XANES Measurements and Interpretation

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Acronyms

XANES

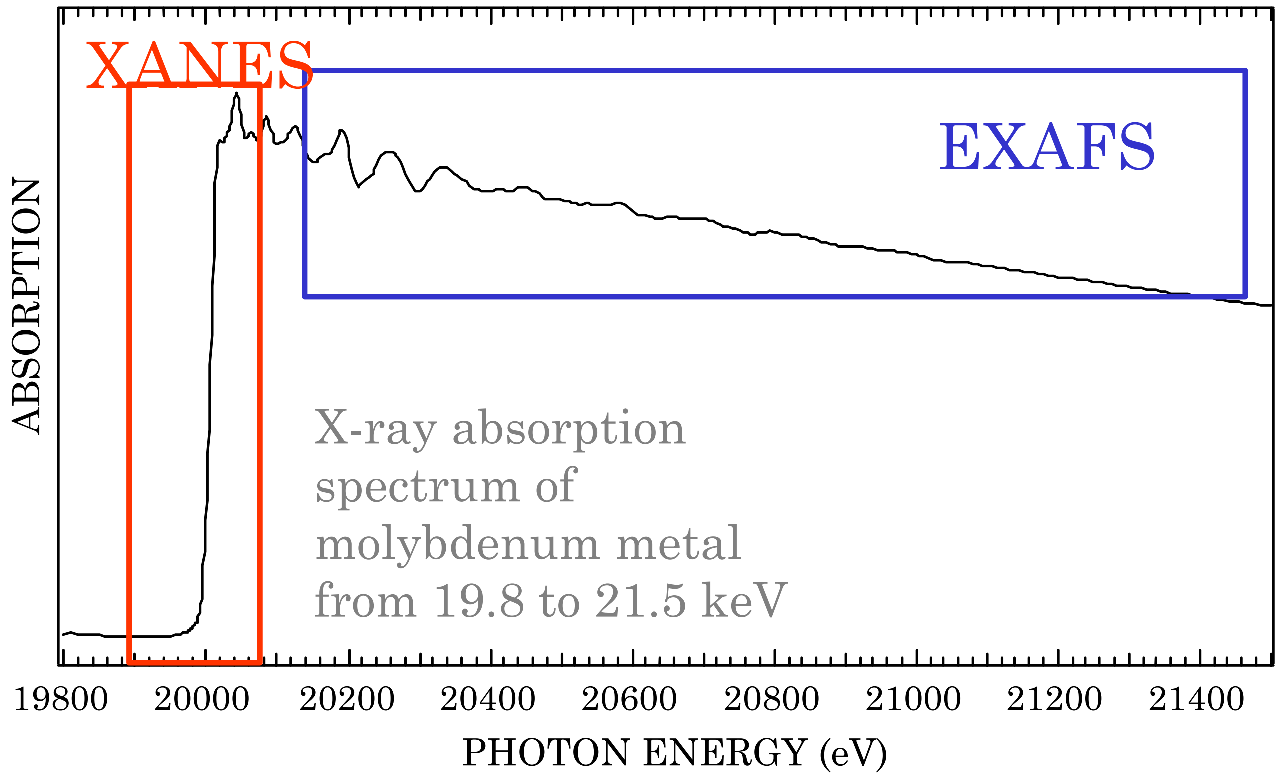
- **X**-ray **A**bsorption **N**ear **E**dge **S**tructure

NEXAFS

- **N**ear-**E**dge **X**-ray **A**bsorption **F**ine **S**tructure

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

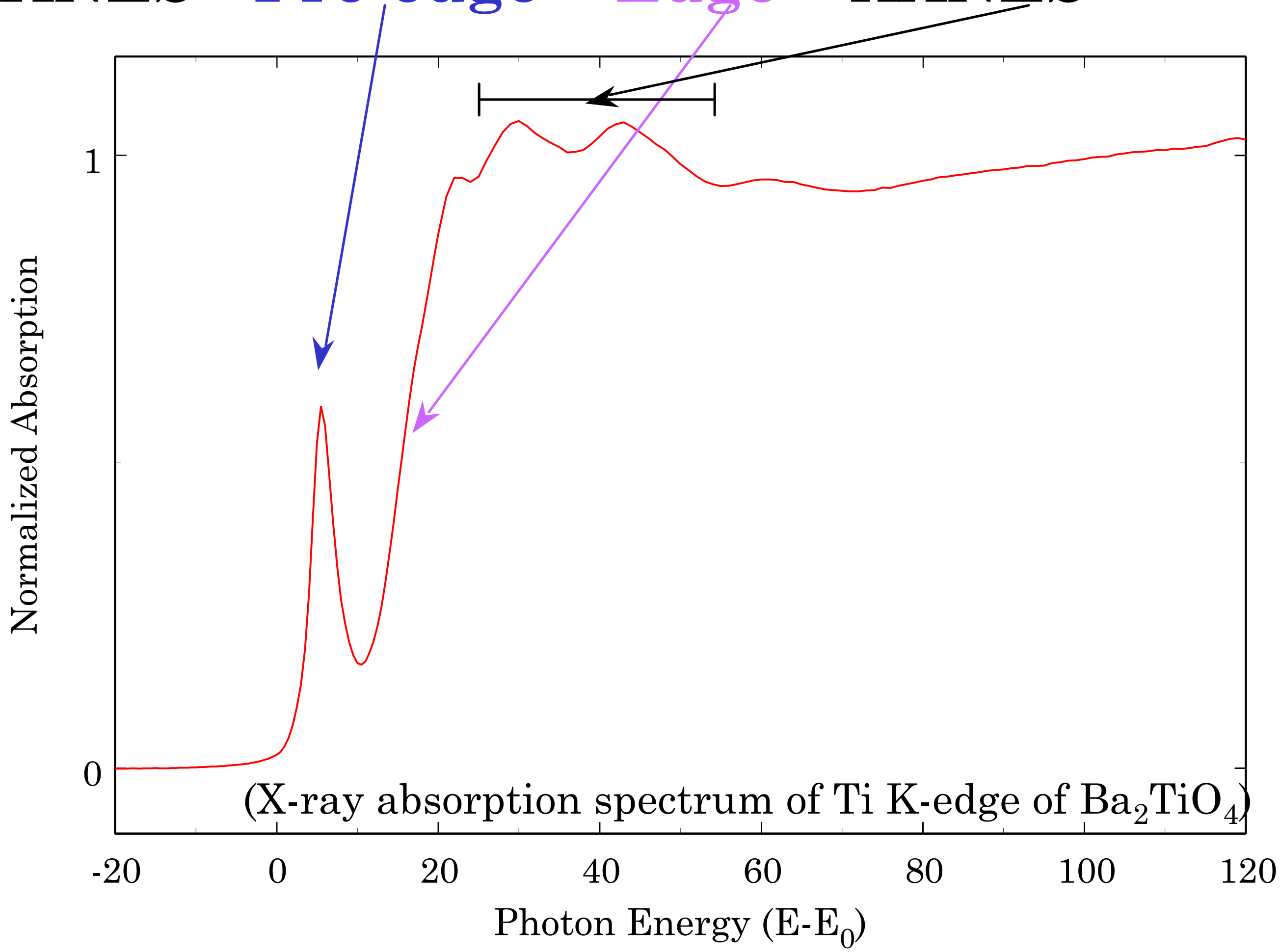
What Is XANES?



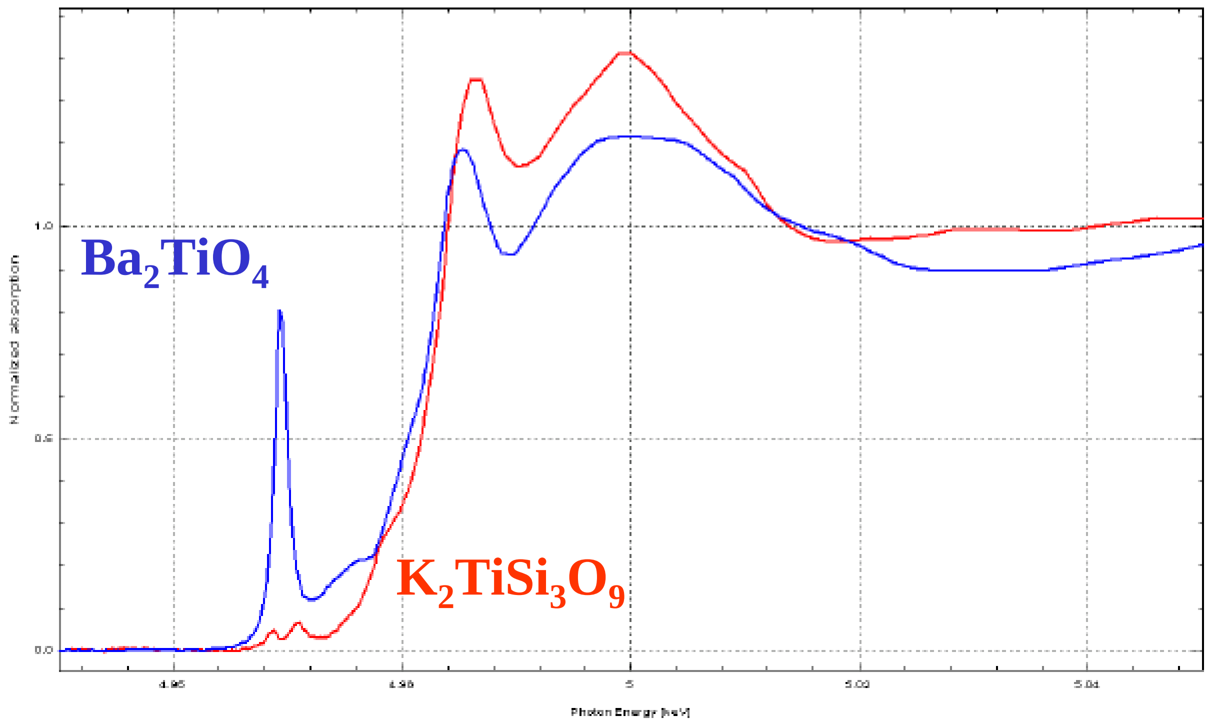
- XANES is region of x-ray absorption spectrum within ~50eV of the absorption edge.
- Suggested that division is that at which wavelength of excited electron is equal to distance between absorbing atom and its nearest neighbor. (λ (Å) $\approx 12/[e(eV)]^{½}$.

