

# *XANES Measurements and Interpretation*

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# *Acronyms*

## **XANES**

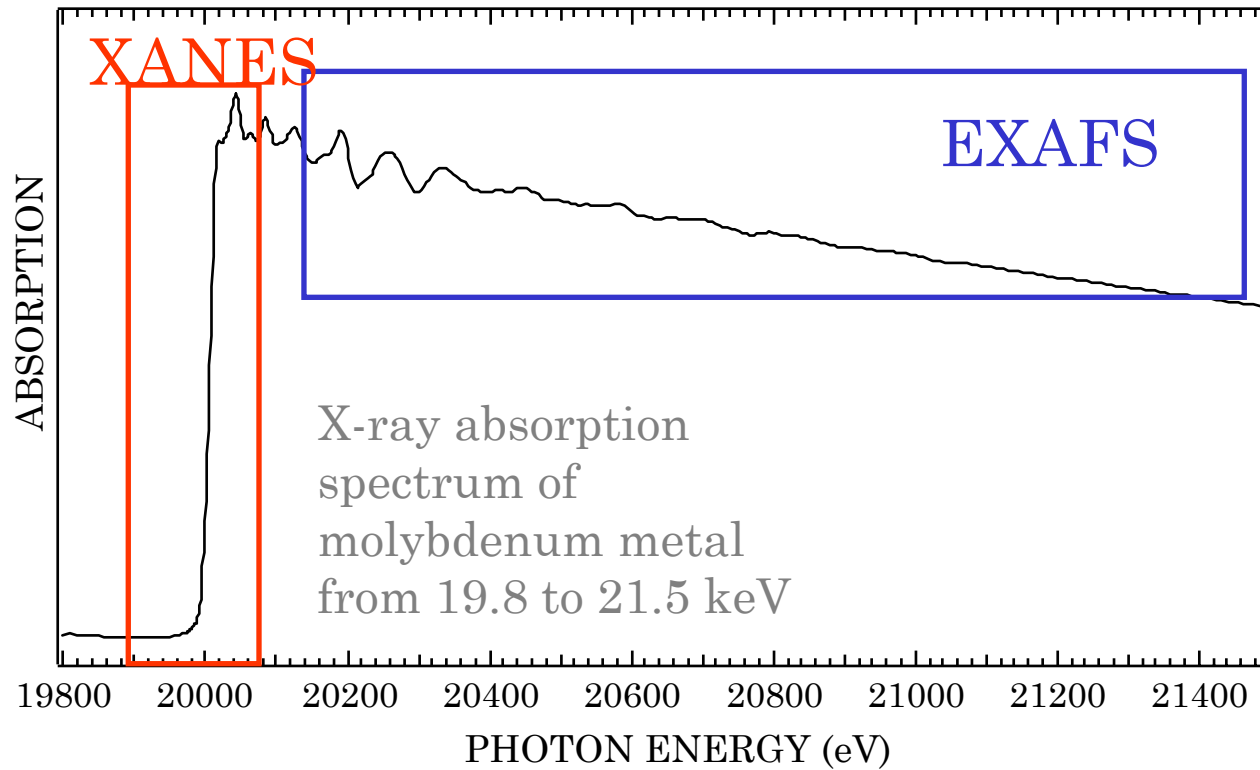
- **X**-ray **A**bsorption **N**ear **E**dge **S**tructure

## **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...

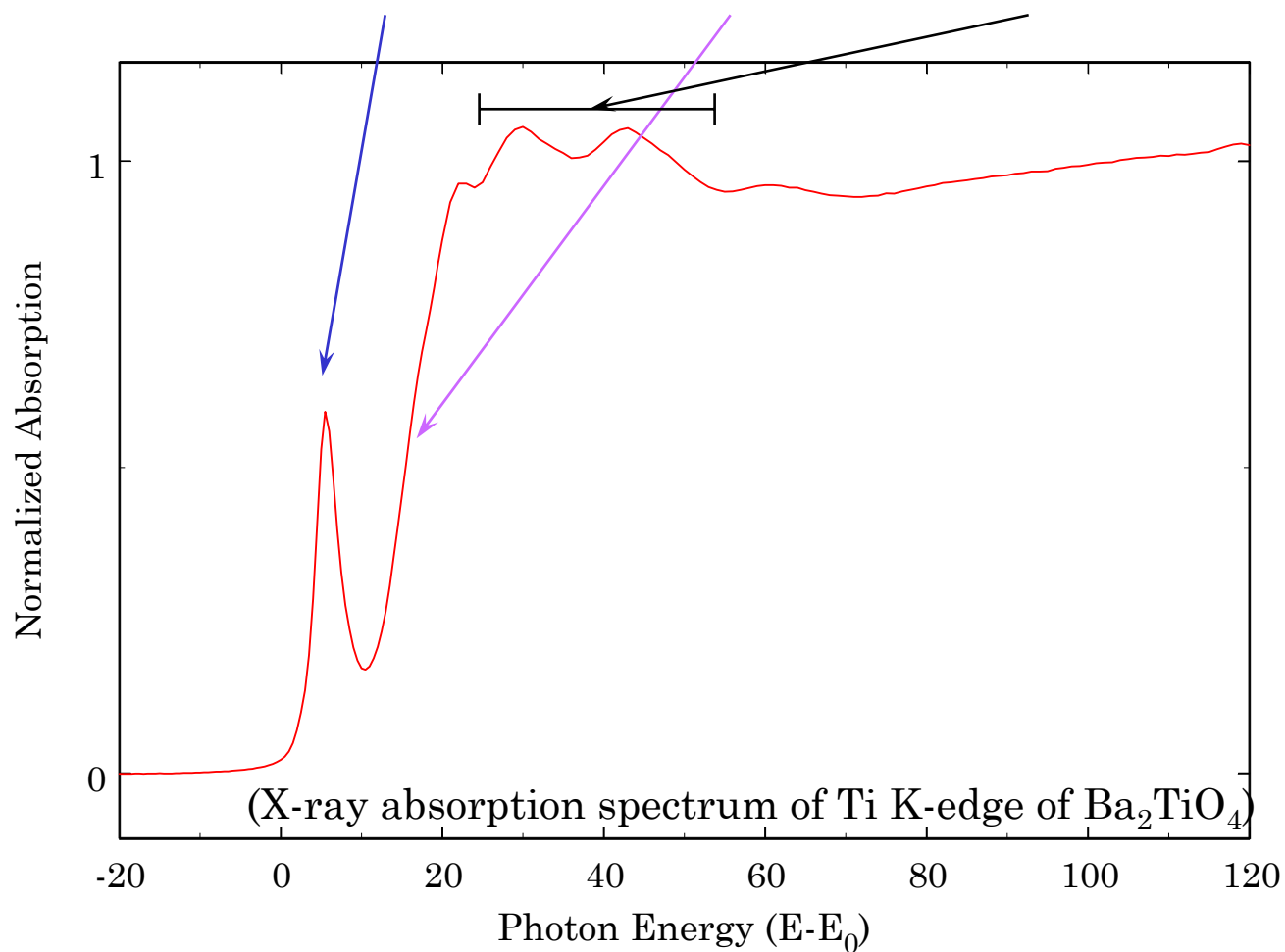
# What Is XANES?



