mo to Ag
“White Line” Intensity: Oxides

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

- Intensity of Re L₃ white line probes Re LDOS

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

*Spectra aligned in energy
Metals & Oxides

- Overall shape of spectrum also different.

White line reflects holes in d-band

No white line

**Au L₃-edge XANES**

![Graph of Au₂O₃ and Au metal](image)

Au₂O₃

Au metal
XANES Peak Fitting in Athena

- Useful for quantification of areas, etc.

EXAFS Data Collection and Analysis Course, APS, July 26-29, 2005
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“White Lines”: large change in absorption coefficient

**Sulfur K-edge XANES of sulfate**

- 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.
Caution about use of absolute intensity of "white line"

Solid sulfur, $S_8$

- Calculation of sulfur K-edge XANES (2.47 keV) for different spherical particles of sulfur.
- Severe distortion of the spectrum for particles 1 µm radius! One absorption length is $\sim 2 \mu m$.

**Quotation from a recent publication on sulfur XANES:**

"Due to their relatively high sulfur concentrations, all standards were powdered and sieved to particles sizes $\leq 10 \mu m$ in diameter to minimize self-absorption effects at the sulfur K-edge"
Pt $L_3$ and $L_2$ Edge XANES

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

- Pt $5d^{5/2}$ 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.

- Only $j=3/2$ probed by $L_2$-edge, both $j = 3/2$ and $j = 5/2$ 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$_3$ XANES

- 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.

10-15Å Pt clusters supported on Al$_2$O$_3$
Experimental *in situ/operando* cells for XAFS experiments used by UOP
Time Evolution of XANES: Kinetics

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

 Photon Energy, keV

Normalized Absorption

RT

Reduction in H$_2$

500°C

Percent Re$_2$O$_7$ remaining

Temperature, ºC

Oxidized Re

Reduced Re

Re

Al$_2$O$_3$

Re-O = 1.72Å

Re-Al = 3.05Å

Re$^{7+}$

EXAFS Data Collection and Analysis Course, APS, July 26-29, 2005

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**Time Evolution of XANES: Kinetics**

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

Heat in H₂ flow

RT

500 °C

80 sec/scan
**Q-XANES & D-XANES**

**Quick XANES**

- Slew monochromator continuously to obtain a XANES spectrum in few seconds (10-ID).
- 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 <1μm diameter.
- 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 – energy alignment is critical.
Linear Combination Fitting in Athena

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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
Linear Combination Fitting

Ni K-edge XANES of in situ sulfiding of a Ni/Al₂O₃ catalyst

Effect of sulfiding

LC-XANES fit to determine amount of oxidized and sulfided Ni present as function of temperature/time

Relative Amount of Ni Sulfide

Temperature, °C

Photon Energy, keV

Normalized Intensity

0.0
0.5
1.0
1.5
2.0
0.0
0.2
0.4
0.6
0.8
Quantification Using Reference Compounds

- Need to be cautious about collecting XANES data of bulk reference compounds in fluorescence – will get incorrect answer in quantitative fitting!

Re $L_3$-edge XANES spectrum of bulk $(NH_4)ReO_4$

White line of spectrum collected in fluorescence severely attenuated.
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.
- Use 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.
- Several examples now in literature in XANES spectroscopy*.


Potential pitfalls and drawbacks of PCA

• Principal components not equal to chemical species.
• Constant ratio of two (chemical) components.
• Temperature increase during measurement.
• Additional information required to transform abstract results in meaningful speciation (either references or concentrations).
• But: Powerful method to reduce ambiguity in qualitative and quantitative analysis of a series of XAS spectra (“model-free”).
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.

- For “experts” only at this time.
**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
Summary

XANES is a much larger signal than EXAFS

XANES can be done at lower concentrations, and less-than-perfect sample conditions.

XANES is easier to crudely interpret than EXAFS

For many systems, the XANES analysis based on linear combinations of known spectra from “model compounds” is sufficient.

More sophisticated linear-algebra techniques, such as principal component analysis can be applied to XANES spectra.

XANES is harder to fully interpret than EXAFS

The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.

This situation is improving…..