What Is XANES?

XANES= Pre-edge + Edge + XANES

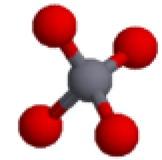


Why Are We Interested In XANES? Local Coordination Environment

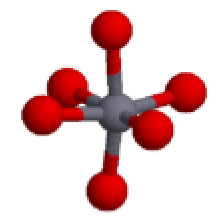


Both Ti^{4+}

Ba_2TiO_4

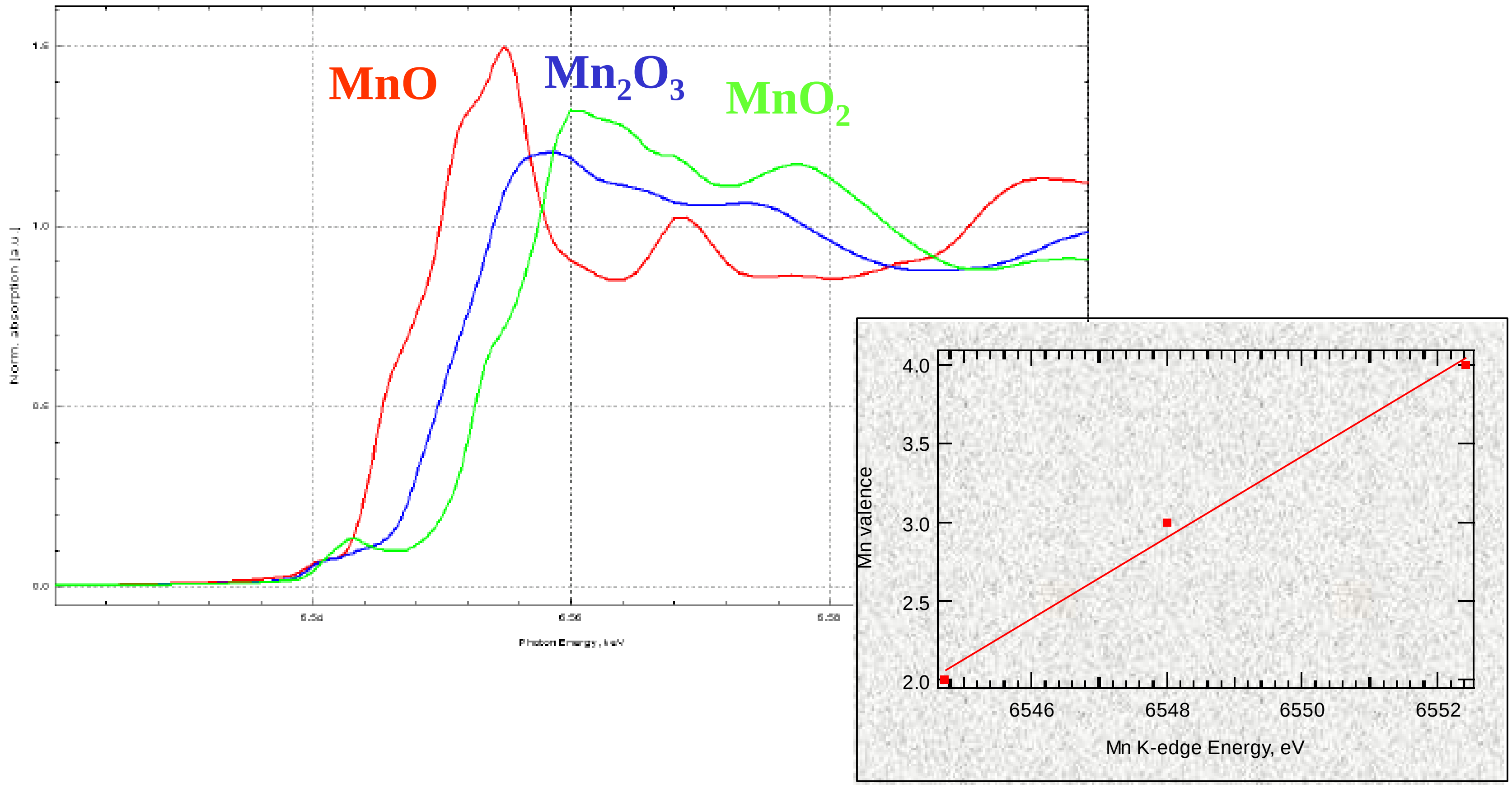


$K_2TiSi_3O_9$



- 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.

Region	Transitions	Information Content
Pre-edge	Features caused by electronic transitions to empty bound states. Transition probability controlled by dipolar selection rules.	Local geometry around absorbing atom. Dependence on oxidation state and bonding characteristics (chemical shift).
Edge	Defines ionization threshold to continuum states.	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).
XANES	Features dominated by multiple-scattering resonances of the photoelectrons ejected at low kinetic energy. Large scattering cross section.	Atomic position of neighbors: interatomic distances and bond angles. Multiple scattering dominates but *ab initio* calculations providing accessible insight (e.g. FEFF8).

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 (1*s* core electron) and L_1 (2*s* 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!

XANES Interpretation

- The EXAFS equation breaks down at low-*k*, which complicated 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

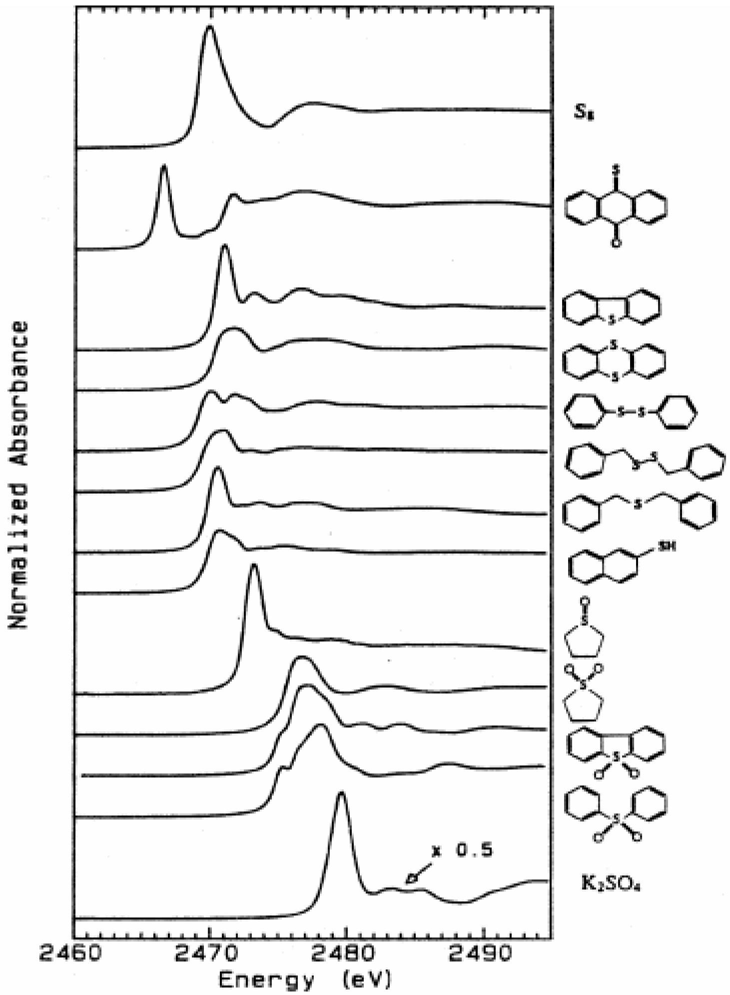
- These chemical and physical interpretations are all related:

  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*).
- 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: benzothiophene, dibenzothiophene.

Can be used as fingerprint.