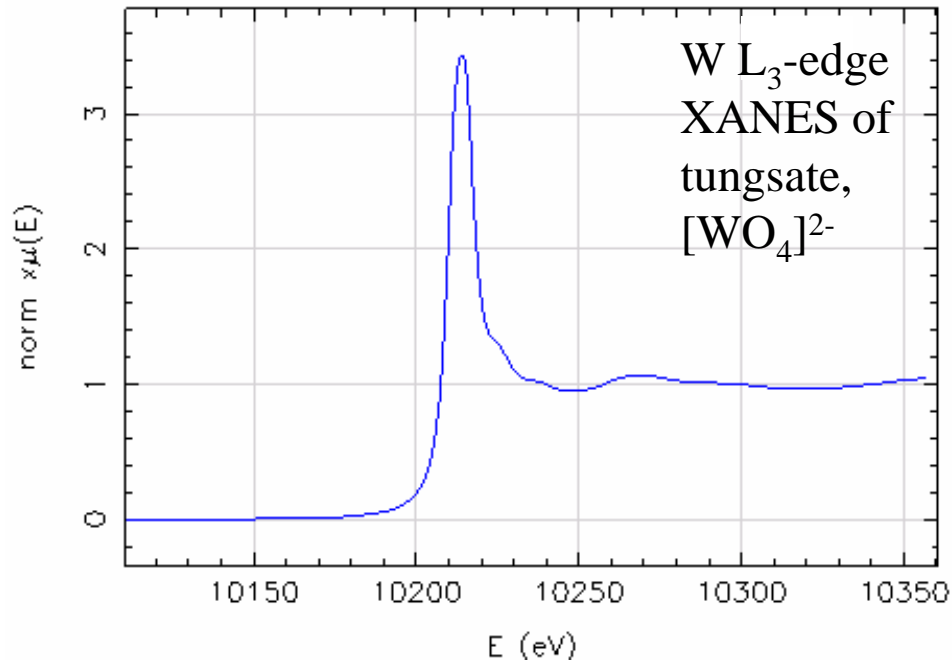
- **XANES is region of x-ray absorption spectrum within ~50eV of the absorption edge.**

