XANES Measurements and Interpretation

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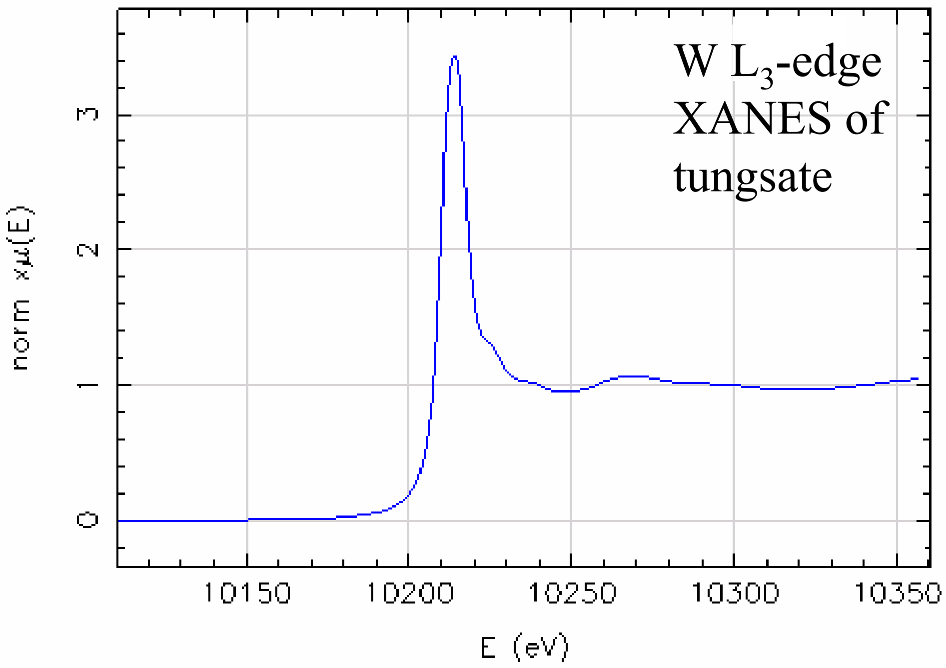
Miscellaneous: E to k

- $k = (2m(E-E_0)/h^2)^{½}$
- $k = (0.2625 \times [E-E_0])^{½}$



E-E0	k
1	0.51
5	1.15
10	1.62
15	1.98
20	2.29
25	2.56
30	2.81
50	3.62
100	5.12
250	8.10
500	11.46
750	14.03
1000	16.20
1500	19.84

Miscellaneous: Absorption edges

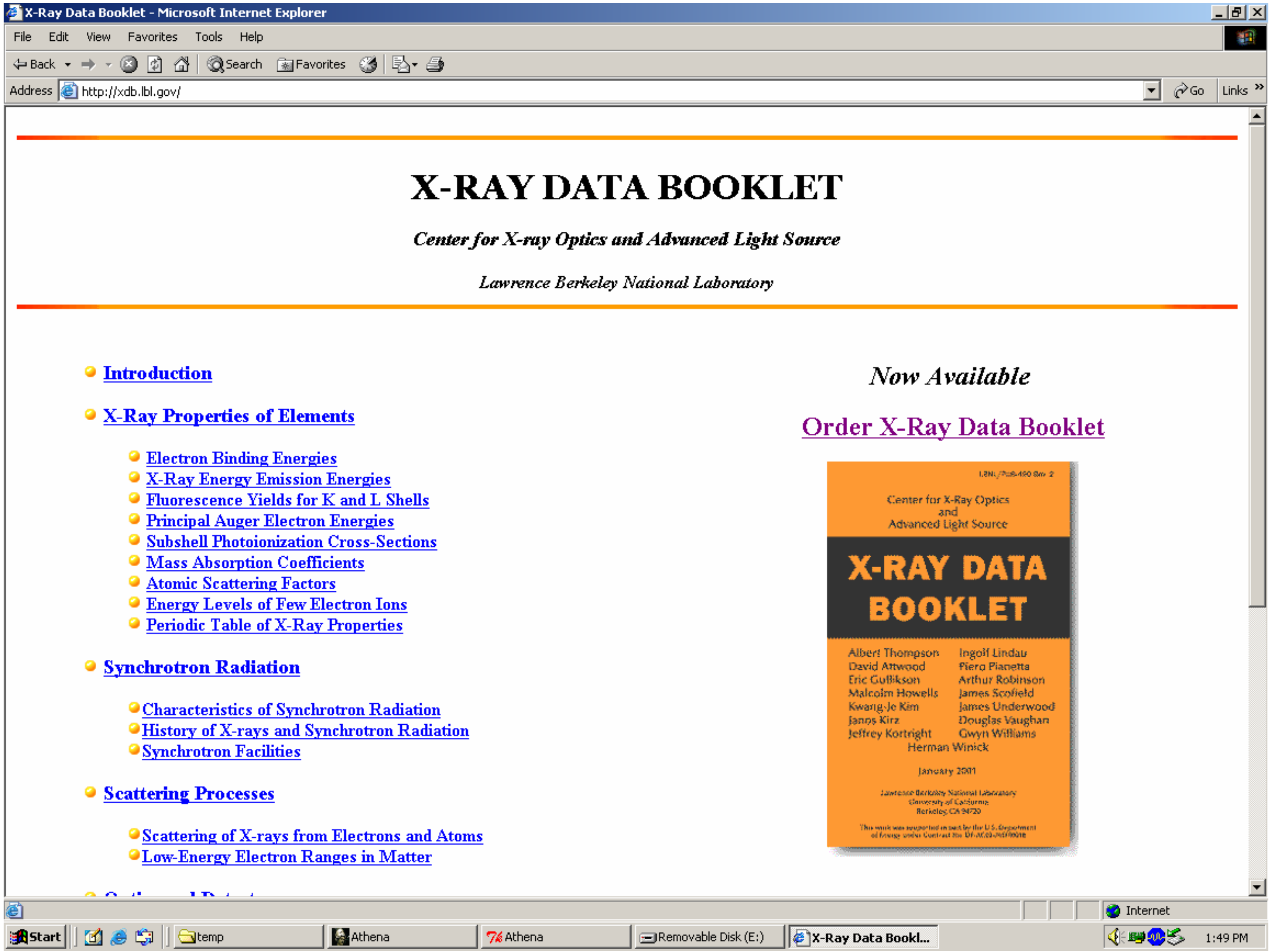
Absorption edge	Core level
K	1*s*
L_{I}	2*s*
L_{II}	2*p*1/2
L_{III}	2*p*3/2
M_{I}	3*s*
M_{II}	3*p*1/2
M_{III}	3*p*3/2
M_{IV}	3*d*3/2
M_{V}	3*d*5/2

Miscellaneous: mesh size

MESH SIZE=	**MICRON SIZE**
50-60 mesh	300-250
80-100	180-150
170-200	90-75
325	45
400-500	38-40
700	22-30
800	20-30
1200	10-20
1600	8-15
1800	6-12
3000	4-8 Very small particles.
8000	2-4
14000	0-2
50000	0-1
100000	0-1/2
200000	0-1/4

MESH SIZE	**MICRON SIZE**
50-60 mesh	300-250 µm
80-100	180-150
170-200	90-75
325	45
400-500	38-40

Miscellaneous: “Yellow book”



X-RAY DATA BOOKLET

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Lawrence Berkeley National Laboratory

- **Introduction**
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  - X-Ray Energy Emission Energies
  - Fluorescence Yields for K and L Shells
  - Principal Auger Electron Energies
  - Subshell Photoionization Cross-Sections
  - Mass Absorption Coefficients
  - Atomic Scattering Factors
  - Energy Levels of Few Electron Ions
  - Periodic Table of X-Ray Properties
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January 2001

Acronyms

XANES

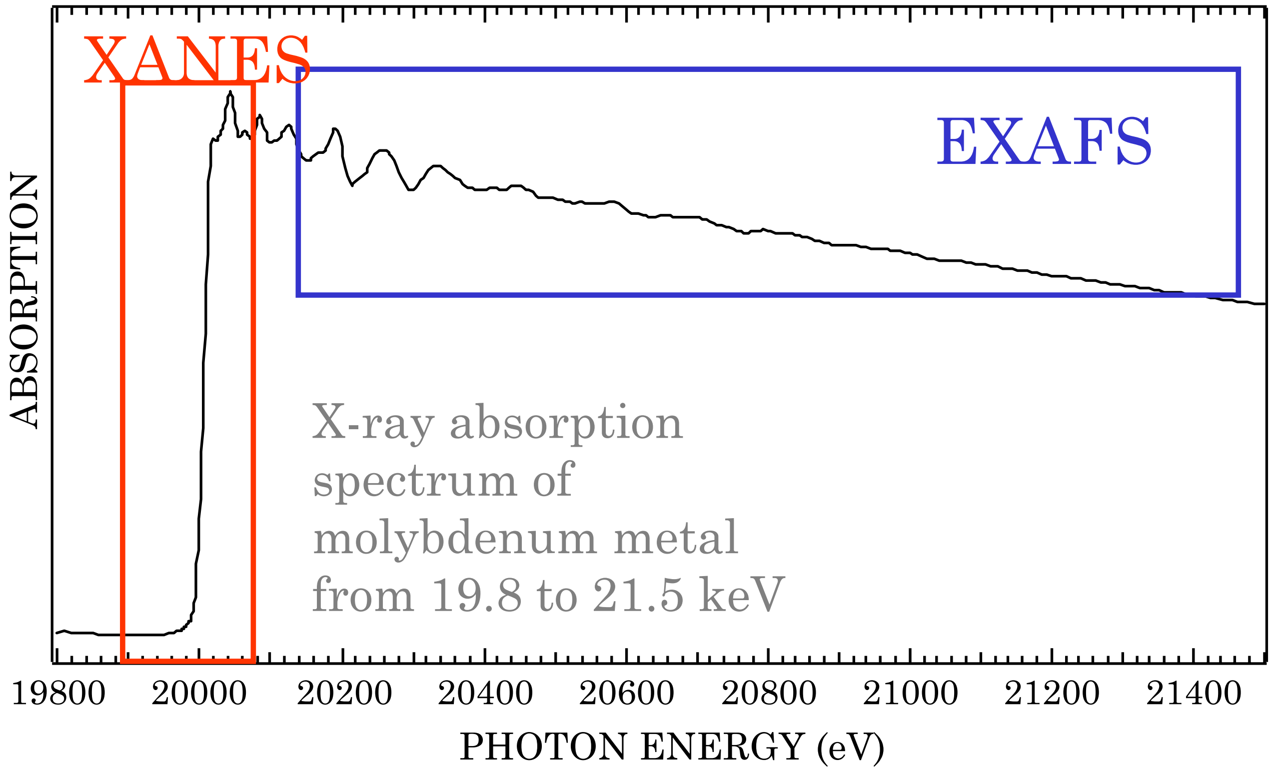
- **X**-ray **A**bsorption **N**ear **E**dge **S**tructure

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?

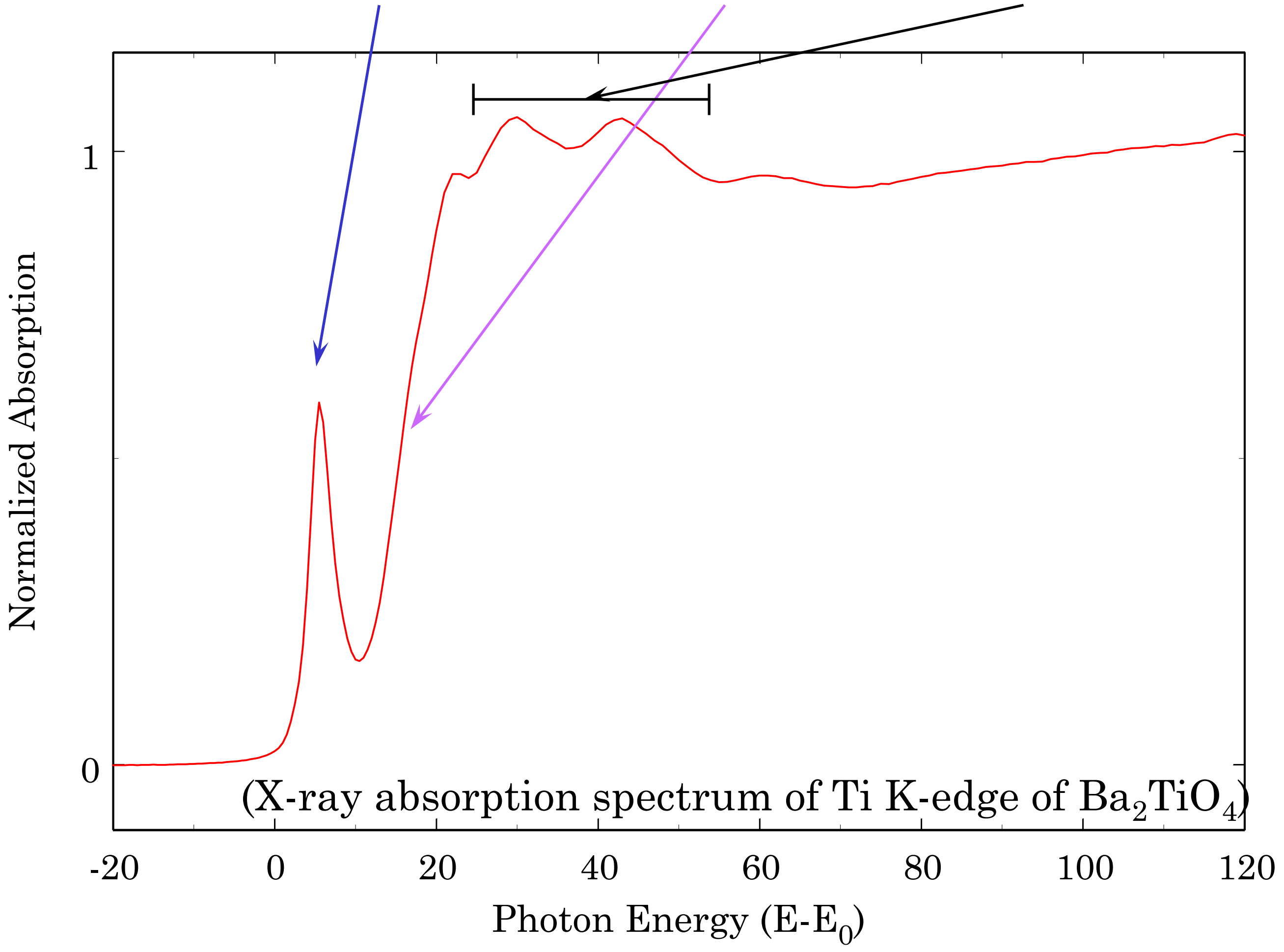


X-ray absorption spectrum of molybdenum metal from 19.8 to 21.5 keV

- 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) $\approx 12/[e(eV)]^{1/2}$.