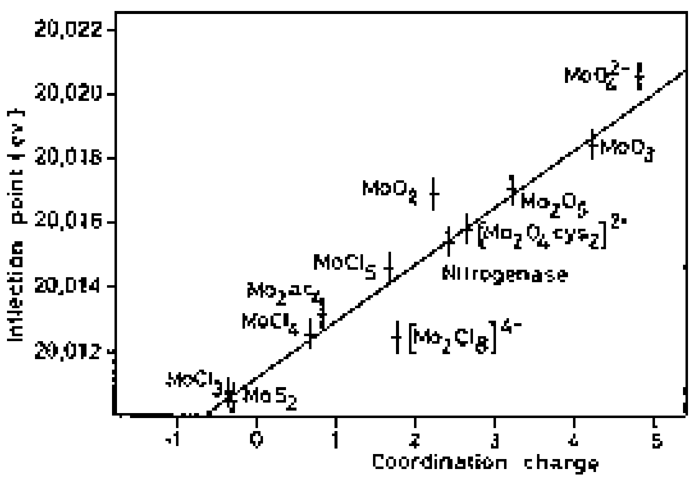
Reference: George and Gorbaty, J. Am. Chem. Soc. 101 (1979) 3182

XANES Analysis: Oxidation State

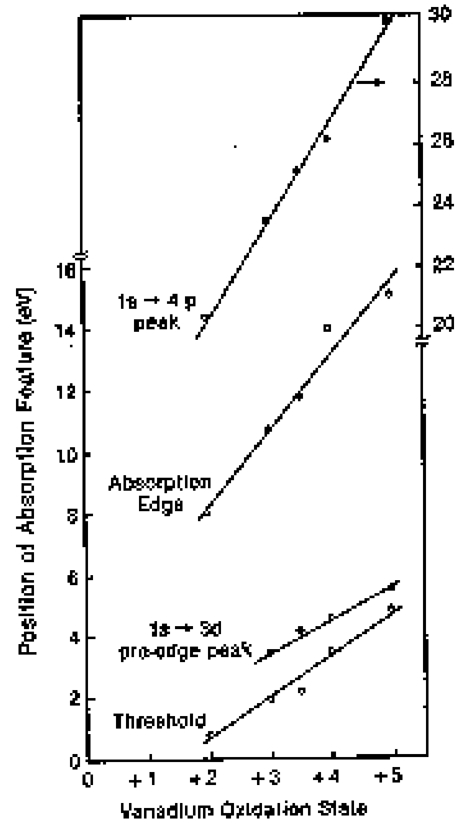
Many, many examples in the literature…...

V K-edge

Mo K-edge

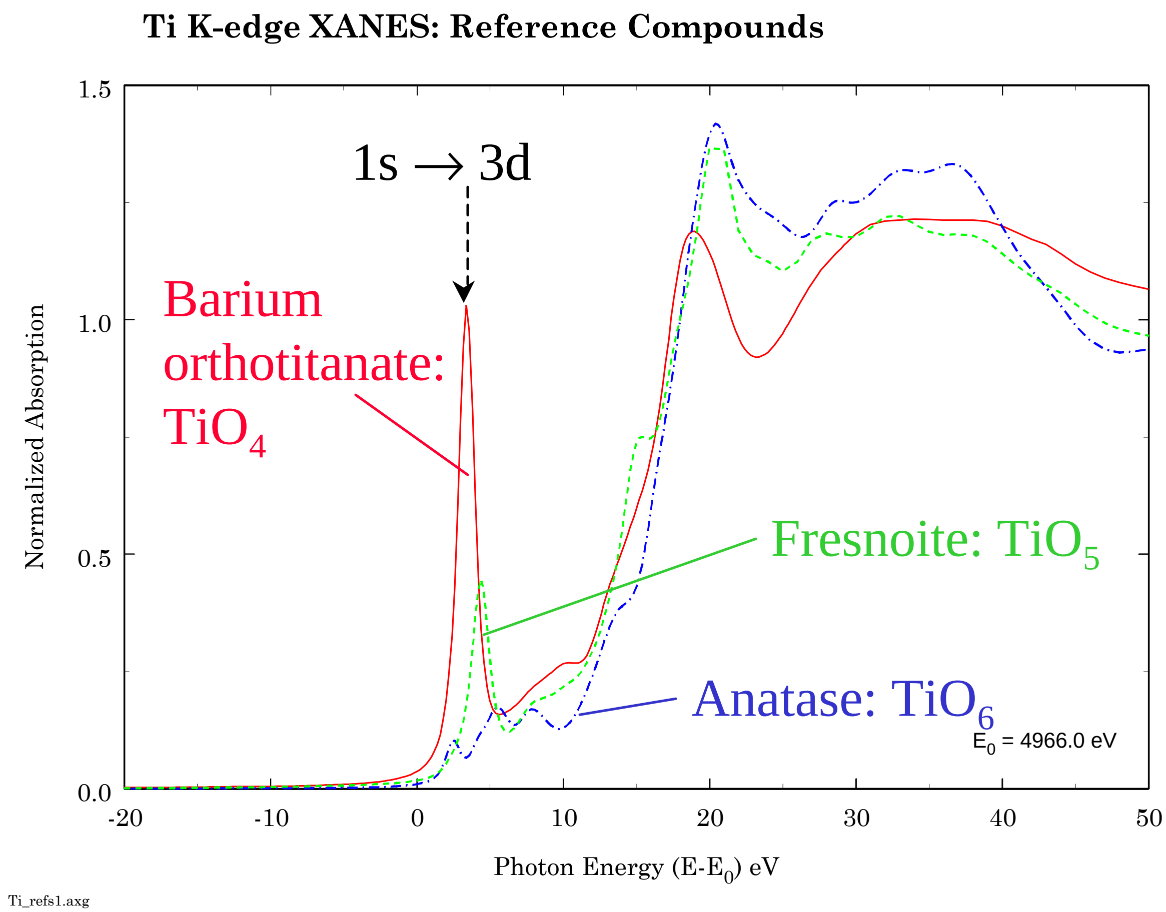


Ref: Cramer et al., JACS, 98 (1976) 1287



Ref: Wong et al., Phys Rev. B 30 (1984) 5596

Local Site Symmetry in Ti-containing Compounds

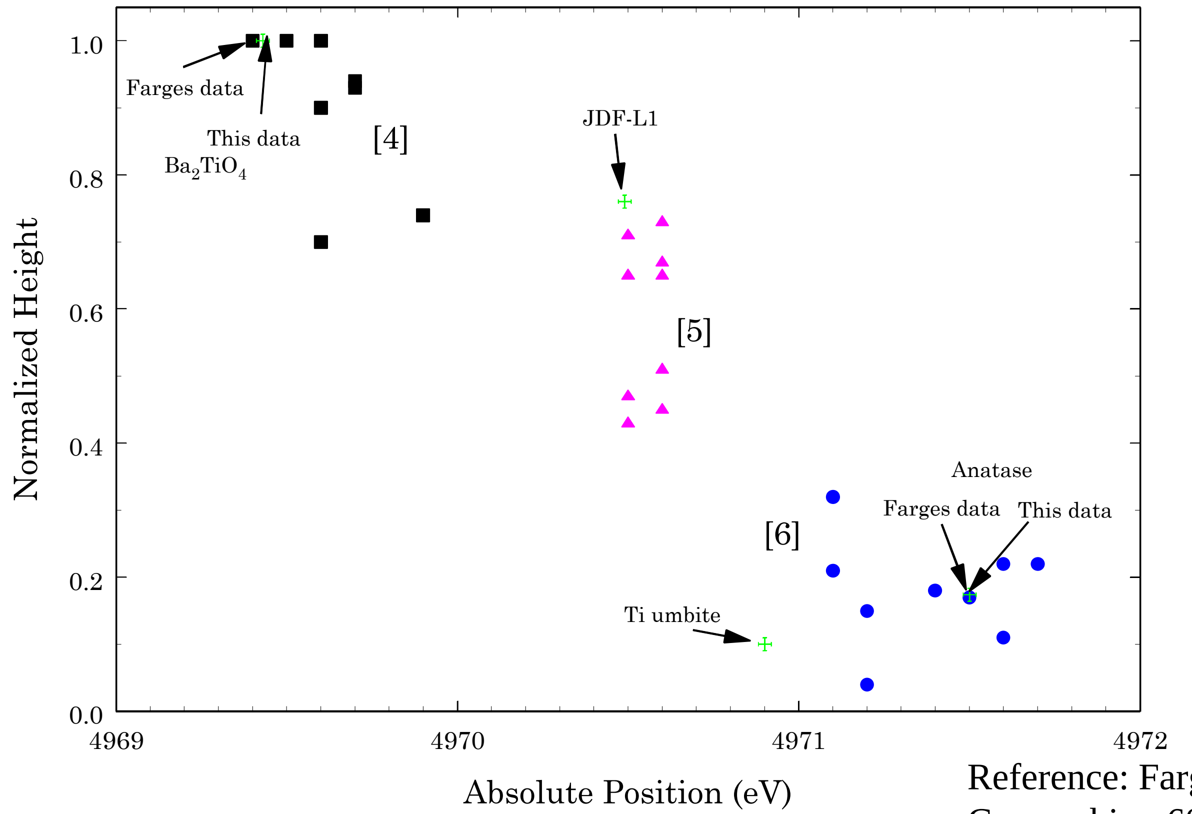


- Symmetry around absorbing atom strongly affects pre-edge transition: ability to differentiate 4, 5, 6-fold coordination.