# What Is XANES?

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

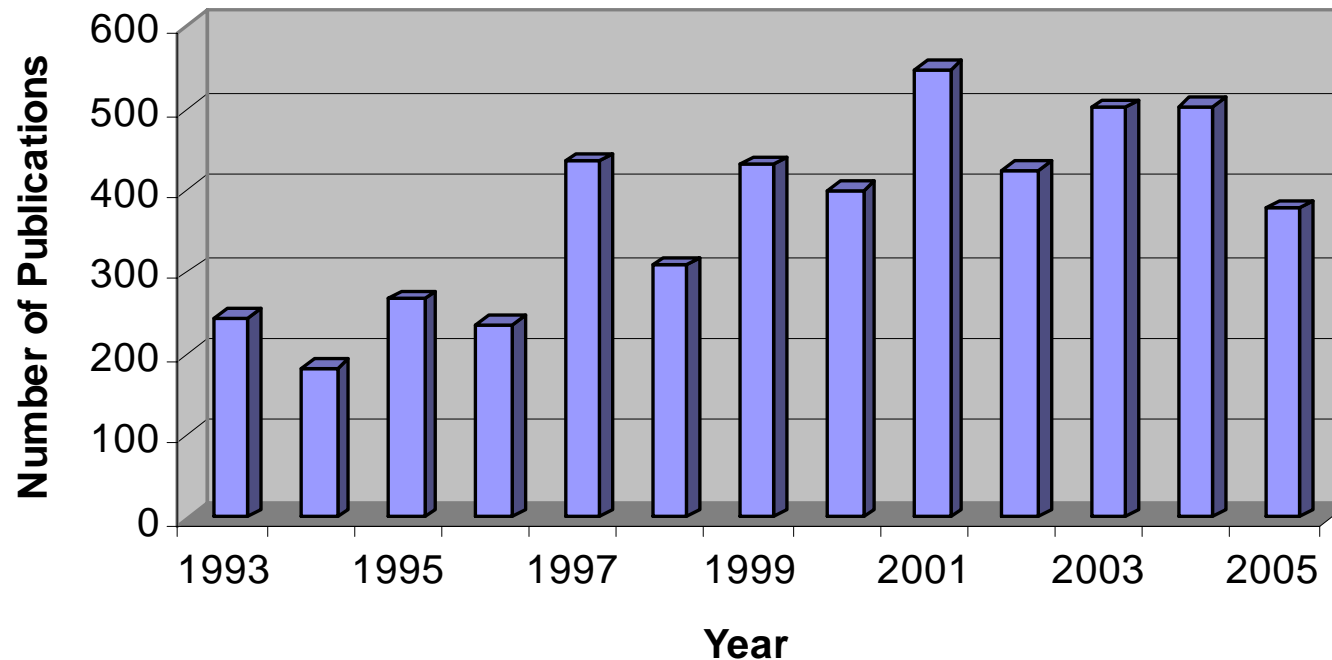


# “White line”



- 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*



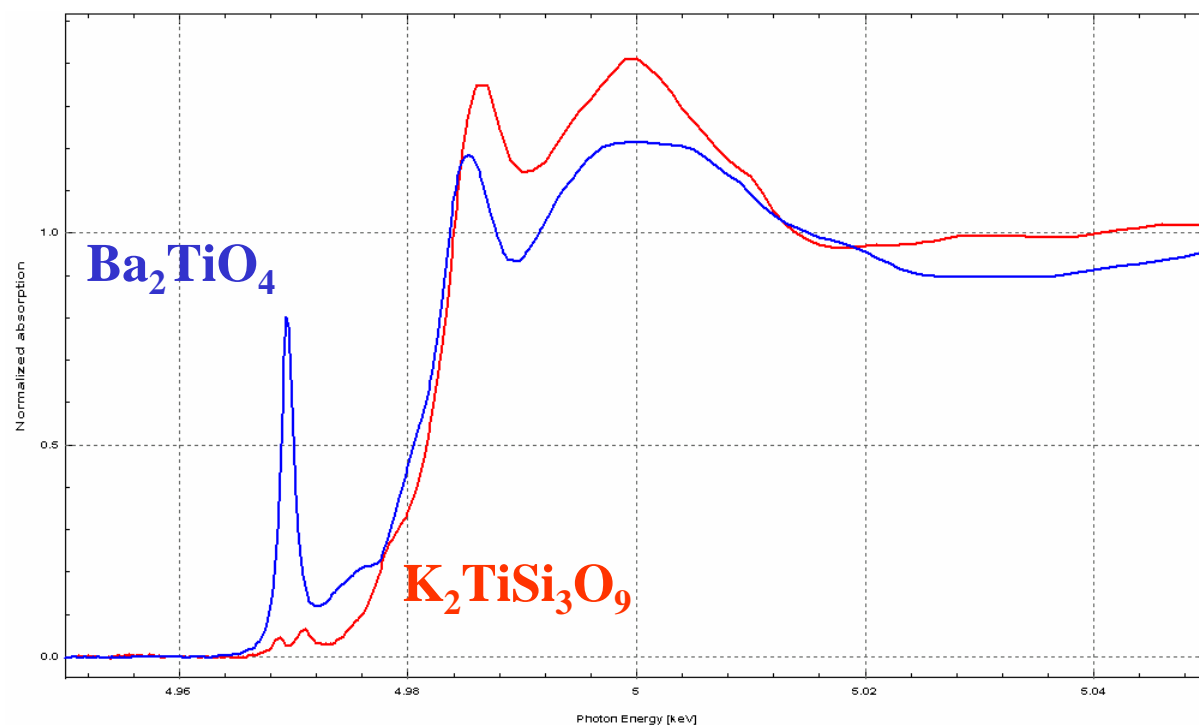
- On average ~500 publications per year in SciFinder!

# *Representative Publications (2005)*

- **Interactions of uranium with bacteria and kaolinite clay.** Chemical Geology (2005), 220(3-4), 237-243.
- **Synthesis, structure, spectroscopy and redox chemistry of square-planar nickel(II) complexes with tetradentate o-phenylenedioxamides and related ligands.** Dalton Transactions (2005), (15), 2516-2526.
- **In situ investigations of structure-activity relationships of a Cu/ZrO<sub>2</sub> catalyst for the steam reforming of methanol.** Journal of Catalysis (2005), 233(2), 297-307.
- **Variations in atmospheric sulphate recorded in stalagmites by synchrotron micro-XRF and XANES analyses.** Earth and Planetary Science Letters (2005), 235(3-4), 729-740.
- **Crystal-Quasicrystal Local Structural Transition in Al-Cu-Fe.** JETP Letters (2005), 81(9), 479-483.
- **Protective Action of Vanadate at Defected Areas of Organic Coatings on Zinc.** Journal of the Electrochemical Society (2005), 152(7), B220-B227.

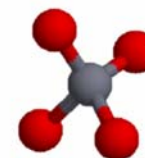
# Why Are We Interested In XANES?