What Is XANES?

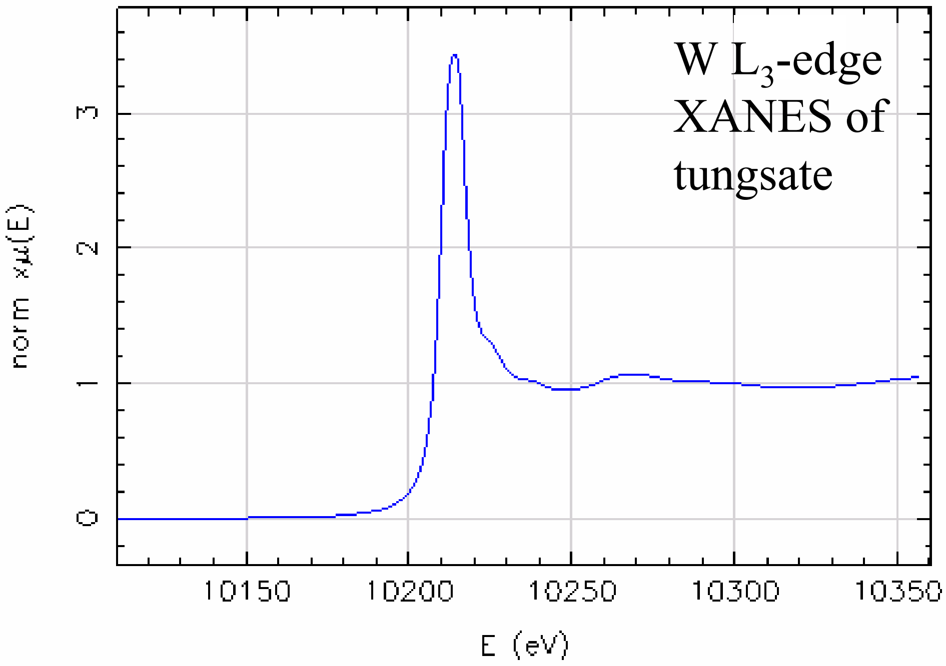
XANES= Pre-edge + Edge + XANES



(X-ray absorption spectrum of Ti K-edge of Ba_2TiO_4)

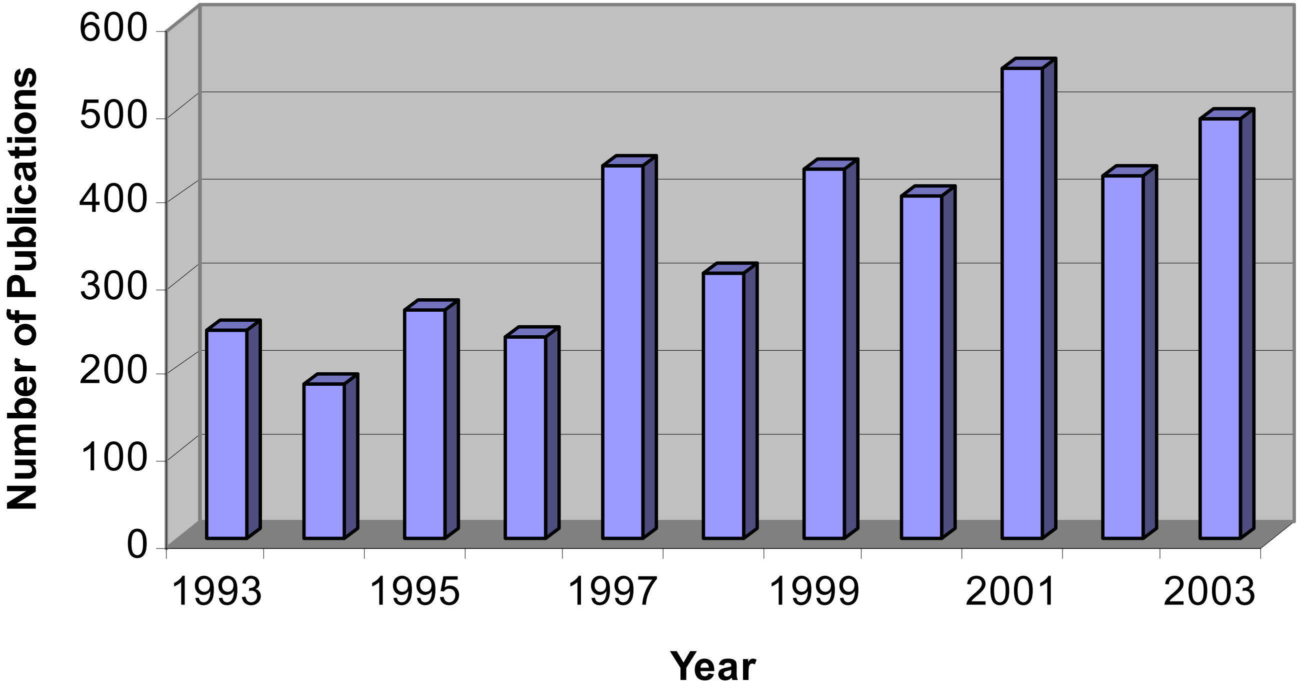
EXAFS Data Collection and Analysis Course, NSLS, June 22-24, 2004

“White line”



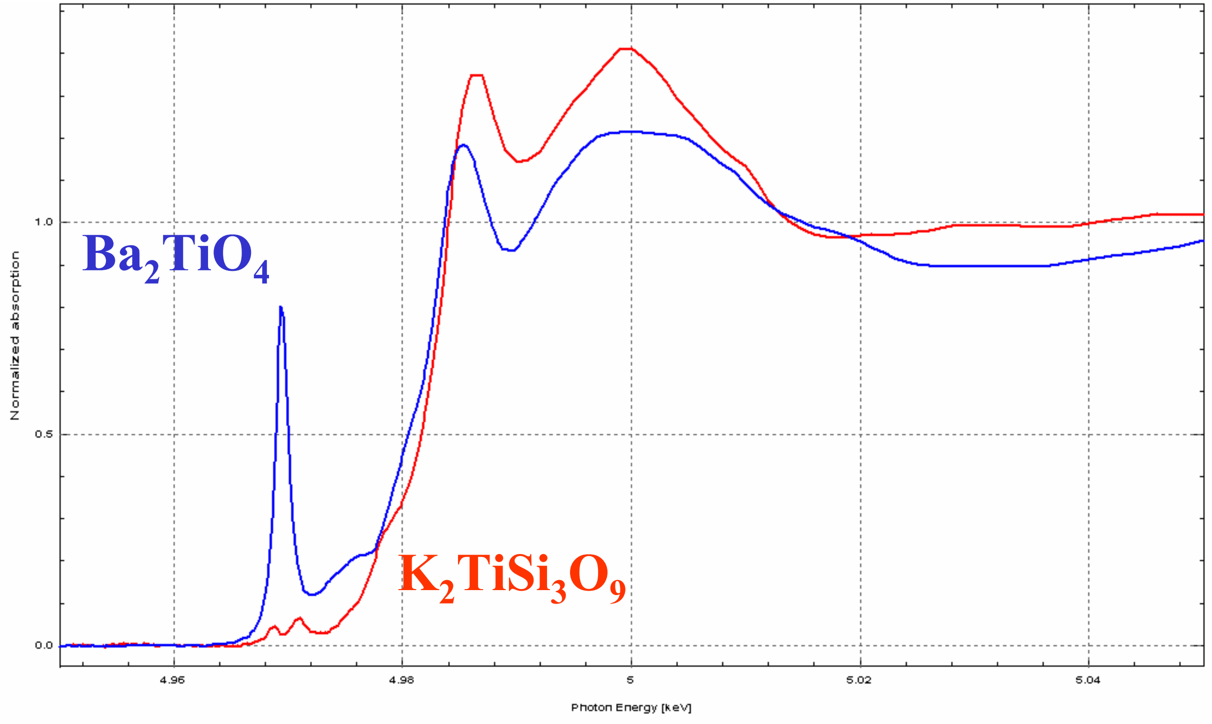
- In years past x-ray absorption spectra were taken with use of photographic plates.
- Absorption edges appeared as unexposed bands on the plate (developed in negative), or “white lines”.
- Very prominent for L-edges of transition metals in high oxidation states.

Number of "XANES" Publications



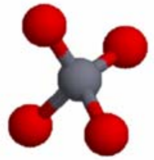
- >500 publications per year!

Why Are We Interested In XANES? Local Coordination Environment



Both Ti^{4+}

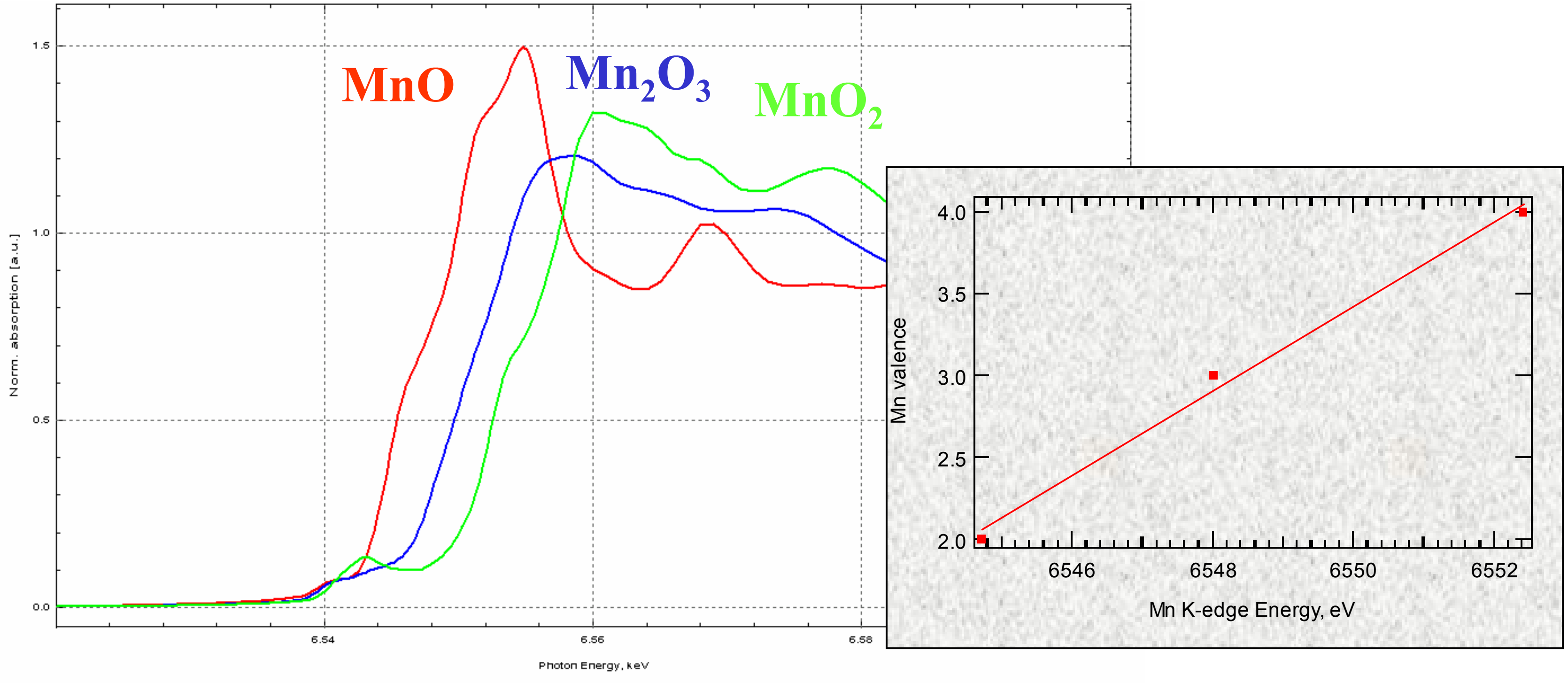
Ba_2TiO_4



$K_2TiSi_3O_9$

- 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.
- First observation was by Berengren for phosphorus in 1920*!

*See “A history of X-ray absorption fine structure”, R. Stumm von Bordwehr, Ann. Phys. Fr. 14 (1989) 377-466)

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 (1s core electron) and L_1 (2s core electron initial state) edges
  - $p \rightarrow d$ for L_2 ($2p_{½}$) 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!

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* 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

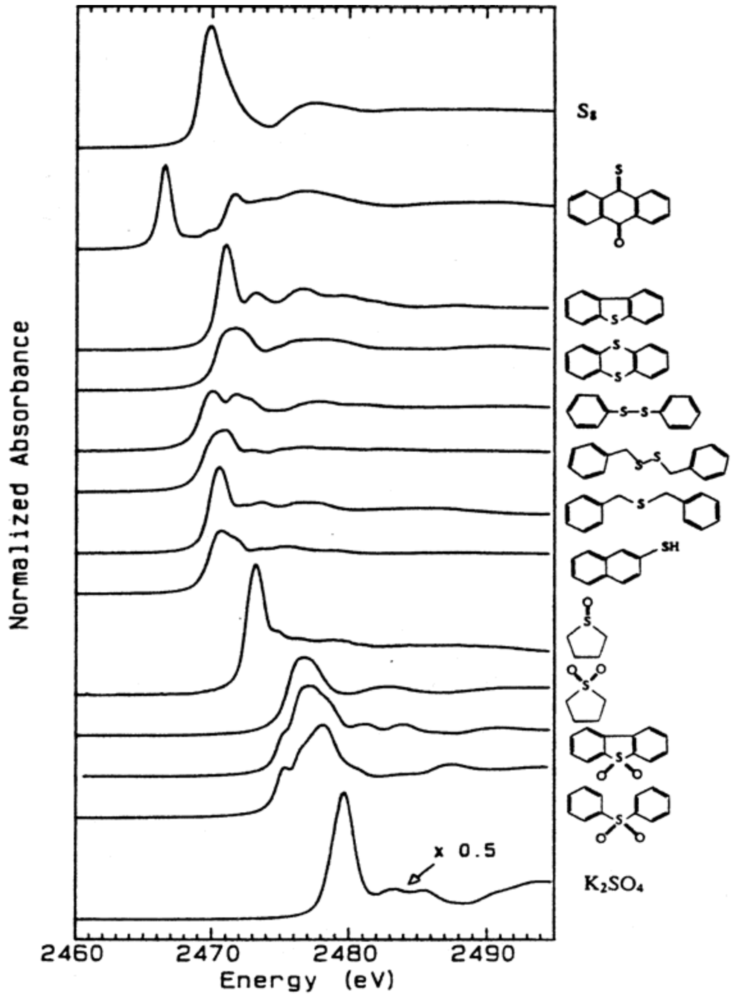
- These chemical and physical interpretations are all related:

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*):
  - $\mathrm{Exp}(-2k^2\sigma^2) = \exp(-2(0.5)^2 \times 0.005) \sim 1$
- 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+}.