Local Site Symmetry in Ti-containing Compounds

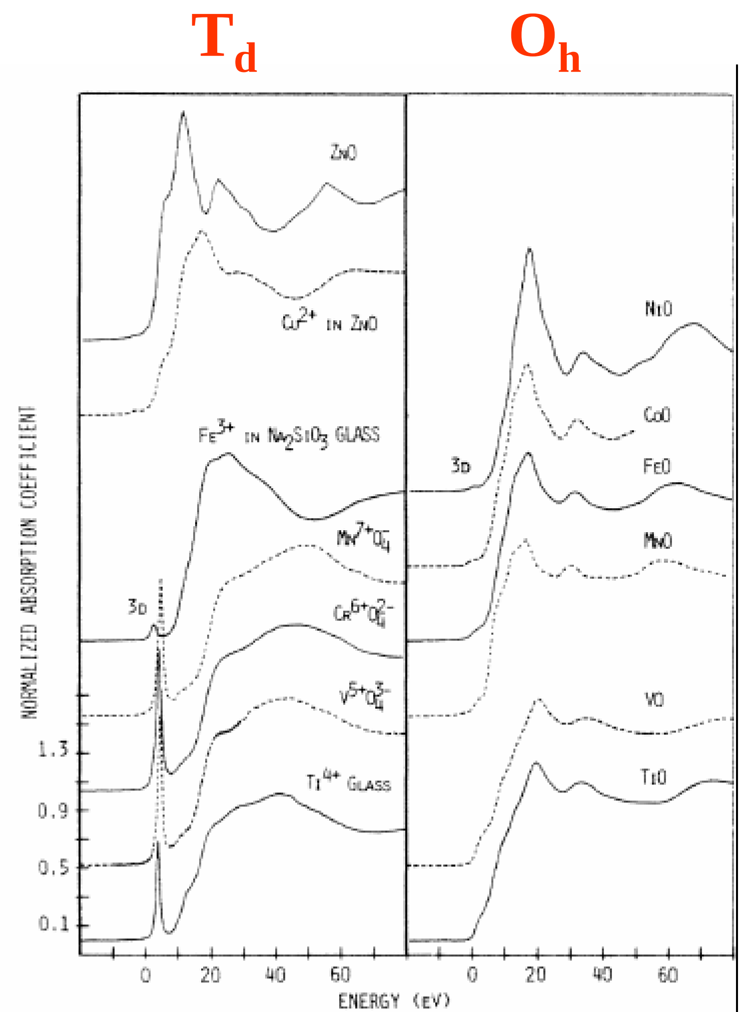
- Correlation between **absolute position and peak height** of pre-edge peak: all 4-fold, 5-fold and 6-fold coordinated Ti compounds fall into separate domains.

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



Reference: Farges et al., Geochim. Cosmochim. 60 (1996) 3023

XANES of 3d Transition Metals: Coordination

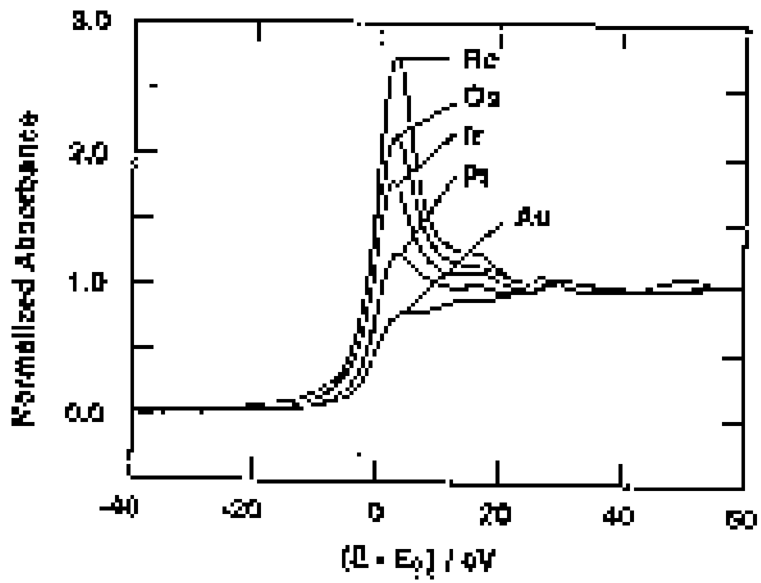


- 1s to 3d pre-edge peak sharp and intense from Ti-Mn, decreases Fe-Cu, absent for Zn.
- Decrease in intensity due to progressive filling of the 3d band.
- Oh symmetry shows only a small pre-edge peak throughout series.

Ref: Lytle et al. Phys. Rev. B 37 (1988) 1550.

"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.



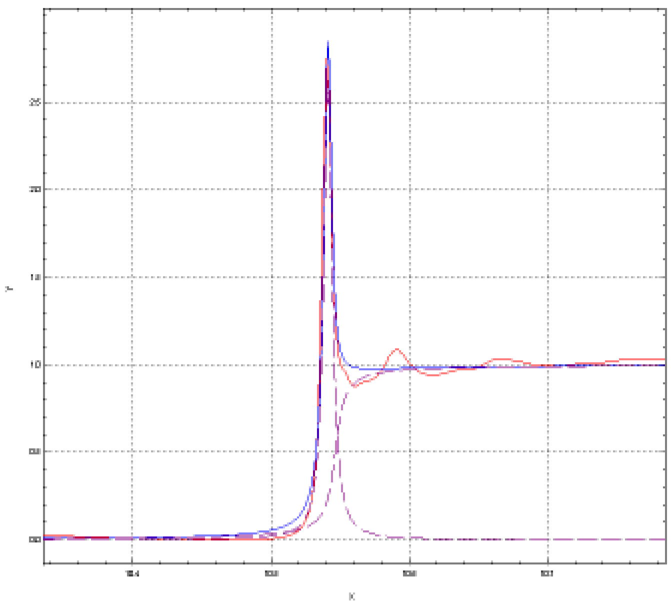
L_3 edge XANES for 5*d* metals

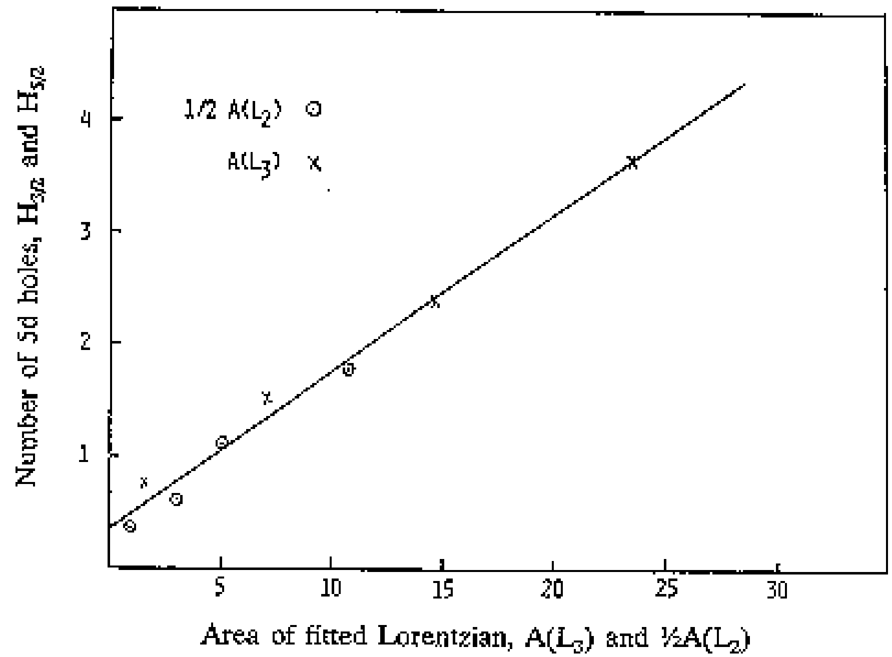
- Transition from 2*p*3/2 to 5*d* states.
- Absence of peak for Au - 5*d* states almost completely occupied.
- For others Pt<Ir<Os<Re, corresponding to increase in number of unoccupied 5*d* states on the atoms.

Reference: G. Meitzner et al., J. Phys. Chem. 96 (1992) 4960

Quantification of “White Line”