## Local Coordination Environment



Both Ti<sup>4+</sup>

Ba<sub>2</sub>TiO<sub>4</sub>



K<sub>2</sub>TiSi<sub>3</sub>O<sub>9</sub>

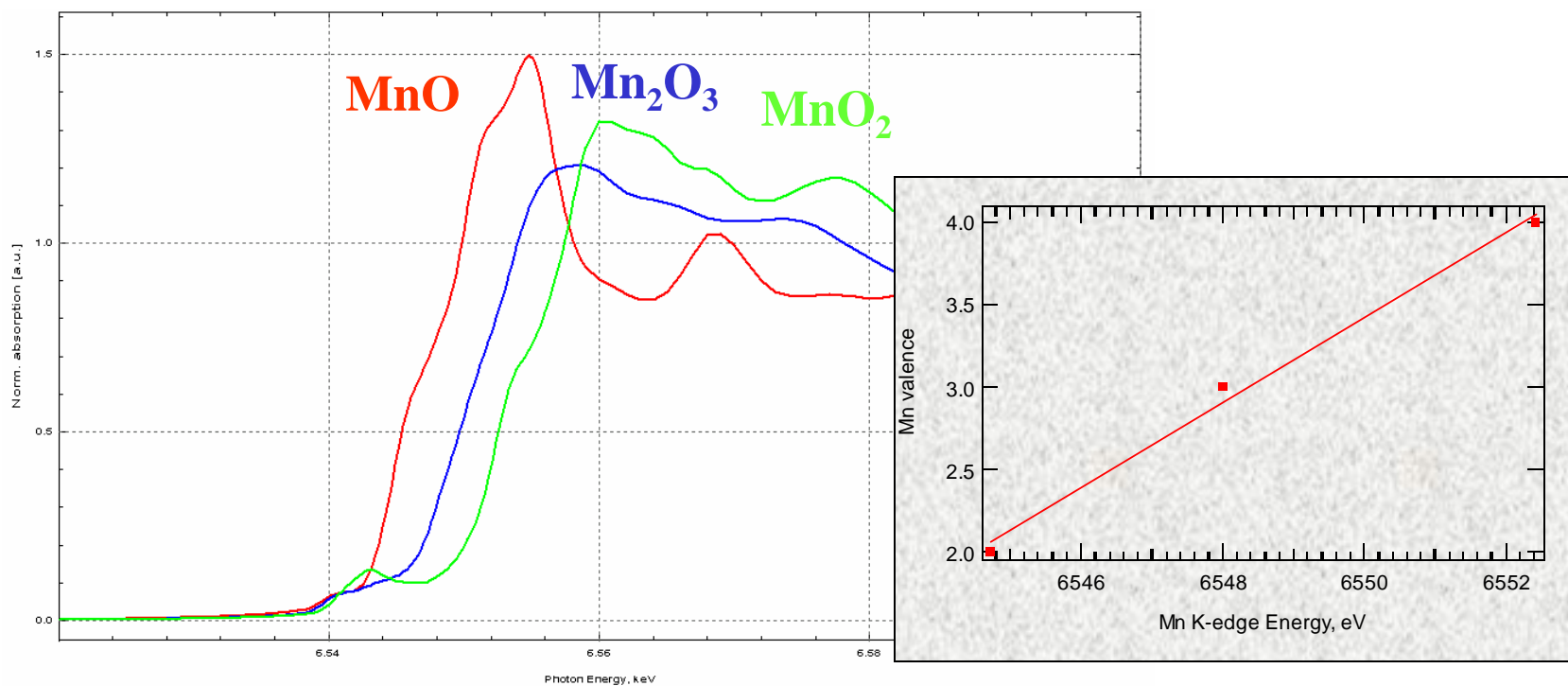


- Ti K-edge XANES shows dramatic dependence on the local coordination chemistry.



# 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 <i>ab initio</i> 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  $L_2$  ( $2p_{1/2}$ ) 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

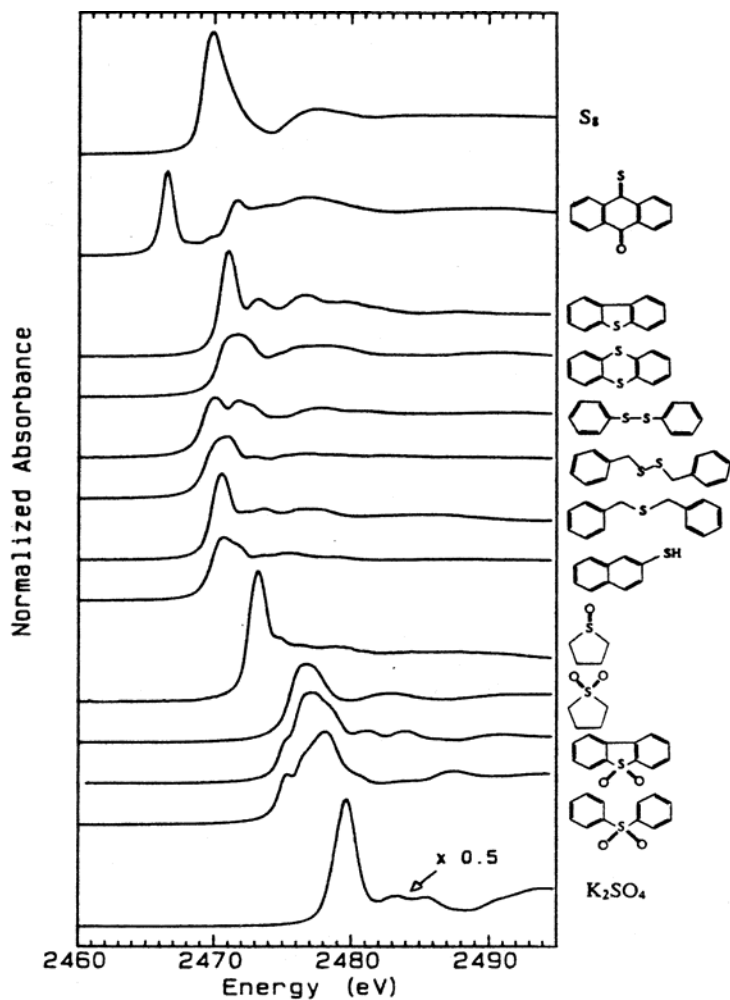
- These chemical and physical interpretations are all related:

**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 (*in situ*):
  - $\text{Exp}(-2k^2\sigma^2) = \text{exp}(-2(0.5)^2 \times 0.005) \sim 1$
- 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  $S^{6+}$ .