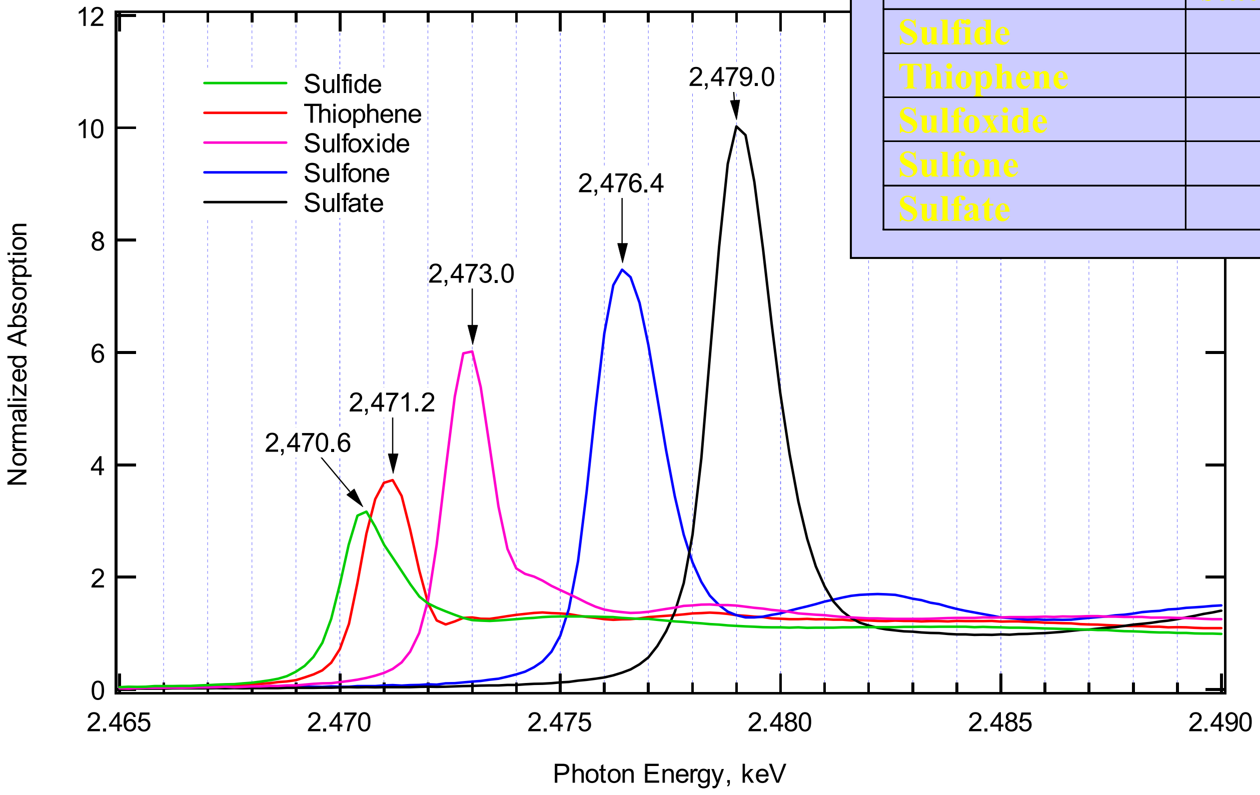
Spectra of S in similar environments similar: thiophene, benzothiophene.

Can be used as fingerprint.

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

XANES Analysis: Oxidation State Sulfur

Sulfur type	Formal oxidation state
Sulfide	2-
Thiophene	1+
Sulfoxide	2+
Sulfone	4+
Sulfate	6+

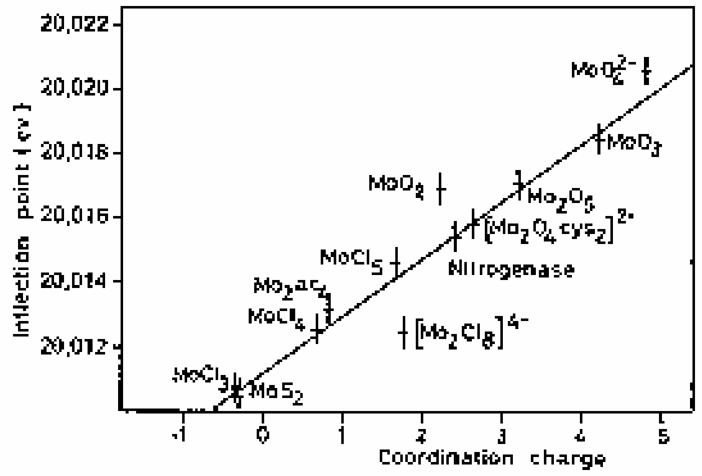


Dodecyl sulfide, thiophene, tetramethylene sulfoxide, tetramethylene sulfone, sulfate(aq)

XANES Analysis: Oxidation State

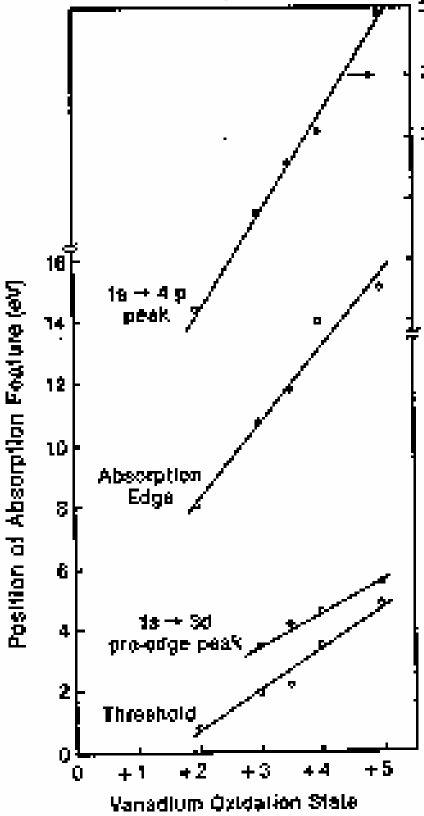
Many, many examples in the literature…...

Mo K-edge



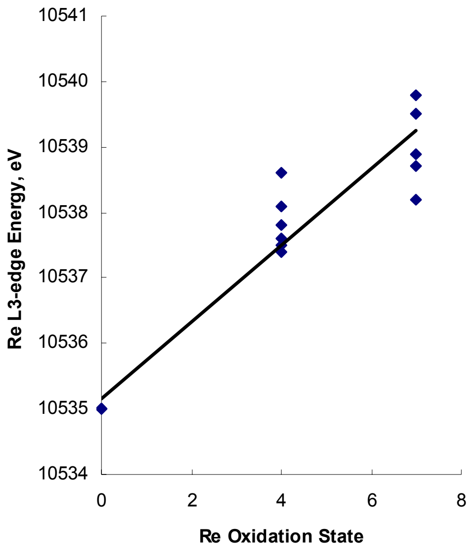
Ref: Cramer et al., JACS, 98 (1976) 1287

V K-edge



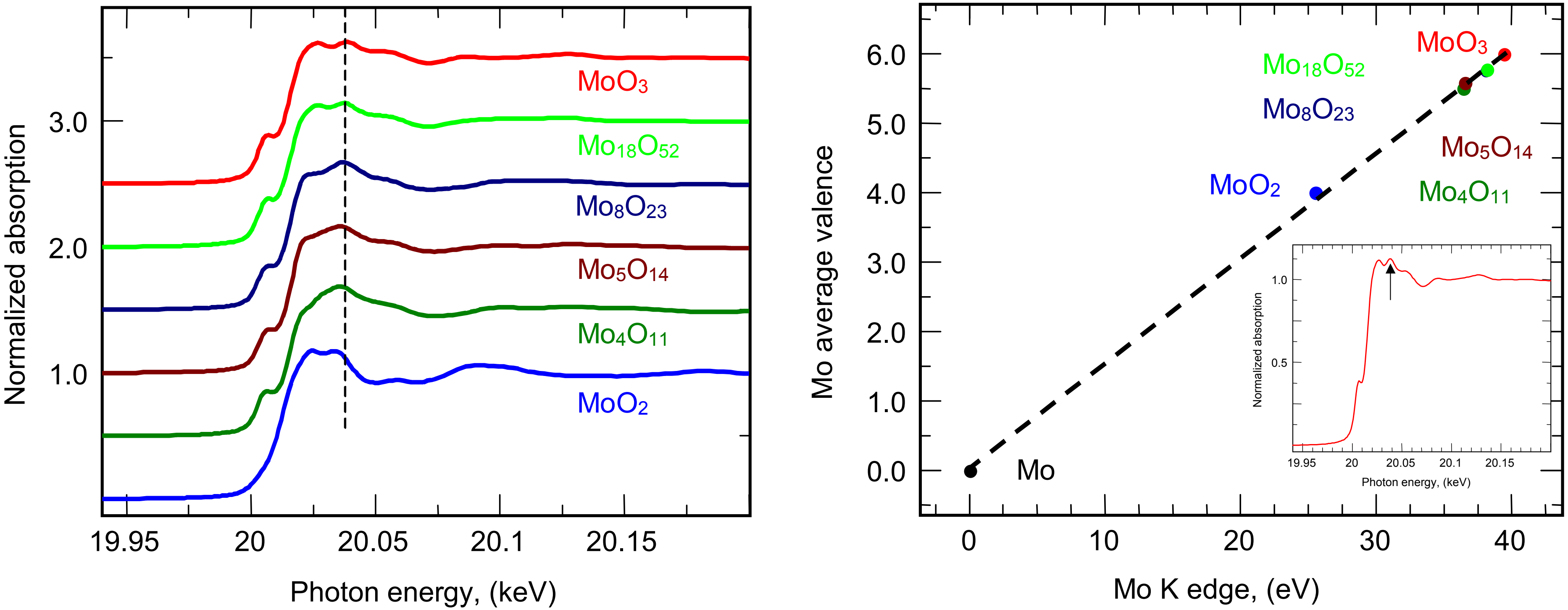
Ref: Wong et al., Phys Rev. B 30 (1984) 5596

Re L_3-edge



XANES Analysis: Oxidation State

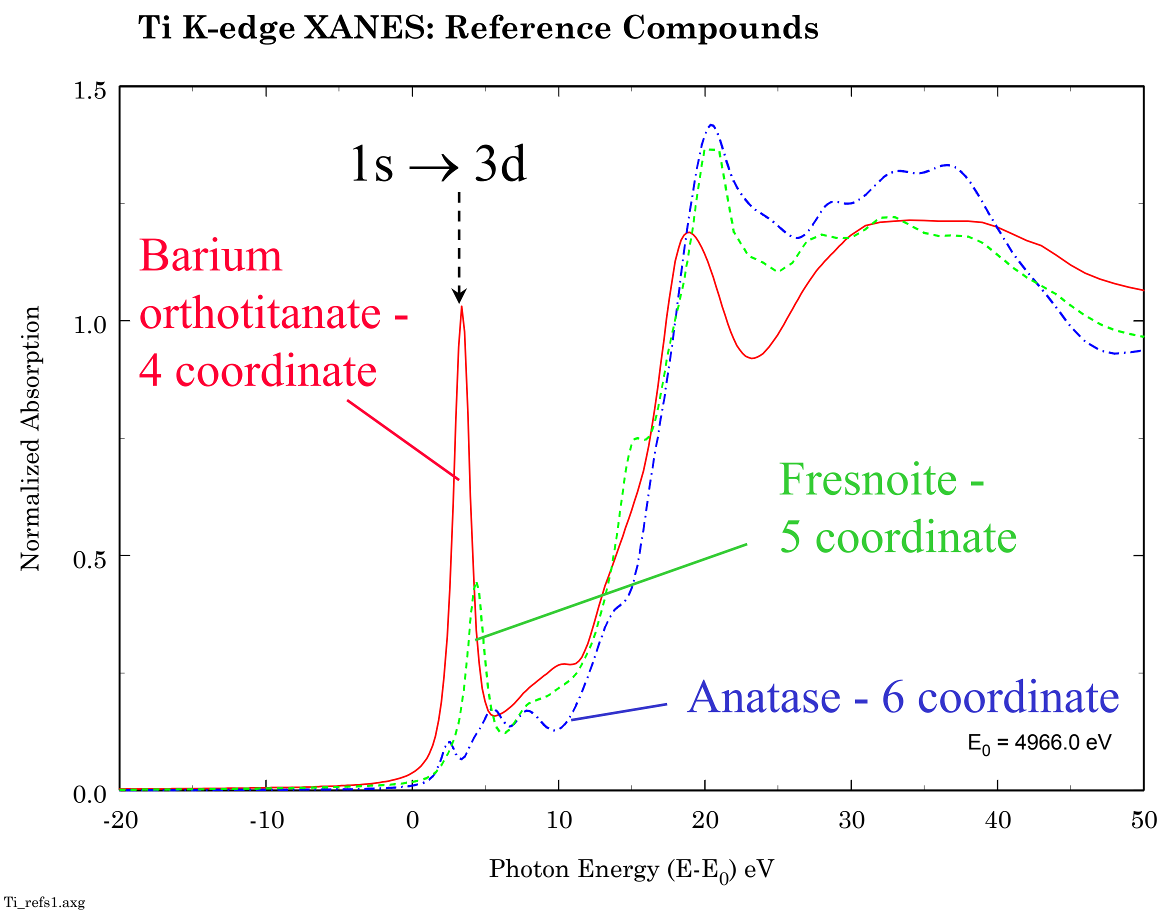
Mo K-edge XANES of Mo oxides



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

T. Ressler et al. J. Cat 210 (2002) 67

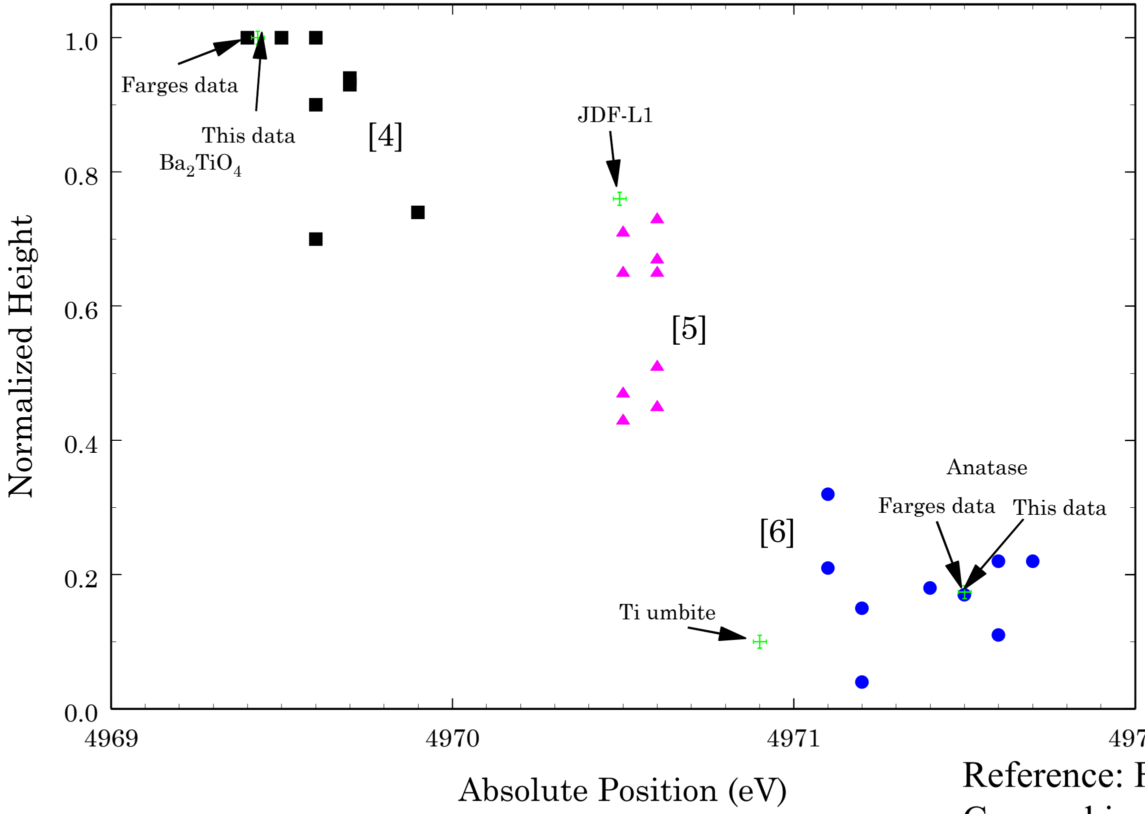
Local Site Symmetry in Ti-containing Compounds