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



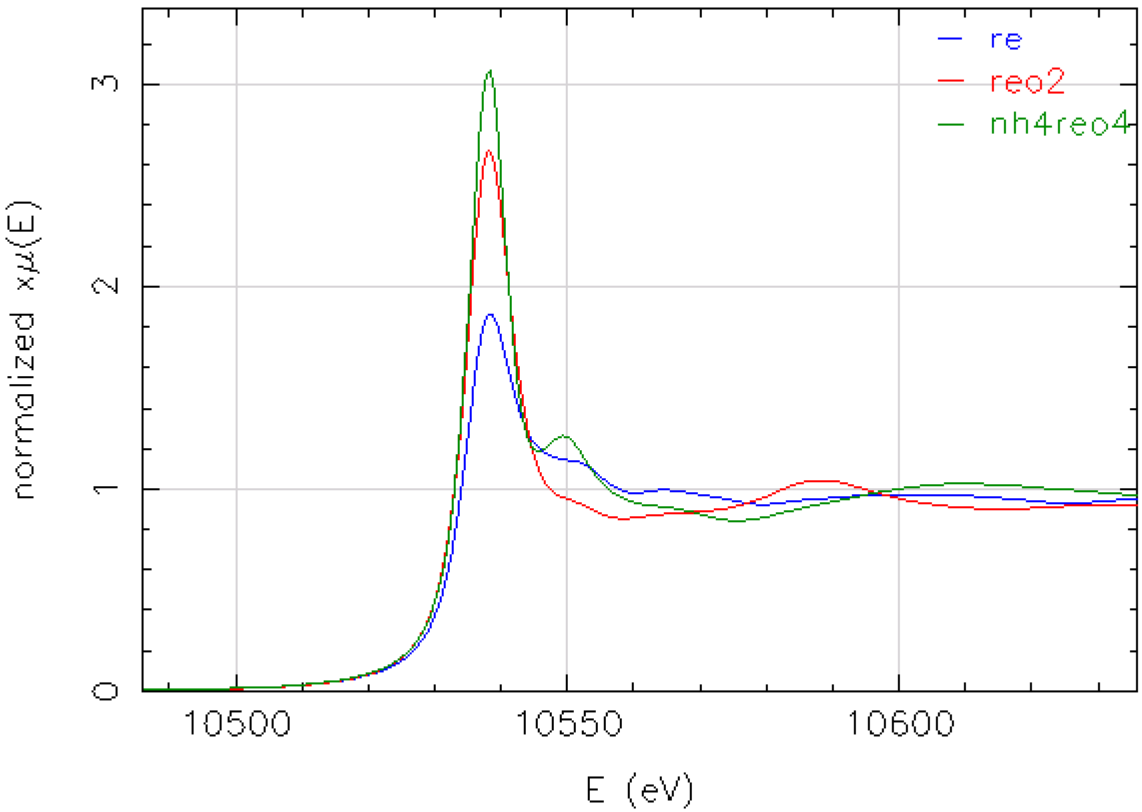


- Linear correlation between white line area and number of 5d-holes for Au-Re

Ref: Lytle et al., Proc. 9th Int. Congr. Catal, Vol 5 (1988) 54

"White Line" Intensity

Re L_3-edge - Transition from 2*p*3/2 to 5*d* states.



Re metal (Re^0) - 5d^5

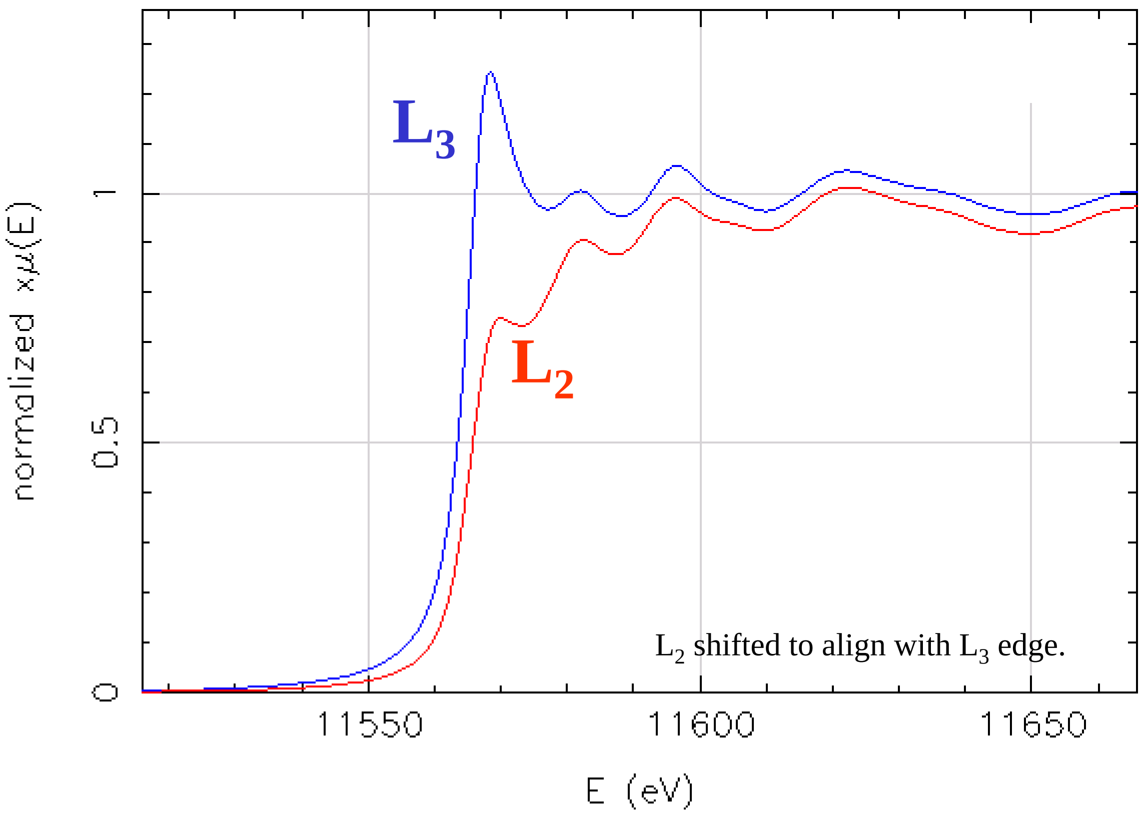
ReO_2 (Re^{4+}) - 5d^1

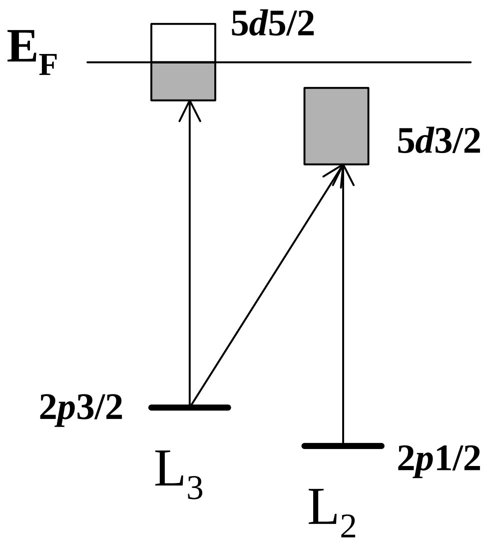
NH_4ReO_4 (Re^{7+}) - 5d^0

- Intensity of Re L_3 white line probes Re LDOS

Pt L_3 and L_2 Edge XANES

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



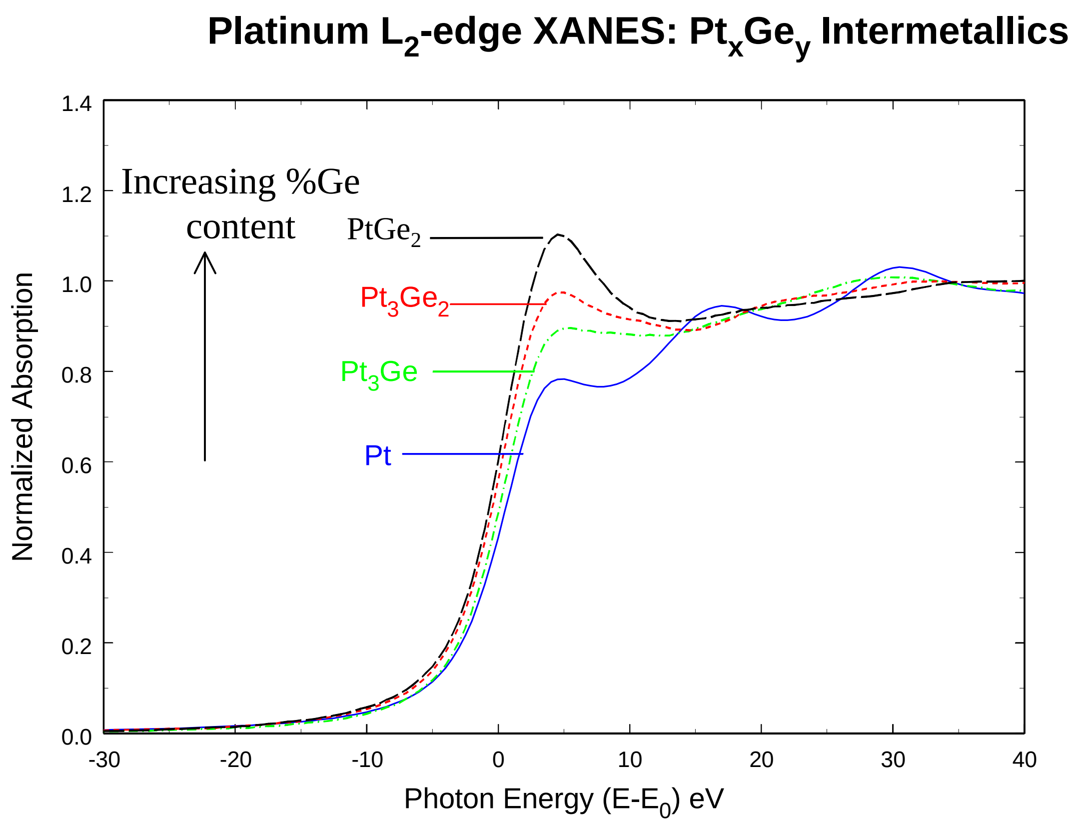


- Pt 5*d*3/2 filled, so no white line.