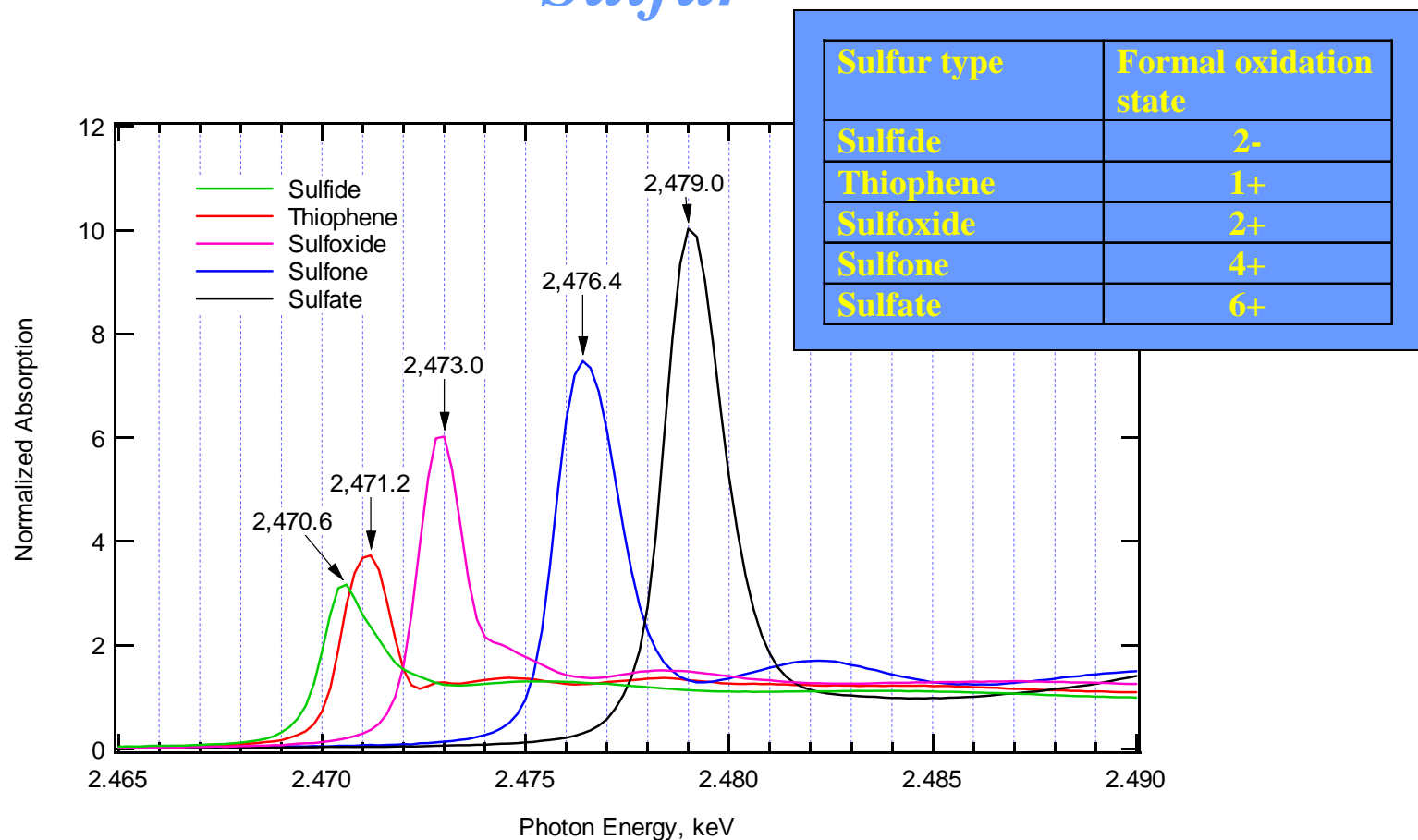
Spectra of S in similar environments similar: thiophene, benzothiophene.

Can be used as fingerprint.

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

# XANES Analysis: Oxidation State

## Sulfur

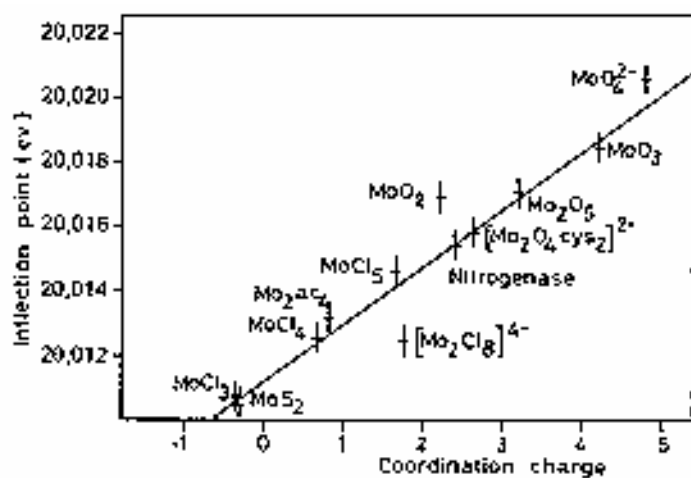


Dodecyl sulfide, thiophene, tetramethylene sulfoxide, tetramethylene sulfone, sulfate(aq)