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

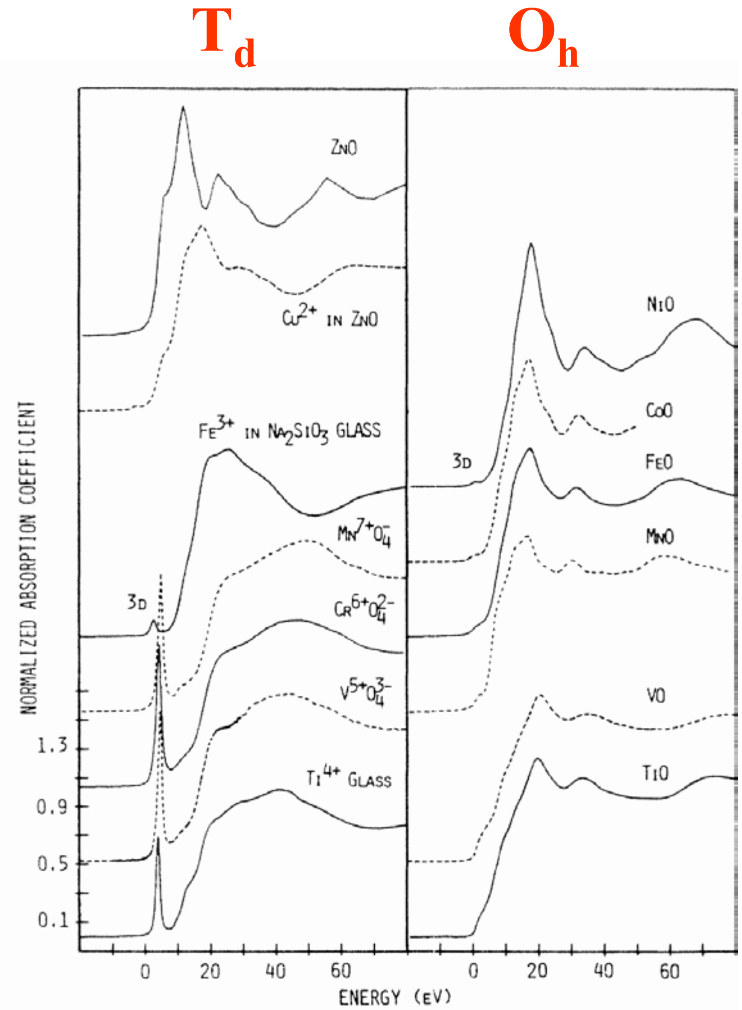
Local Site Symmetry in Ti-containing Compounds

- 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

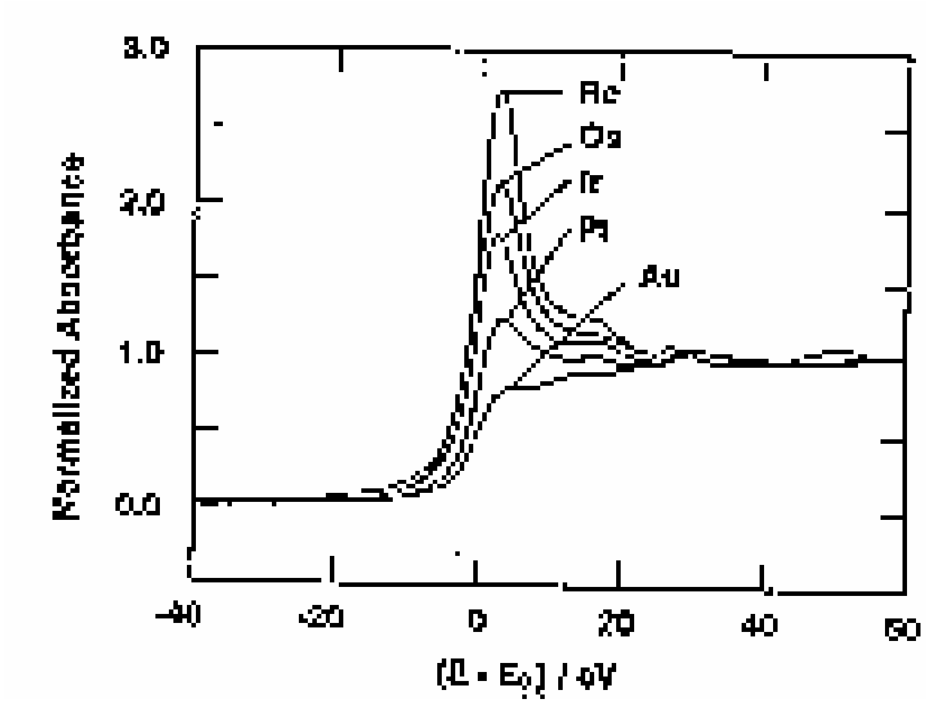
XANES of 3d Transition Metals: Coordination



- 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.

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

"White line" Intensity of Group VIII Metals



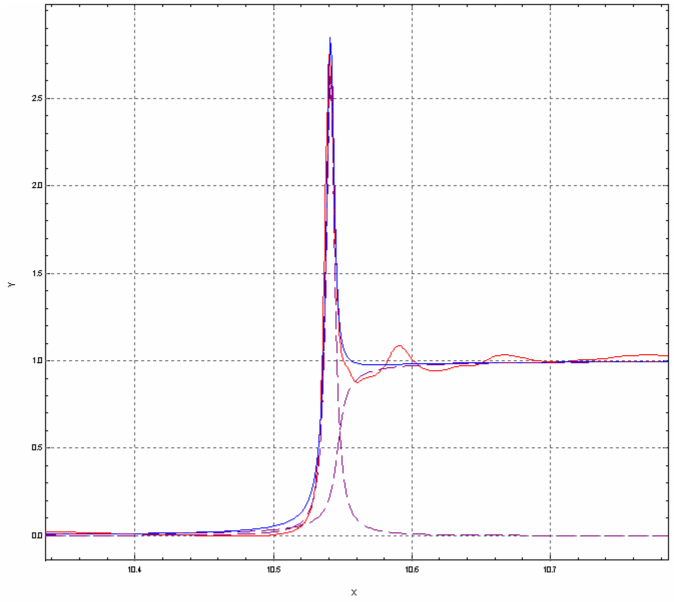
L_3 edge XANES for 5*d* metals

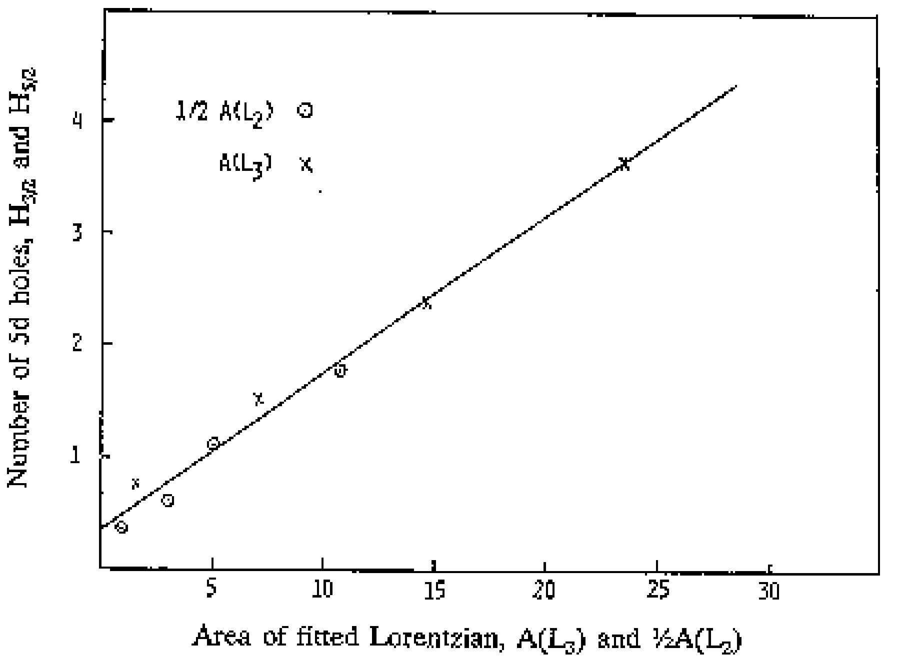
- Transition from 2*p*3/2 to 5*d* states.
- Absence of peak for Au: 5*d* states almost completely occupied (d^{10}).
- For others Pt (d^9)<Ir (d^7)<Os (d^6)<Re (d^5), corresponding to increase in number of unoccupied 5*d* states on the atoms.

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.