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

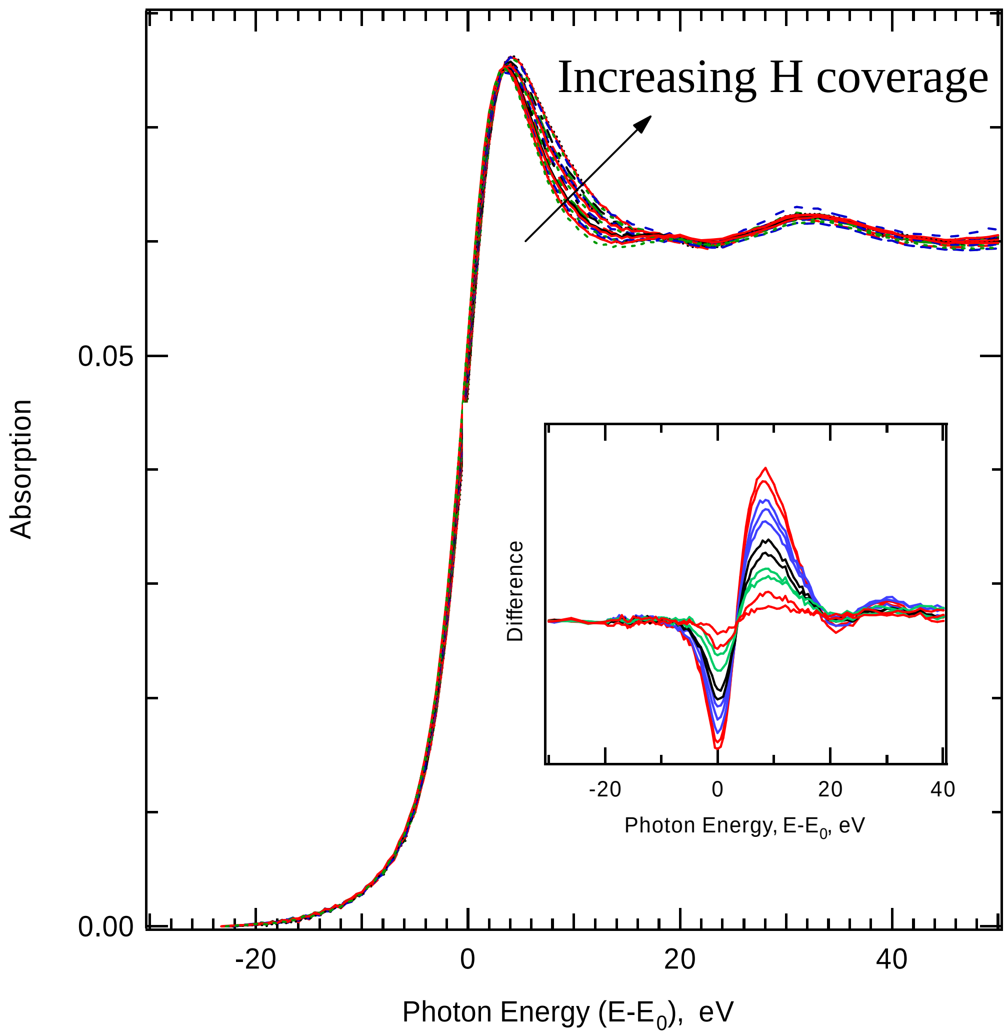
- *j*=3/2 probed by L_2-edge, *j*=5/2 probed by L_3-edge.

XANES to Probe Charge Transfer in Alloys



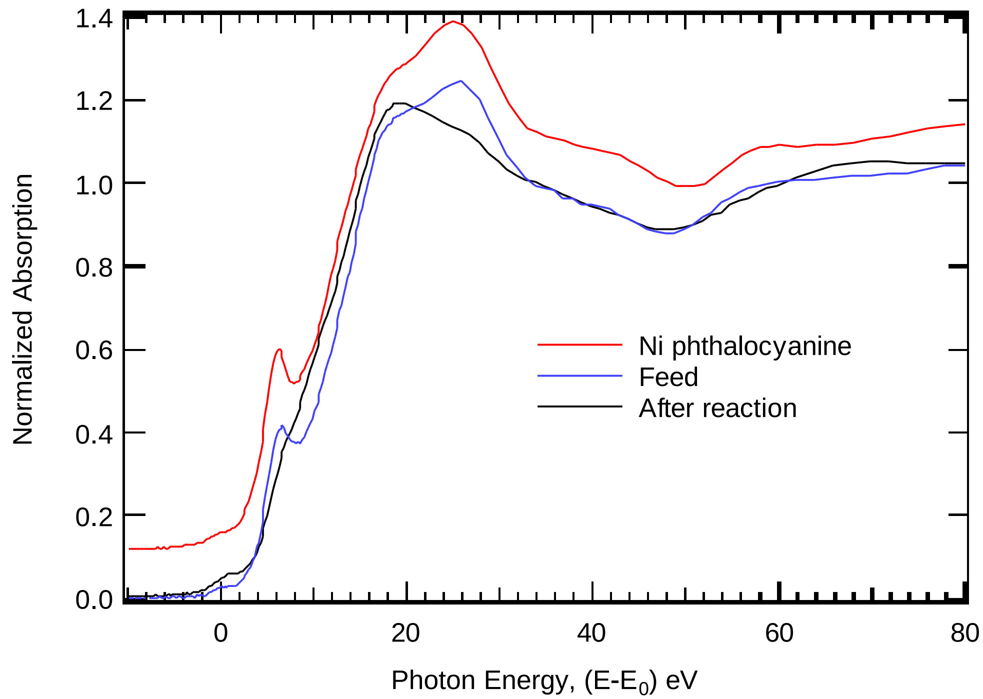
- Transition is 2*p* to 5*d*: Pt *d*-band full, so “no” intensity at edge.
- PtGe intermetallics: charge transfer from *d*-band of Pt to Ge, resulting in significant intensity at edge.
- Use as signature of Pt-Ge intermetallic formation.

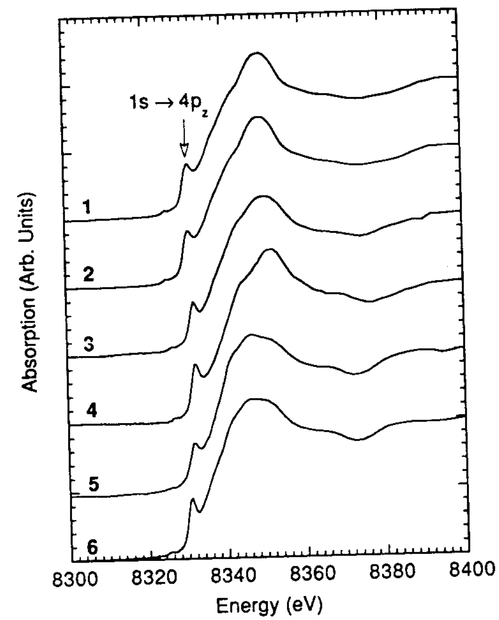
Effect of Adsorbed Hydrogen on Pt L_3 XANES



- White-line intensity decreases and spectra broaden to higher energies as H is added.
- Difference signal typically leads to broad structure ~8 eV above absorption edge.
- Several different interpretations in the literature.

Symmetry: Ni K-edge





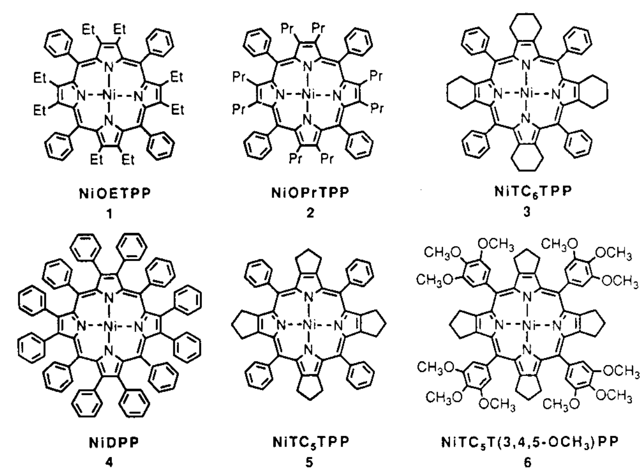


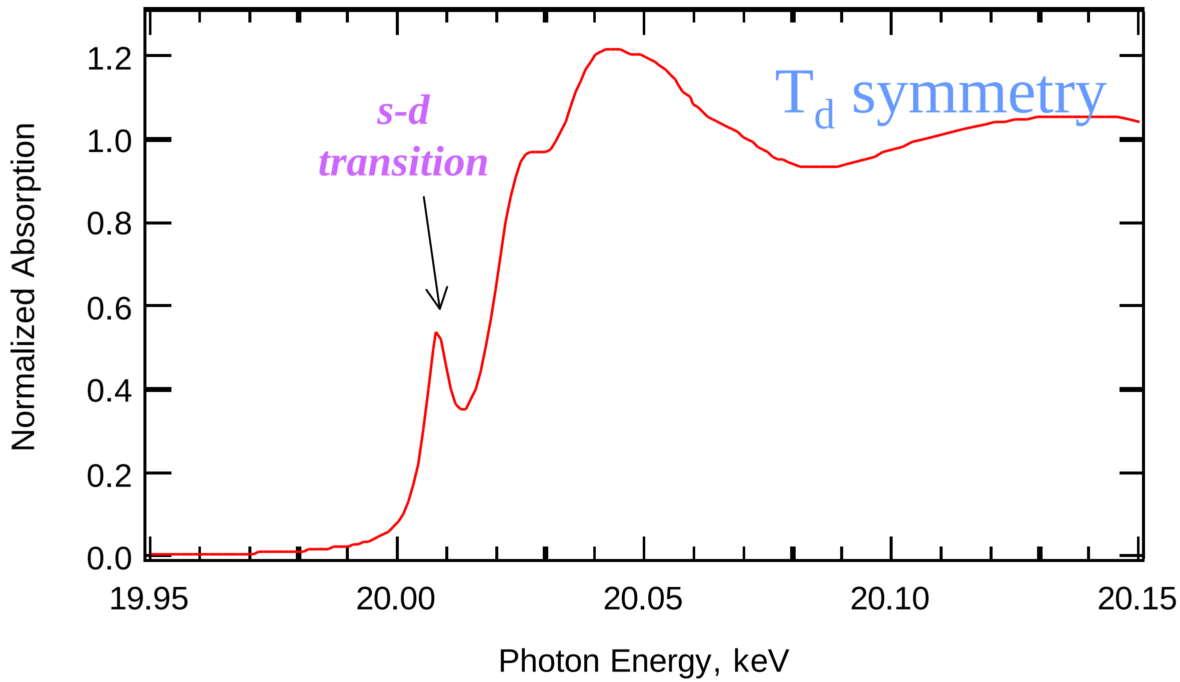
Figure 1. Structural formulas of NiOETPP (**1**), NiOPrTPP (**2**), NiTC$_6$-TPP (**3**), NiDPP (**4**), NiTC$_5$TPP (**5**), and NiTC$_5$T(OMeP)P (**6**).