# XANES Analysis: Oxidation State

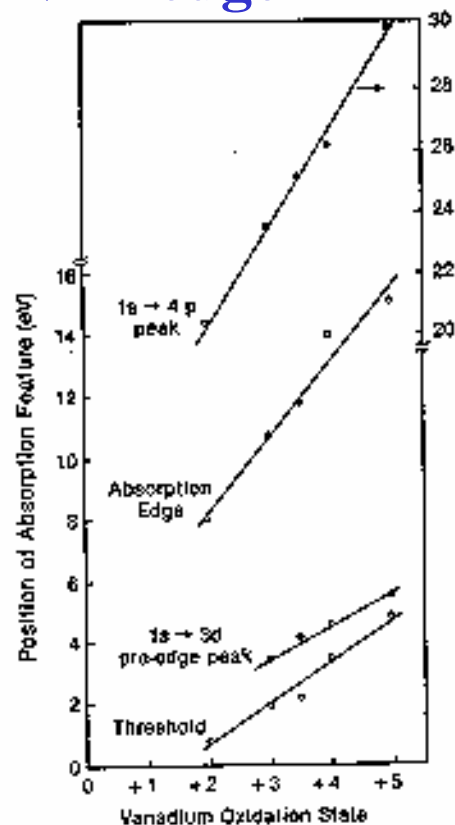
Many, many examples in the literature.....

## Mo K-edge



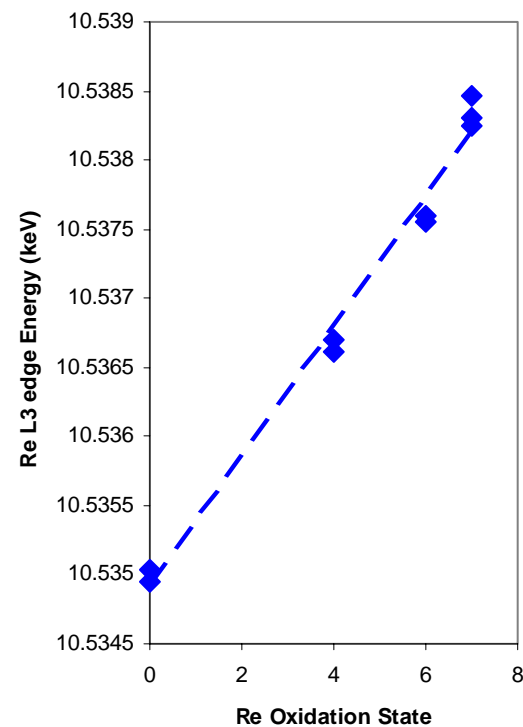
Ref: Cramer et al., JACS, 98 (1976) 1287

## V K-edge



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

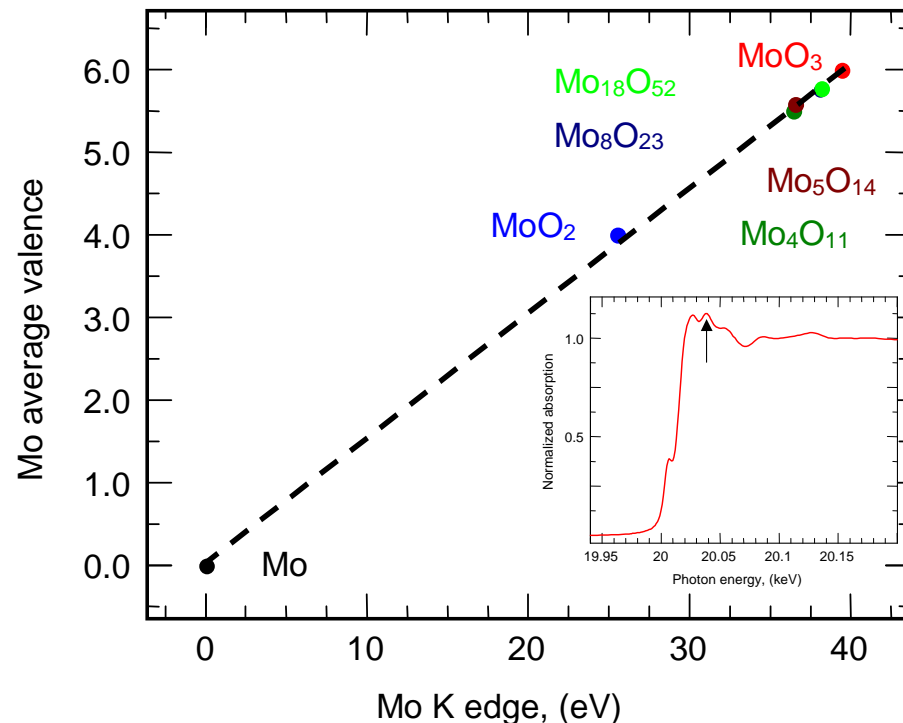
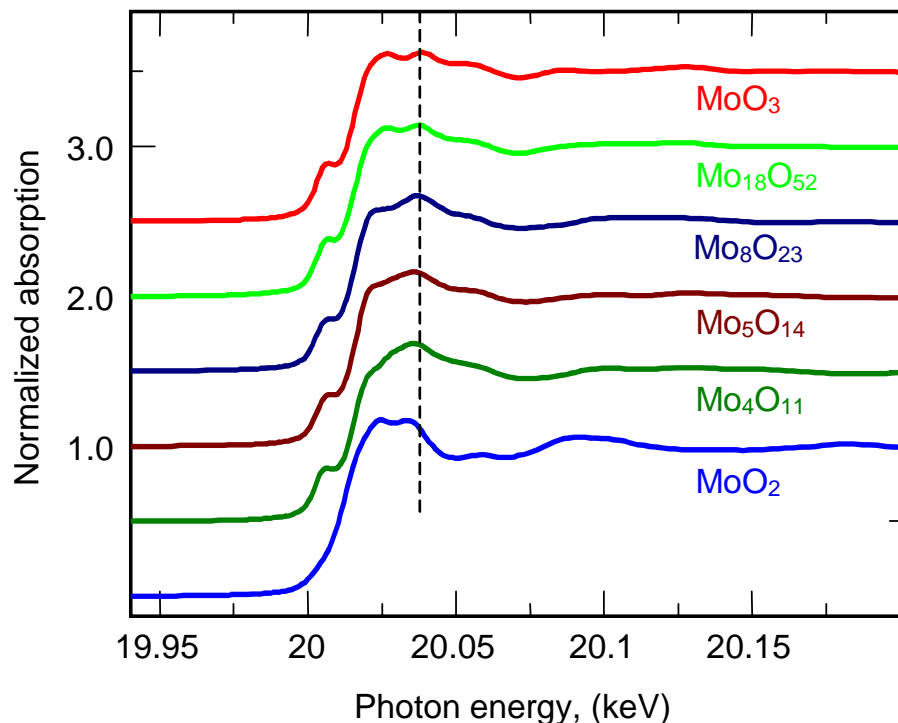
## Re L<sub>3</sub>-edge