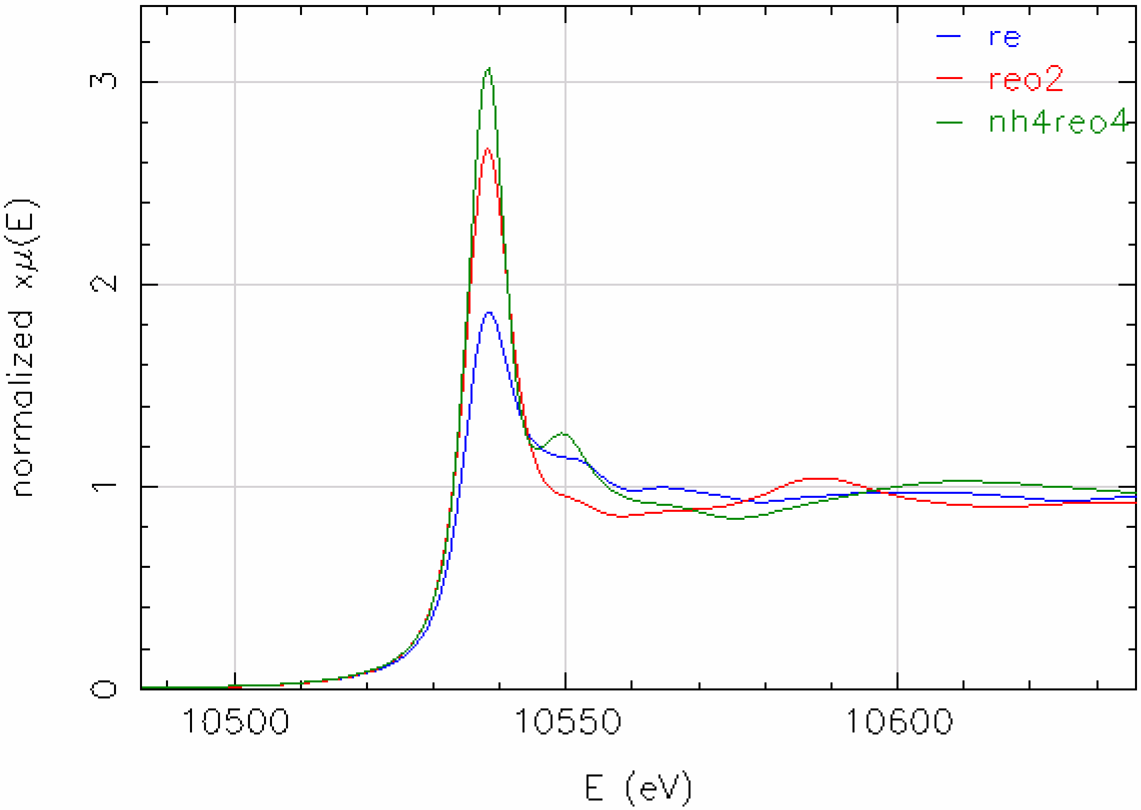


- Linear correlation between white line area and number of 5d-holes for Au-Re

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

“White Line” Intensity: Oxides

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



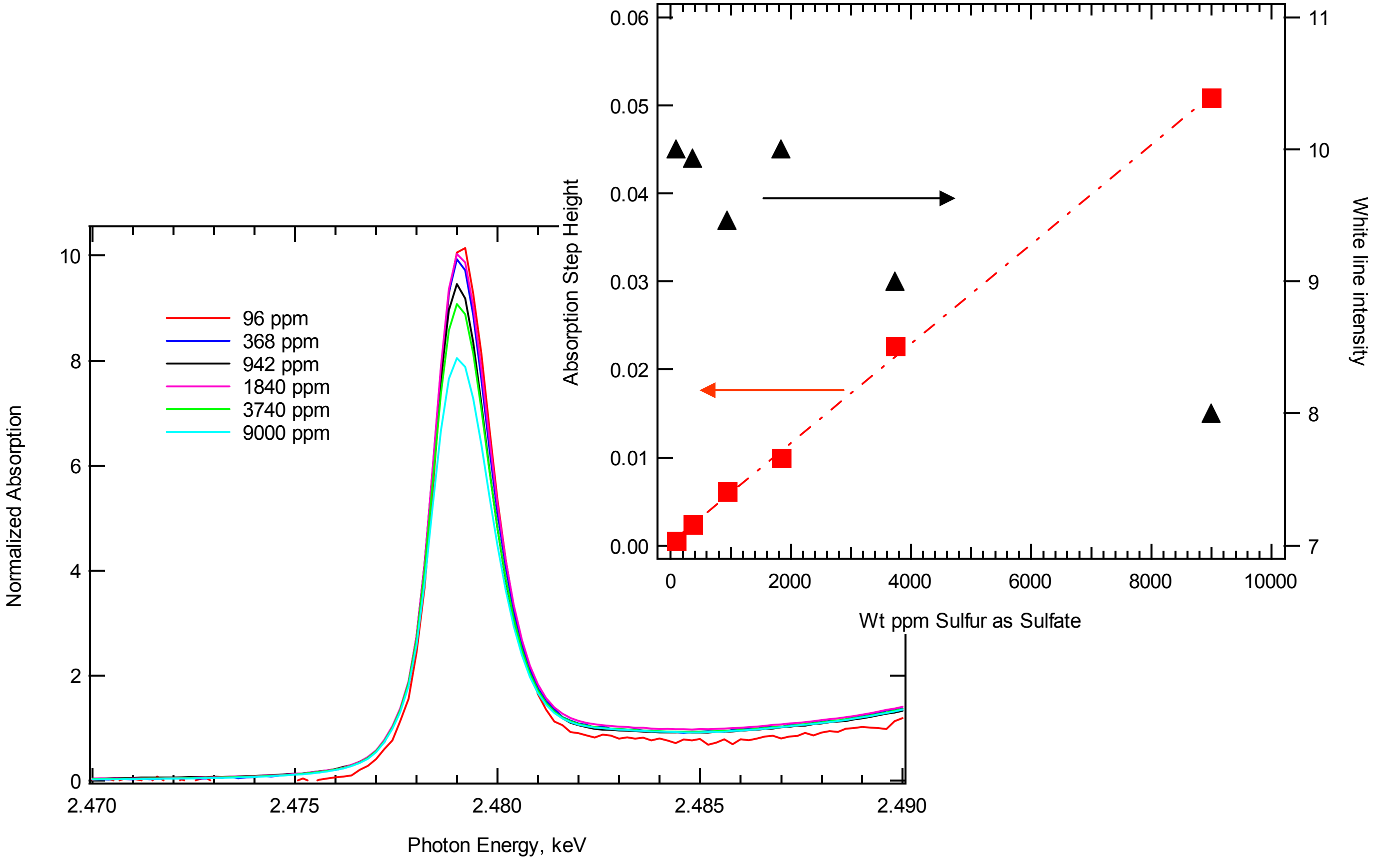
Re metal (Re^0) - $5d^5$

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

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

- Intensity of Re L_3 white line probes Re LDOS

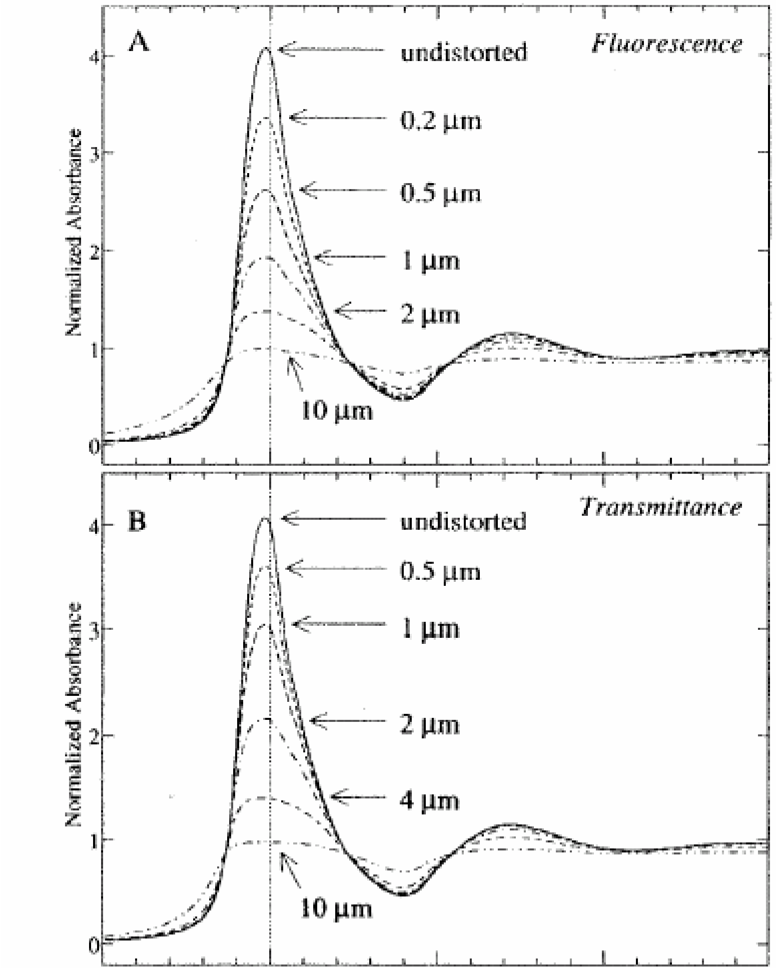
"White Lines": large change in absorption coefficient



- 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.

Caution about use of absolute intensity of "white line"

Solid sulfur, S_8



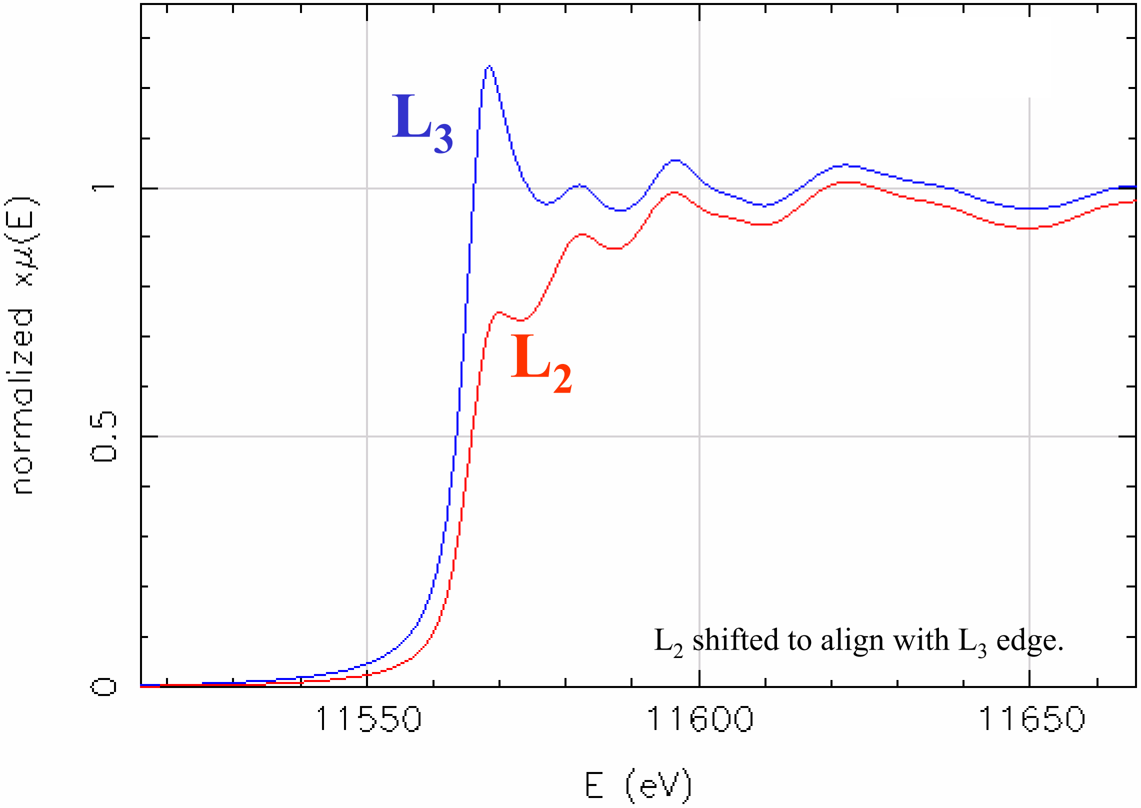
- Calculation of sulfur K-edge XANES (2.47 keV) for different spherical particles of sulfur.
- Severe distortion of the spectrum for particles 1 µm radius! One absorption length is ~ 2 µm.

"Due to their relatively high sulfur concentrations, all standards were powdered and sieved to particles sizes ≤10µm in diameter to minimize self-absorption effects at the sulfur K-edge"

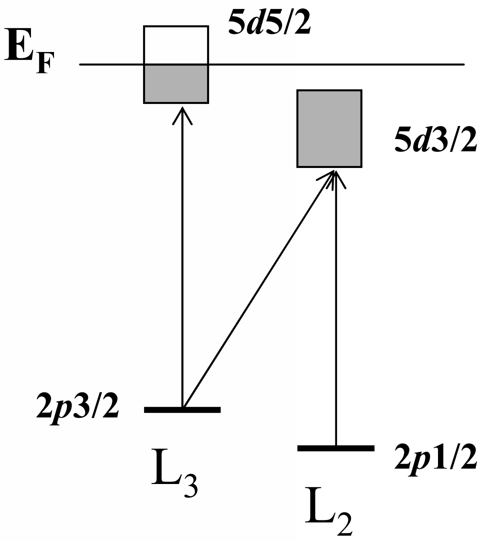
Pickering et al. Biochem 40 92001) 8138

Pt L_3 and L_2 Edge XANES

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



L_2 shifted to align with L_3 edge.



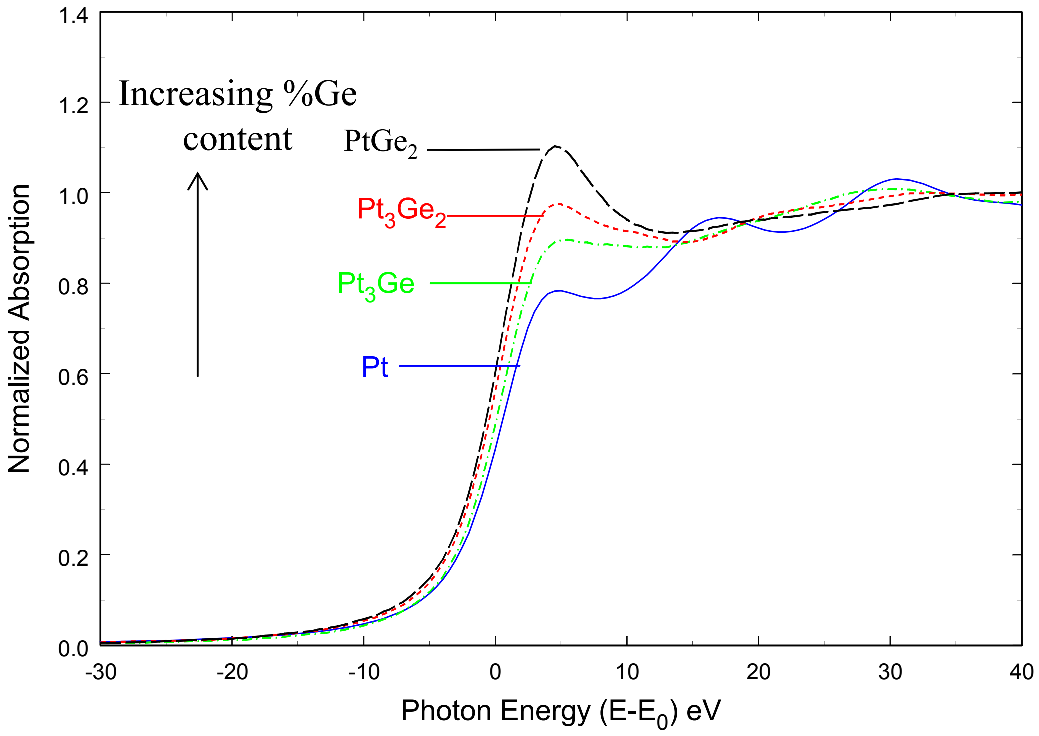
- Pt 5*d*3/2 filled, so no white line.

- 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.

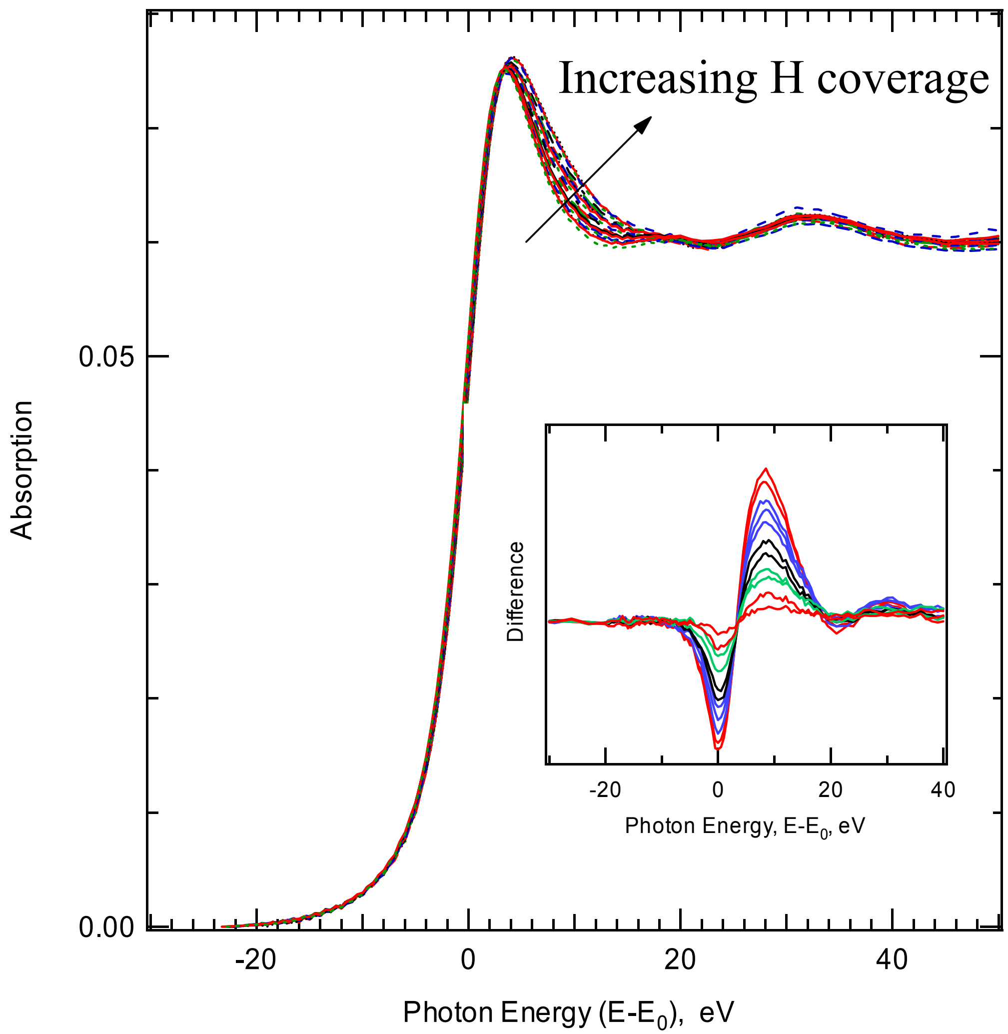
XANES to Probe Charge Transfer in Alloys