- Only square planar Ni compounds exhibit intense pre-edge peak at 5 eV.
- Ni in feed predominantly square planar Ni^{2+}. This converted to different species during reaction.

Ref: Barkigia et al, JACS, 115 (1993) 3627

Which Edge to Choose: Energy Resolution

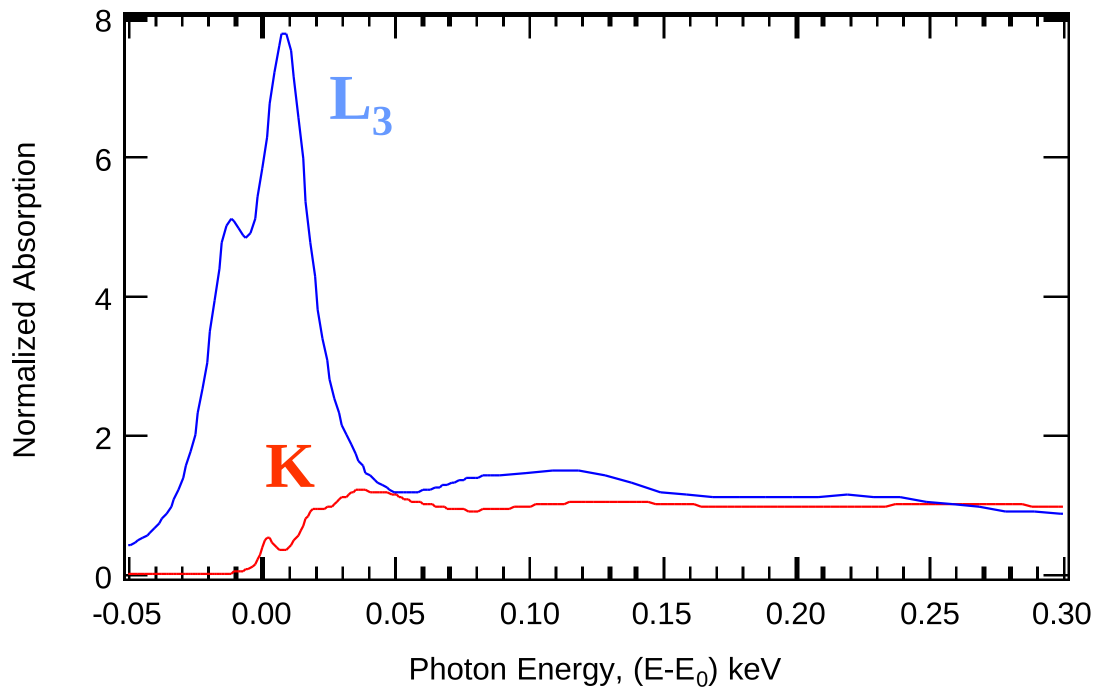
Mo K-edge XANES of Na_2MoO_4



- 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_3-edge (2.5 keV) XANES of Na_2MoO_4 with that of Mo K-edge (20.0 keV).

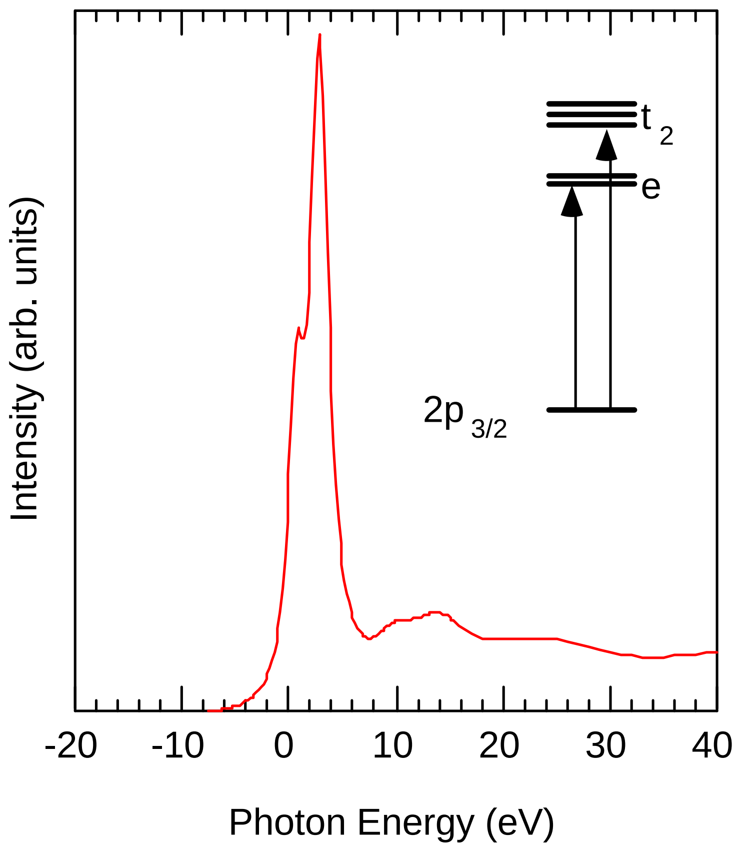


- Mo L_3-edge at 2.5 keV, 0.5 eV spectral resolution!

Which Edge to Choose: Energy Resolution

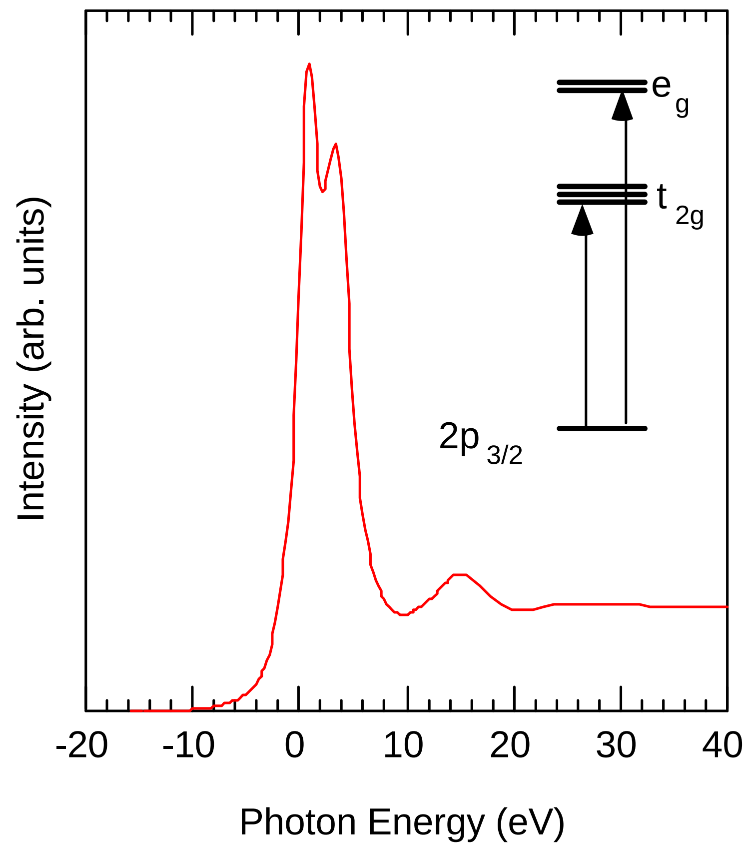
Sodium Molybdate, $NaMoO_4$
Mo atom tetrahedral coordination