# XANES Analysis: Oxidation State

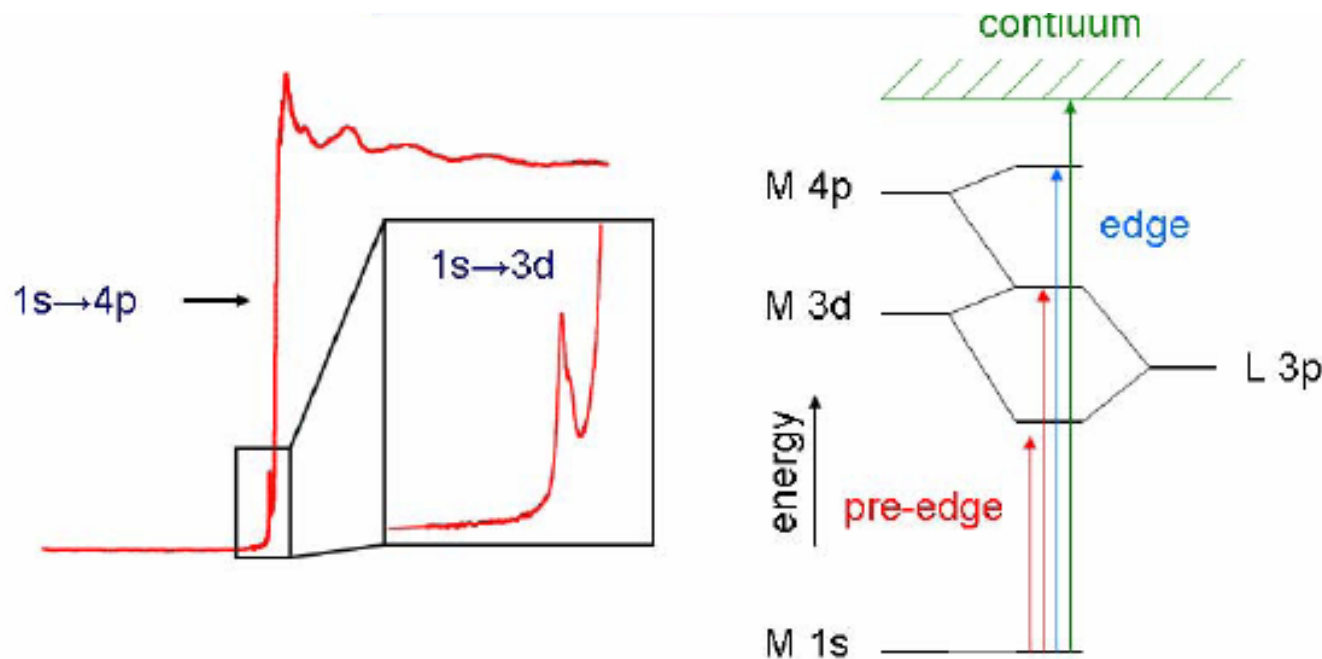
## Mo K-edge XANES of Mo oxides



- 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

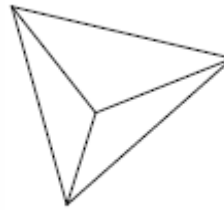
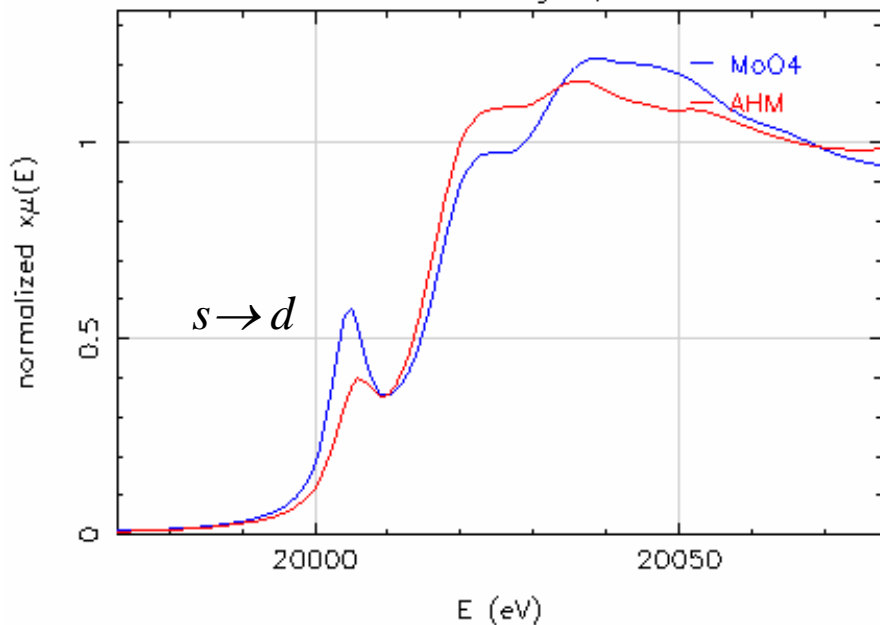
# Metal K-edge XANES



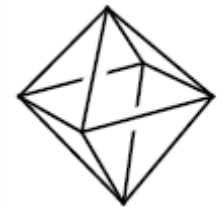
- Intense edge absorption due to dipole allowed  $s \rightarrow p$  transition ( $\Delta l = \pm 1$ ).
- Weaker pre-edge feature results from mixing of 3d-4p orbitals of suitable symmetry (or from quadrupolar allowed transition – ~2 orders magnitude weaker).