Platinum L_2-edge XANES: Pt_xGe_y Intermetallics



- 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

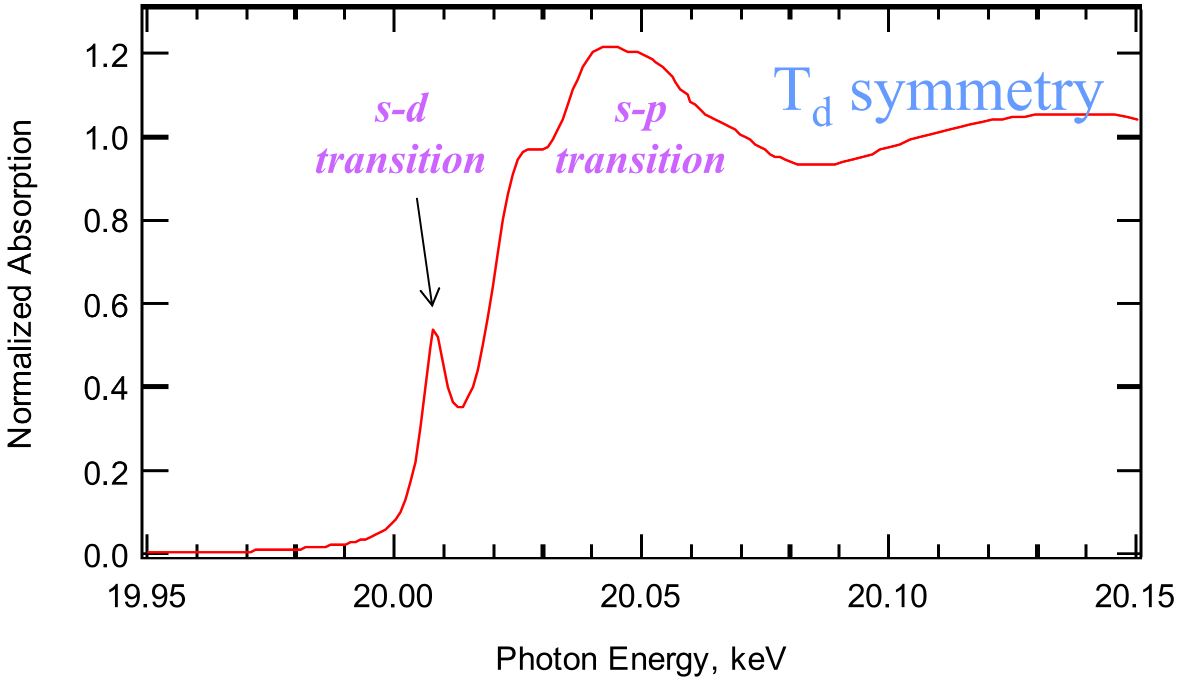


10-15Å Pt clusters supported on Al_2O_3

- 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.

Which Edge to Choose: Energy Resolution

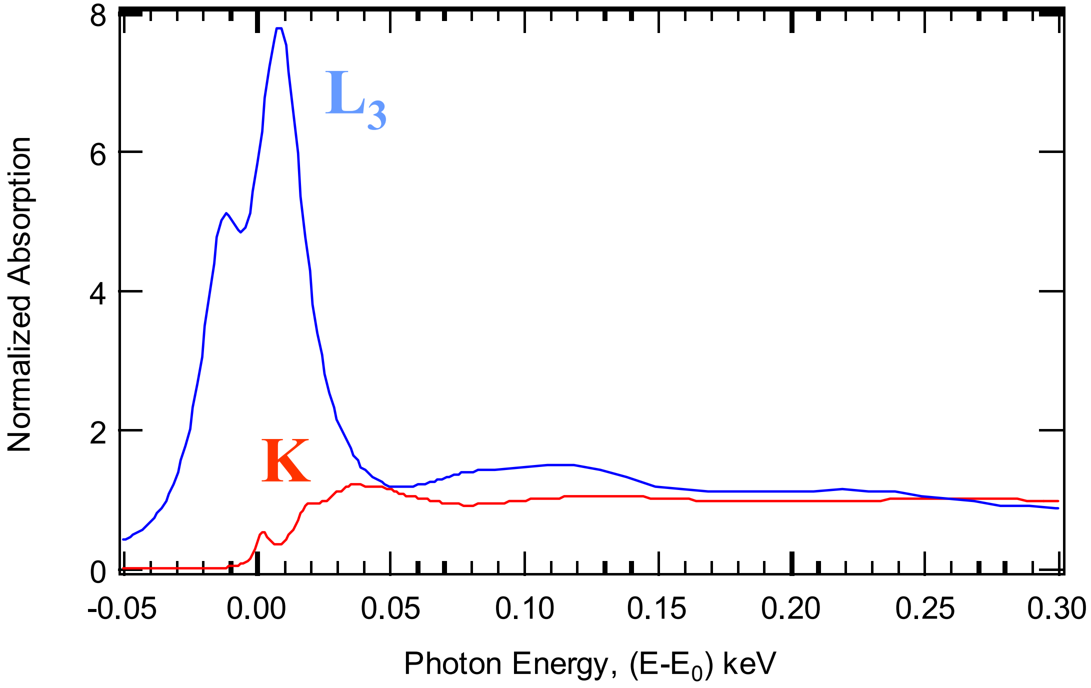
Mo K-edge XANES of Na_2MoO_4



- 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).

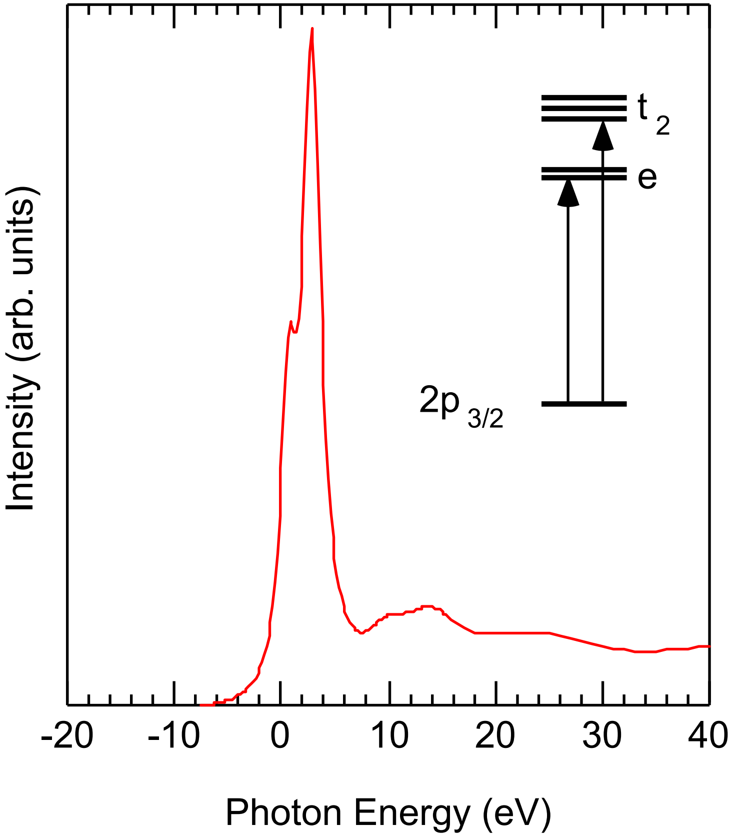


- Mo L_3-edge at 2.5 keV, 0.5 eV spectral resolution!

Which Edge to Choose: Energy Resolution

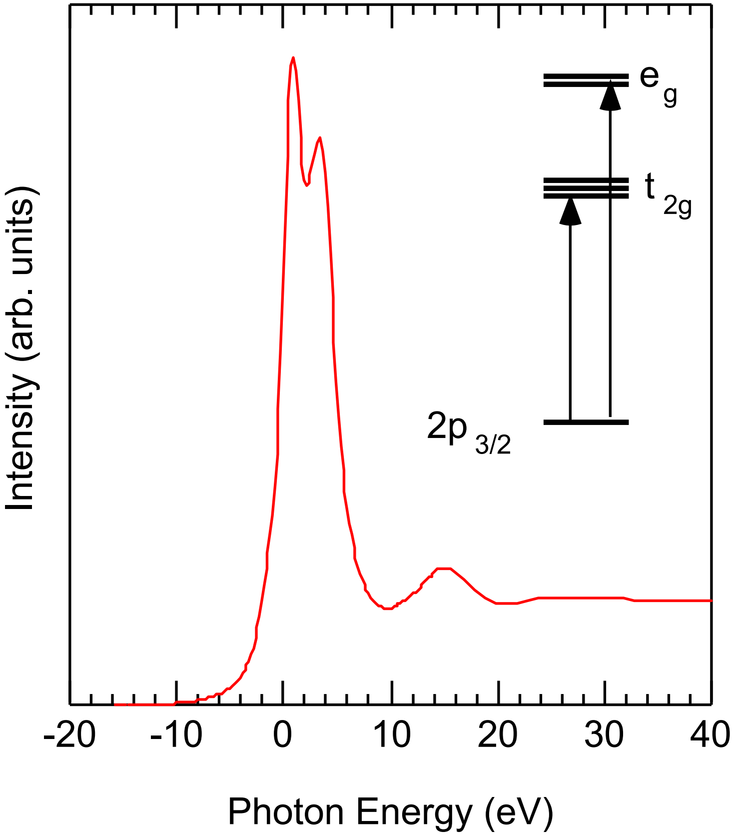
Sodium Molybdate, $NaMoO_4$
Mo atom tetrahedral coordination

Mo L_3-edge XANES



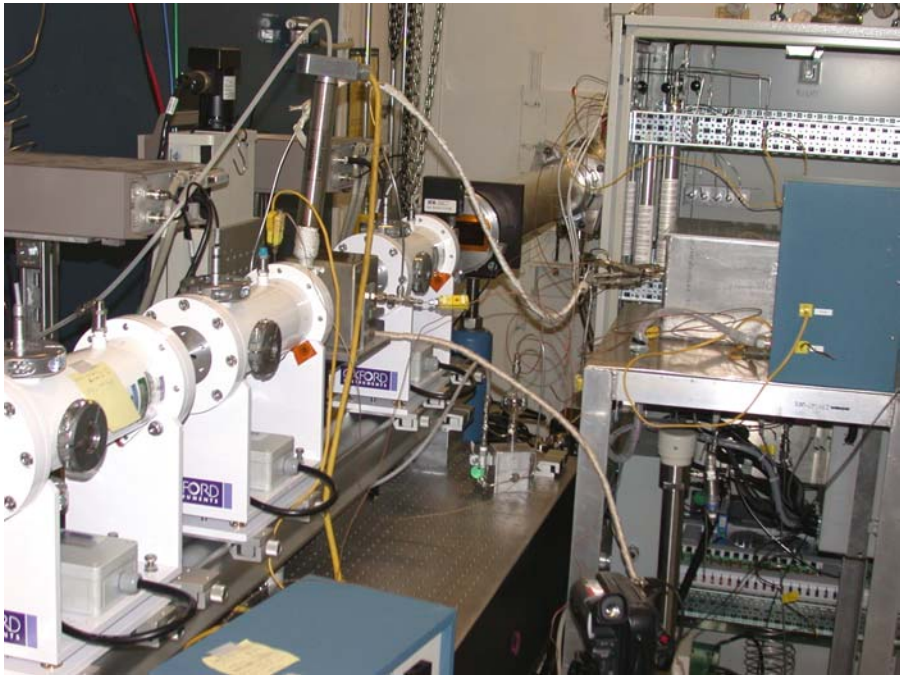
Cobalt Molybdate, $CoMoO_6$
Mo atom octahedral coordination