Mo L_3-edge XANES



Cobalt Molybdate, $CoMoO_6$
Mo atom octahedral coordination

Mo L_3-edge XANES



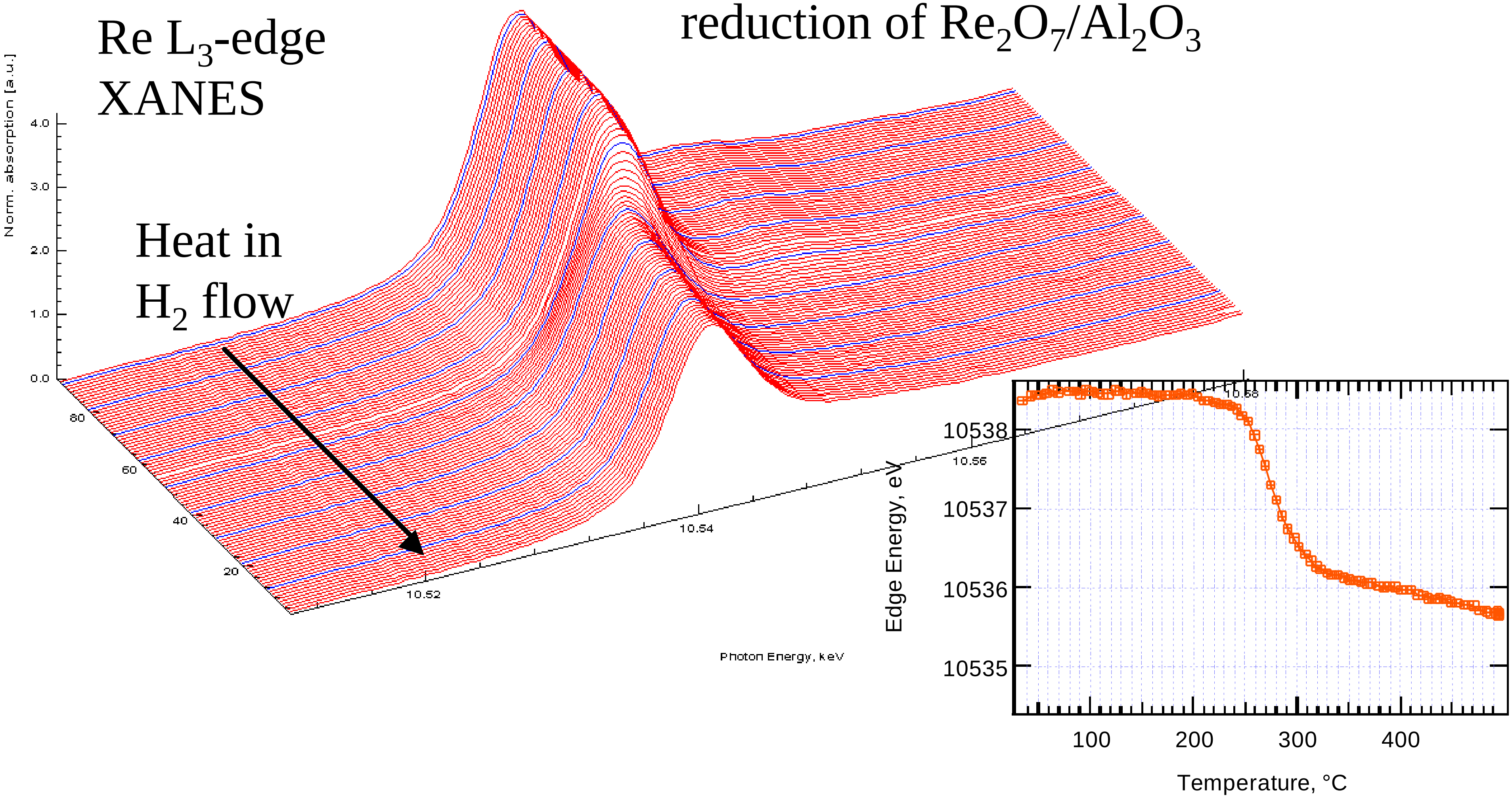
- **DE tetrahedral = 2.2-2.5 eV; DE octahedral = 3.25-4.2 eV**

Time Evolution of XANES

In situ temperature programmed reduction of Re_2O_7/Al_2O_3

Re L_3-edge XANES

Heat in H_2 flow



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

- Specialized application of XANES.
- Focus x-ray beam to <10μm diameter.
- 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)
- See http://www.bnl.gov/x26a/ for information.

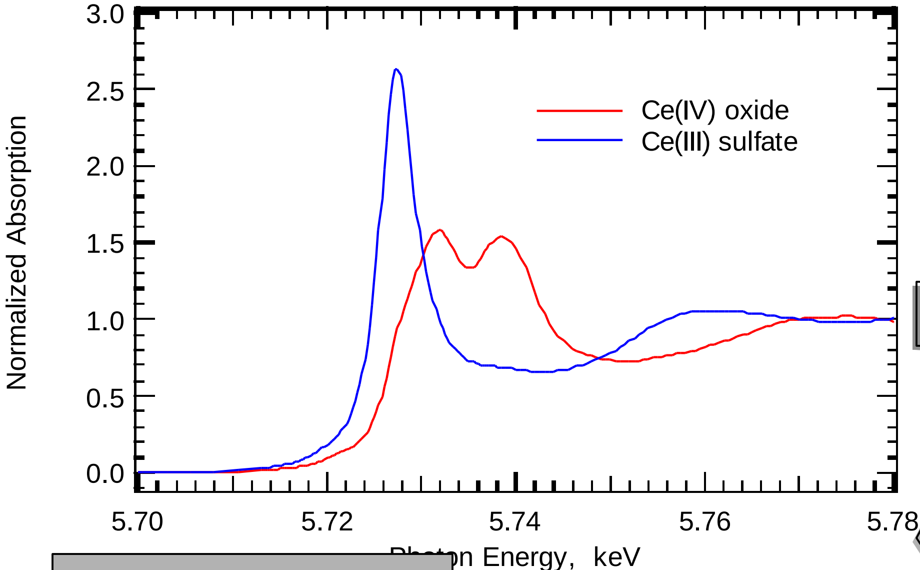
Analysis of Mixtures

- 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

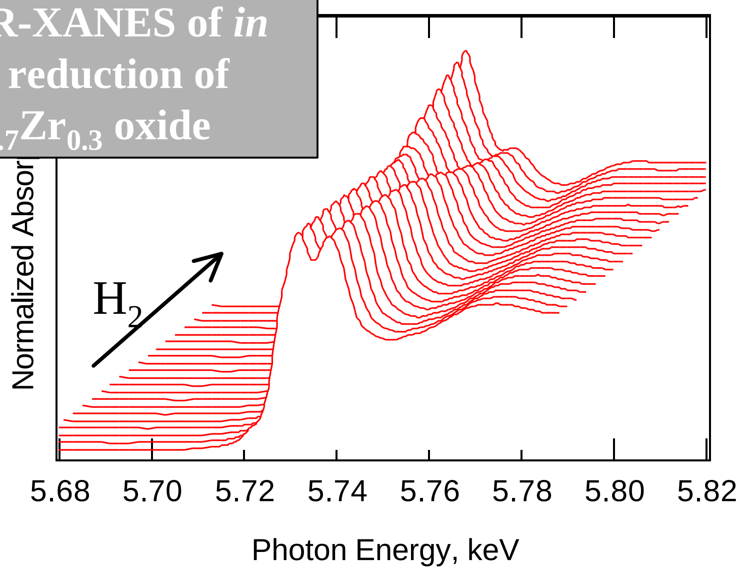
- Use a linear combination of spectra of various reference samples.
- Allows quantification of species in multiple-component mixture from their fingerprint in the XANES region.
- Use a least-squares algorithm to refine the sum of a given number of reference spectra to an experimental spectrum.
- Simple method, easy to implement.
- Must have spectra of the reference compounds.

Linear Combination Fitting

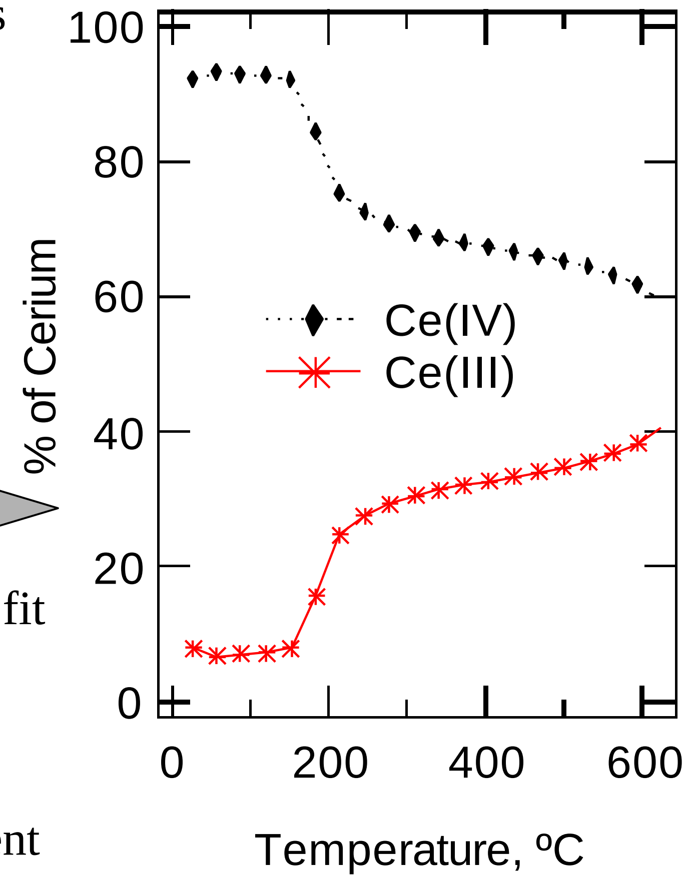


Fit experimental data to linear combination of known reference compounds

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 for many years 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...

*Determination of molybdenum surface environment of molybdenum/titania catalysts by EXAFS, XANES and PCA. Mikrochimica Acta 109 (1992) 281.

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 error.
- Growing popularity in XANES spectroscopy.

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…..