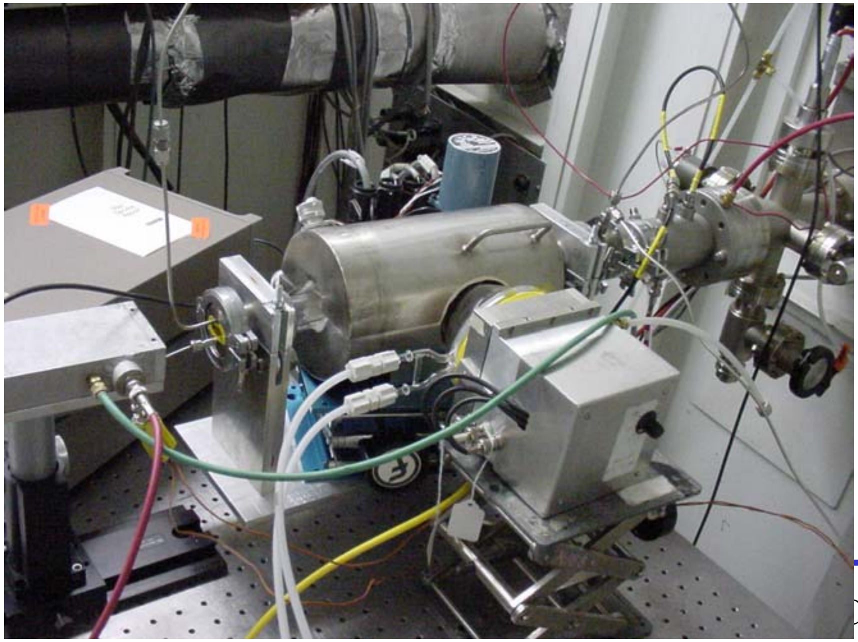
Mo L_3-edge XANES

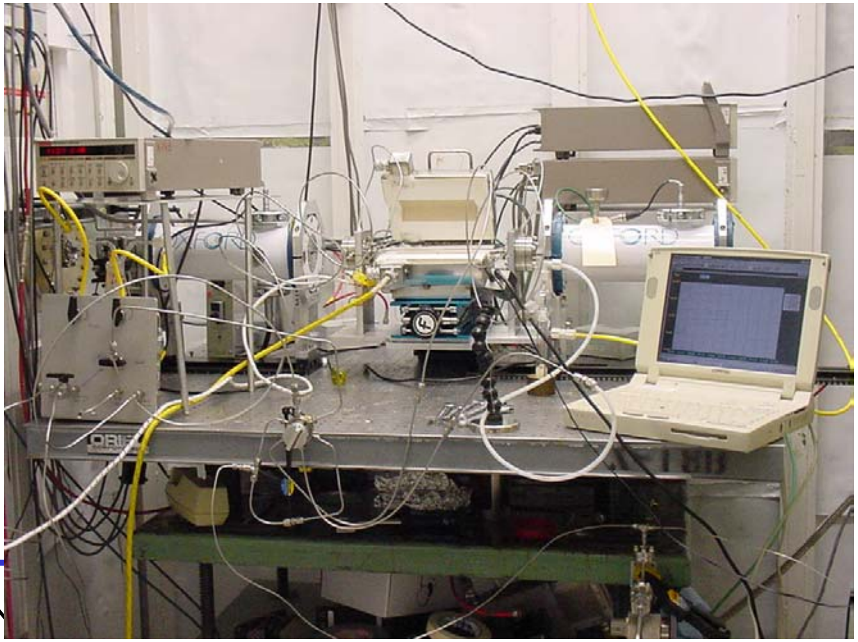


- **ΔE tetrahedral = 2.2-2.5 eV; ΔE octahedral = 3.25-4.2 eV**

Experimental *in situ/operando* cells for XAFS experiments used by UOP

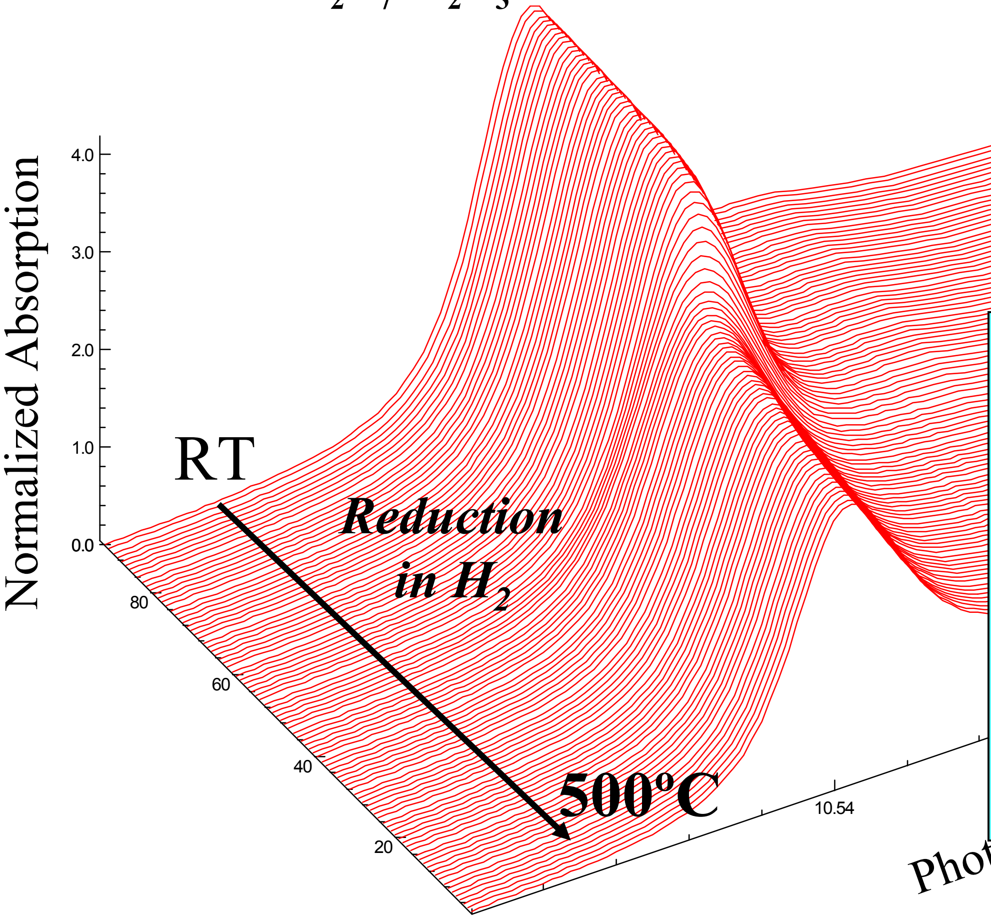


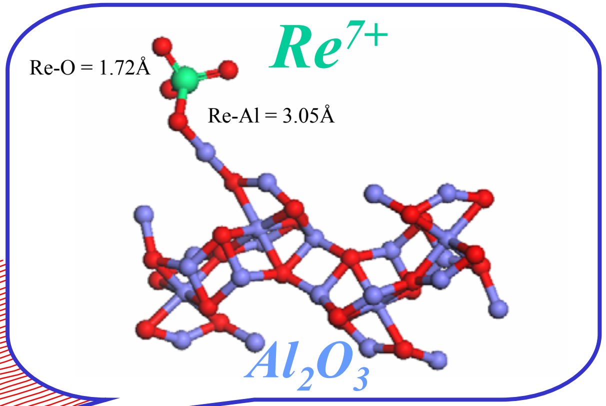


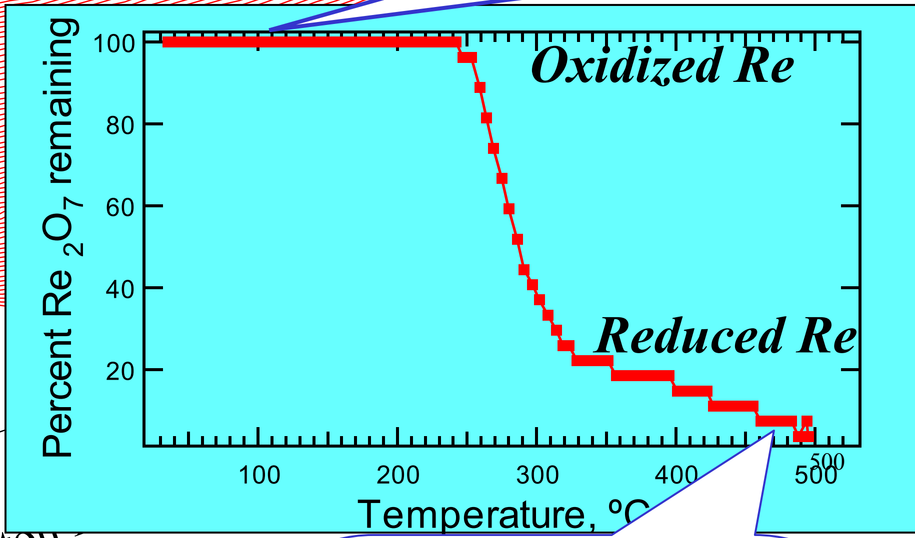


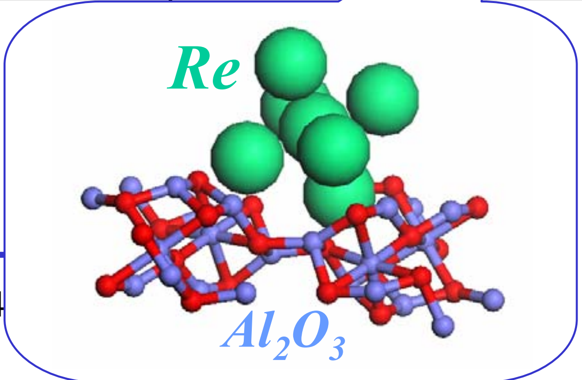
Time Evolution of XANES: Kinetics

In situ temperature programmed reduction of Re_2O_7/Al_2O_3



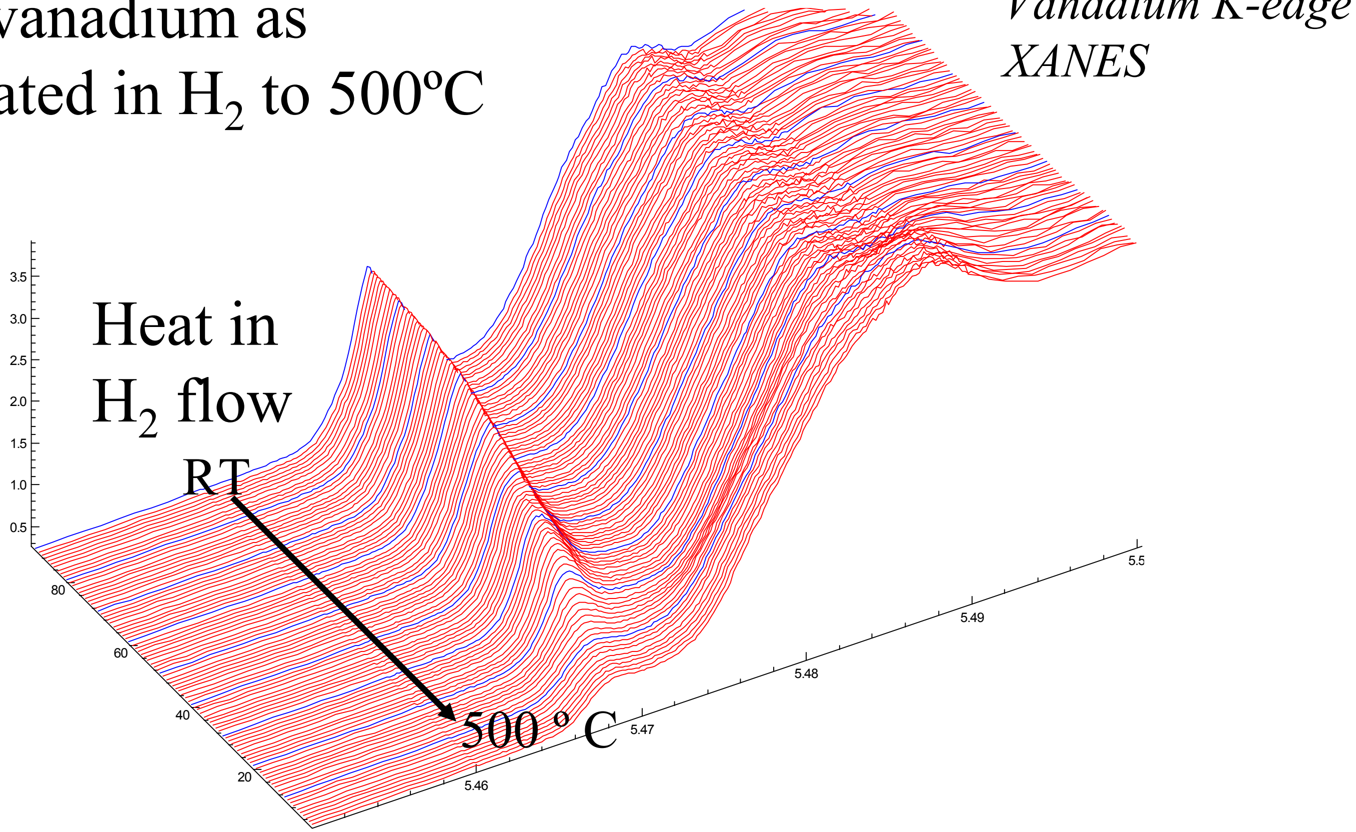






Time Evolution of XANES: Kinetics

TPR-XANES showing reduction of vanadium as catalyst is heated in H_2 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)
- See http://www.bnl.gov/x26a/ for information.

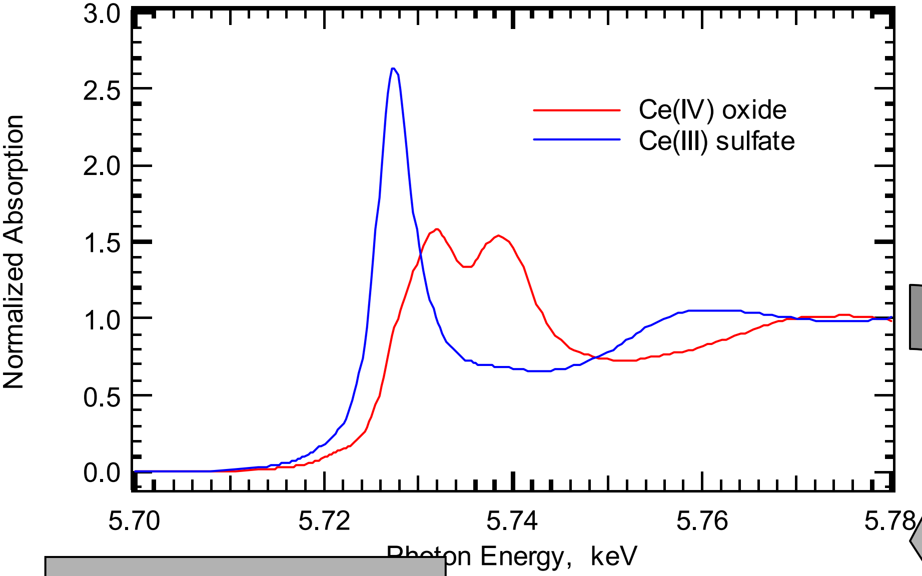
Analysis of Mixtures

- 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

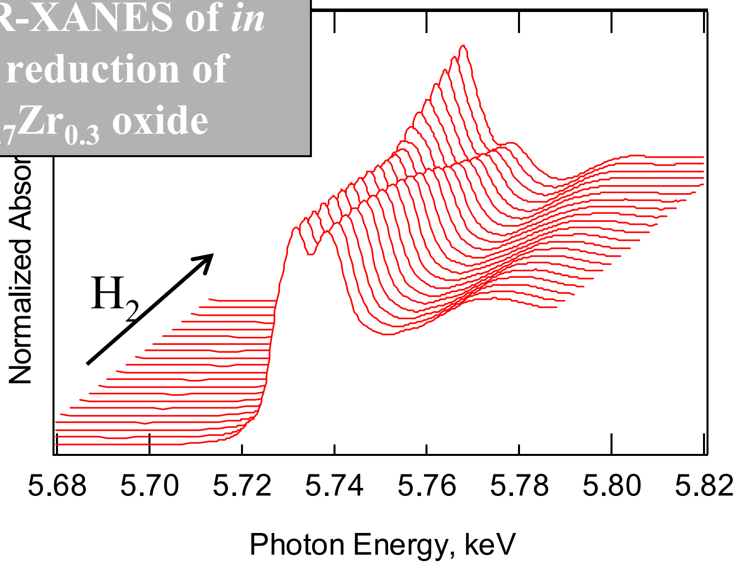
- Use a linear combination of spectra of various reference samples.
- Allows quantification of species in multiple-component mixture from their fingerprint in the XANES region.
- Use a least-squares algorithm to refine the sum of a given number of reference spectra to an experimental spectrum.
- Simple method, easy to implement.
- **Must have good quality spectra of the reference compounds recorded under similar conditions – energy alignment is critical.**

Linear Combination Fitting

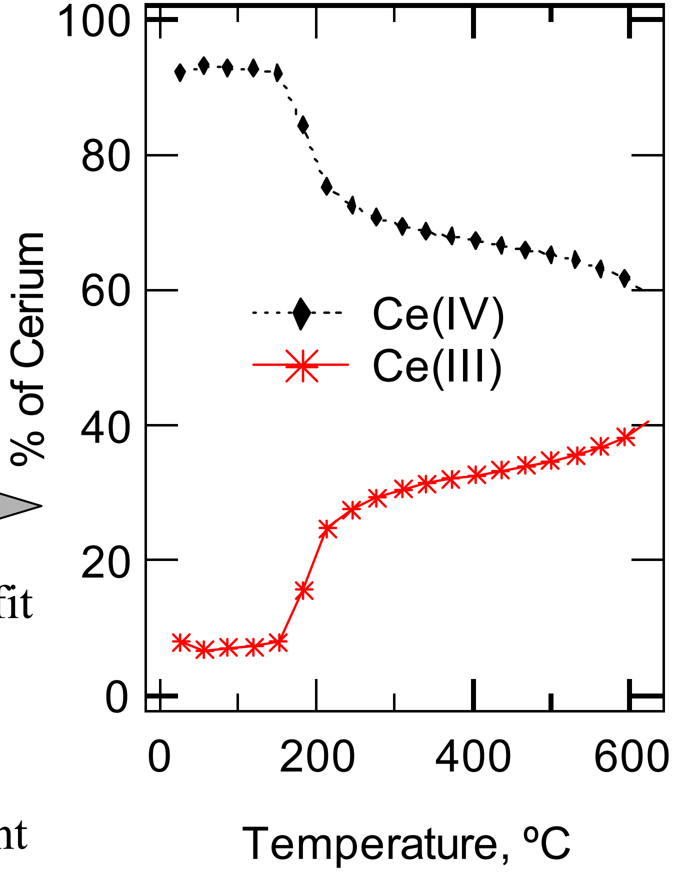


Fit experimental data to linear combination of known reference compounds

TPR-XANES of *in situ* reduction of $Ce_{0.7}Zr_{0.3}$ oxide

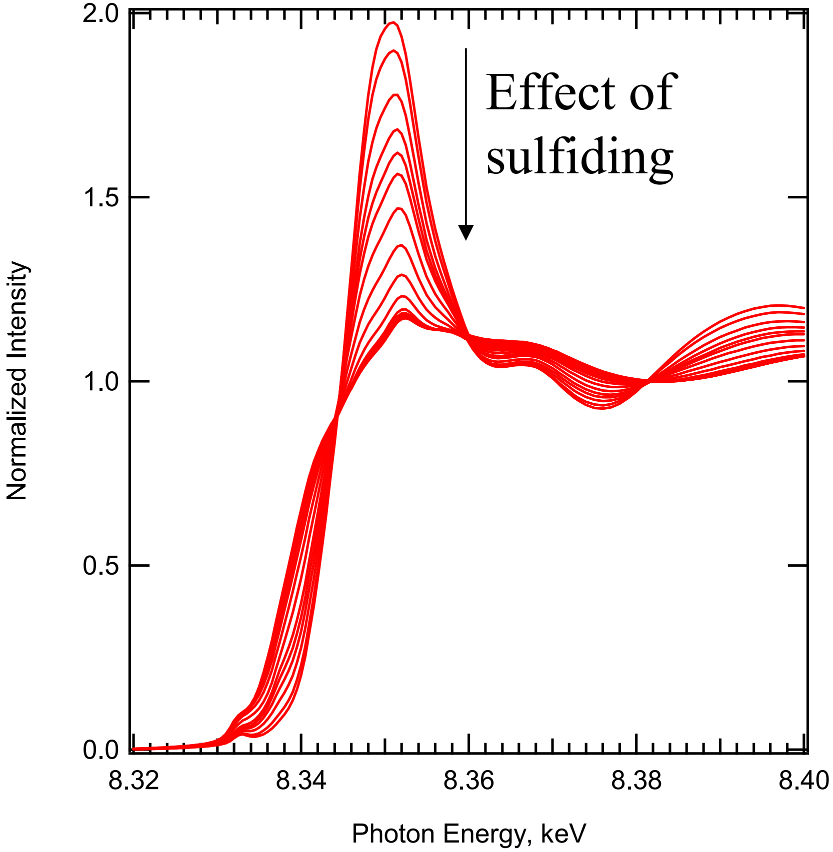


LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature

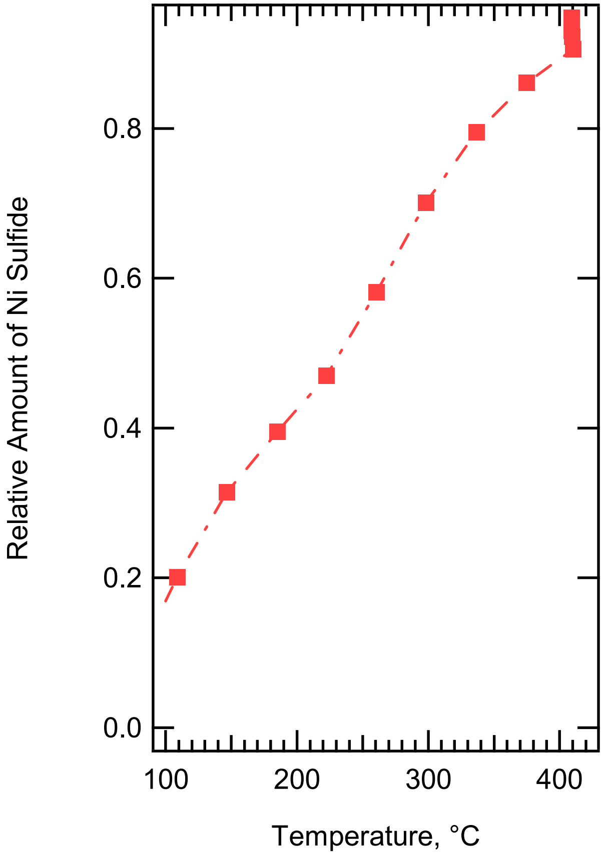


Linear Combination Fitting

Ni K-edge XANES of in situ sulfiding of a Ni/Al_2O_3 catalyst



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



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...

[†] Factor Analysis in Chemistry, 2nd Ed. John Wiley & Sons, NY, 1991

*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 (statistical) error.
- No *a priori* assumptions on number/type of components.
- Growing popularity in XANES spectroscopy*.

*"Principal component analysis approach for modeling sulfur K-XANES spectra in humic acids", S. Beauchemin et al., Soil. Sci. Soc.Am.J., 66 (2002) 83.

"Quantitative speciation of Mn-bearing particulates emitted from autos burning mcp-Mn gasolines using XANES spectroscopy", T. Ressler et al., Environ. Sci. Technol., 34 (2000) 950.

"EXAFS and principal component analysis: a new shell game", S. Wasserman et al., J. Synch. Rad., 6 (1999) 284.

"The kinetic significance of V^{5+} in n-butane oxidation catalyzed by vanadium phosphates", G.W. Coulston et al., Science, 275 (1997) 191

"XANES-TPR study of Cu-Pd bimetallic catalysts: application of factor analysis", M.Fernandez-Garcia et al., J. Phys. Chem 99 (1995) 12565.

Potential pitfalls and drawbacks of PCA

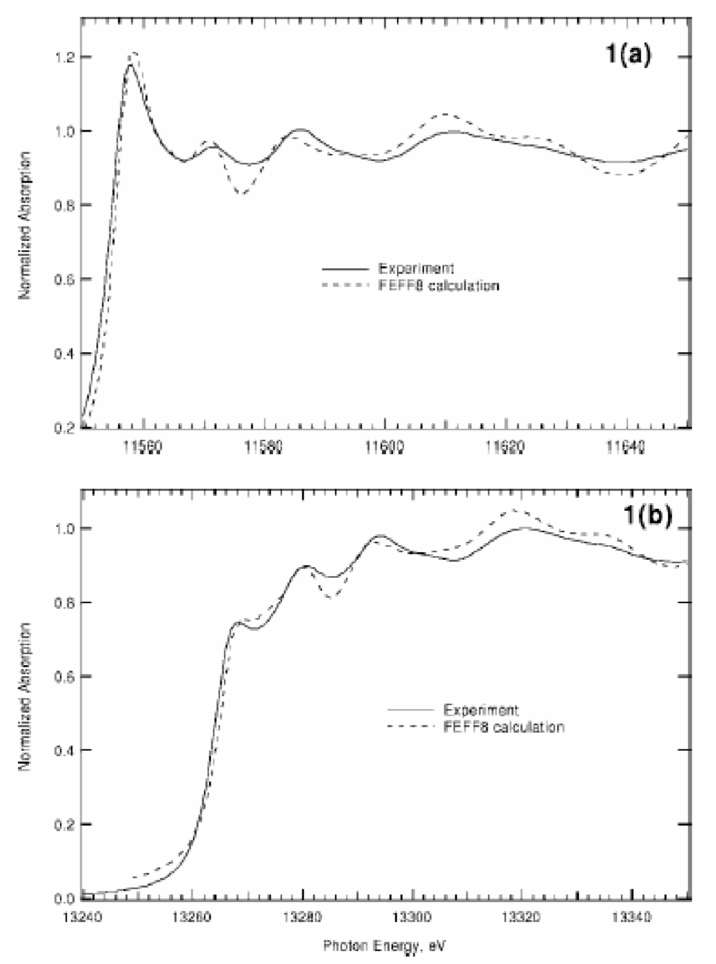
- **Principal components not equal to chemical species.**
- **Constant ratio of two (chemical) components.**
- **Temperature increase during measurement.**
- **Additional information required to transform abstract results in meaningful speciation (either references or concentrations).**
- **But: Powerful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

Feff8.1 and XANES

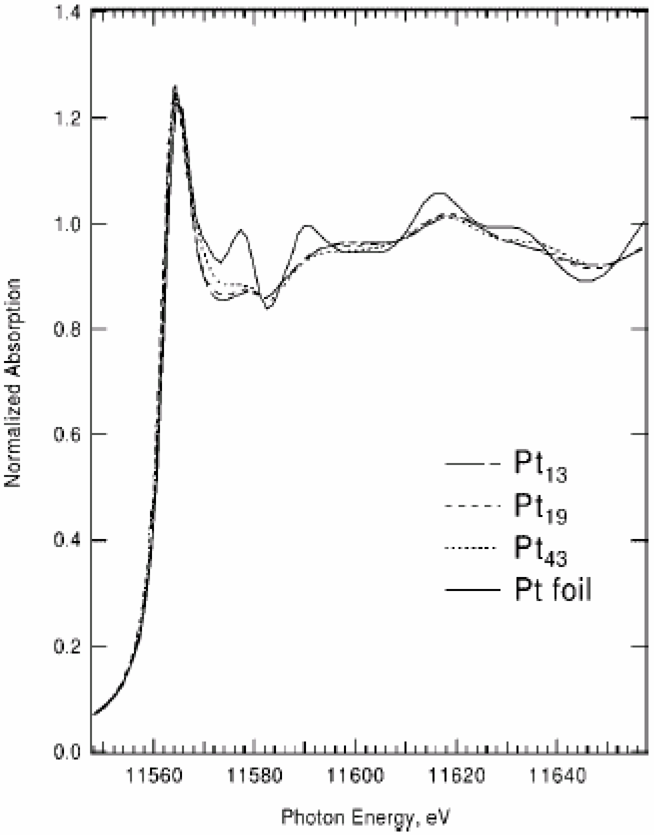
- Dramatic progress in past decade both in theory and *ab initio* calculations.
- Significant progress has been made in understanding XANES.
- Quantitative theory central to quantitative interpretation of XAFS spectra in terms of local geometric and electronic structure.
- Will hear more about Feff tomorrow!

Feff8.1 and XANES: Pt L-edges

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

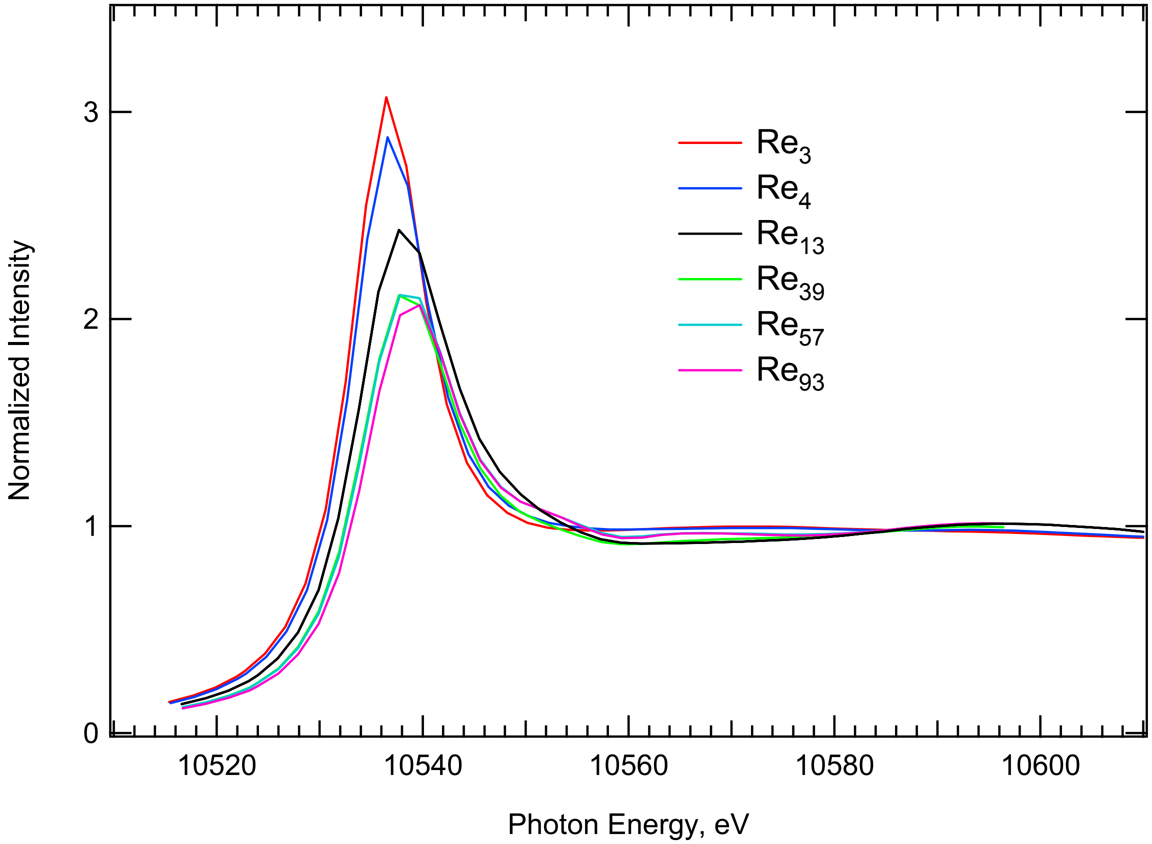


Pt L_3-edge XANES as function of Pt cluster size



Preliminary FEFF8 Calculations

Naked Re Clusters



- **Large white line variation with Re cluster size.**
- **Convergence at ~39 atom cluster.**

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…..