# Molybdenum Oxides

## Mo K-edge XANES



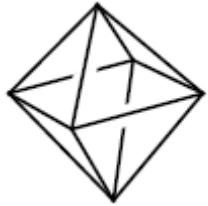
**Tetrahedral  
coordination**



**Octahedral  
coordination**

- 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*

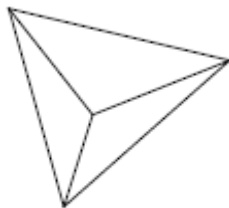


## **Pure octahedral case**

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.

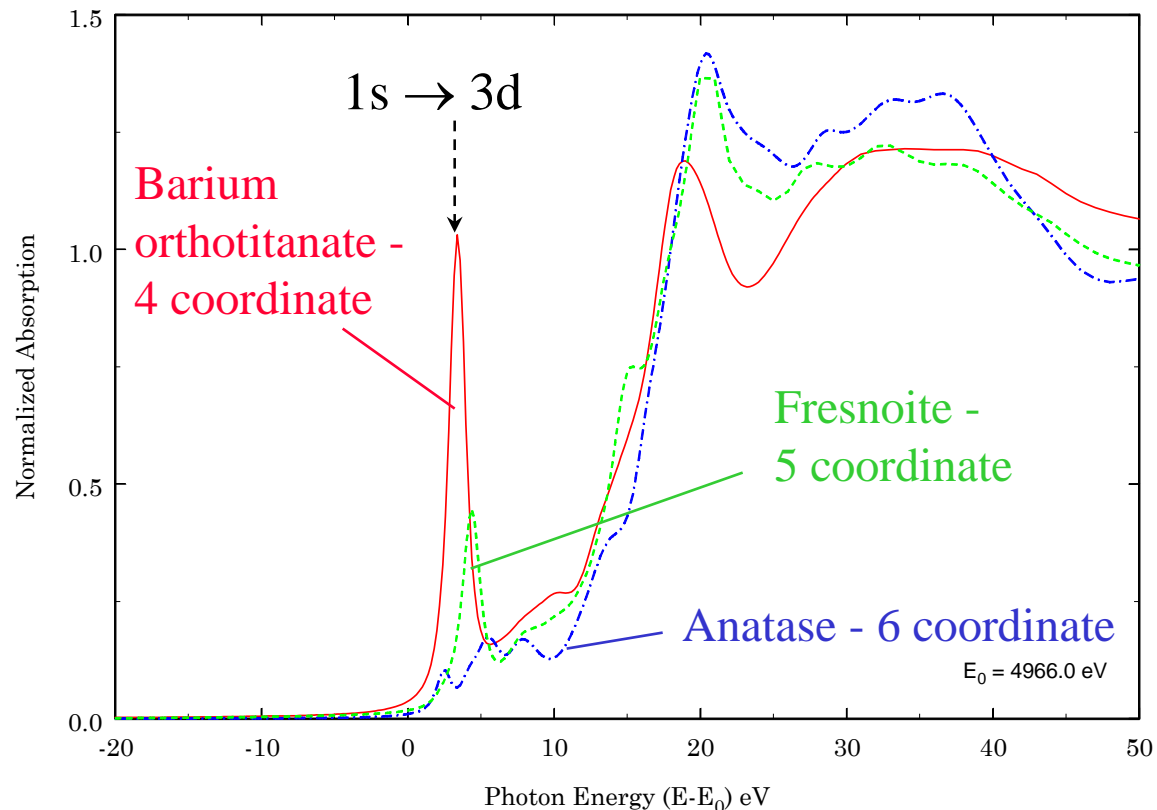


## **Pure tetrahedral**

Largest pre-edge intensity.

# Local Site Symmetry in Ti-containing Compounds

Ti K-edge XANES: Reference Compounds



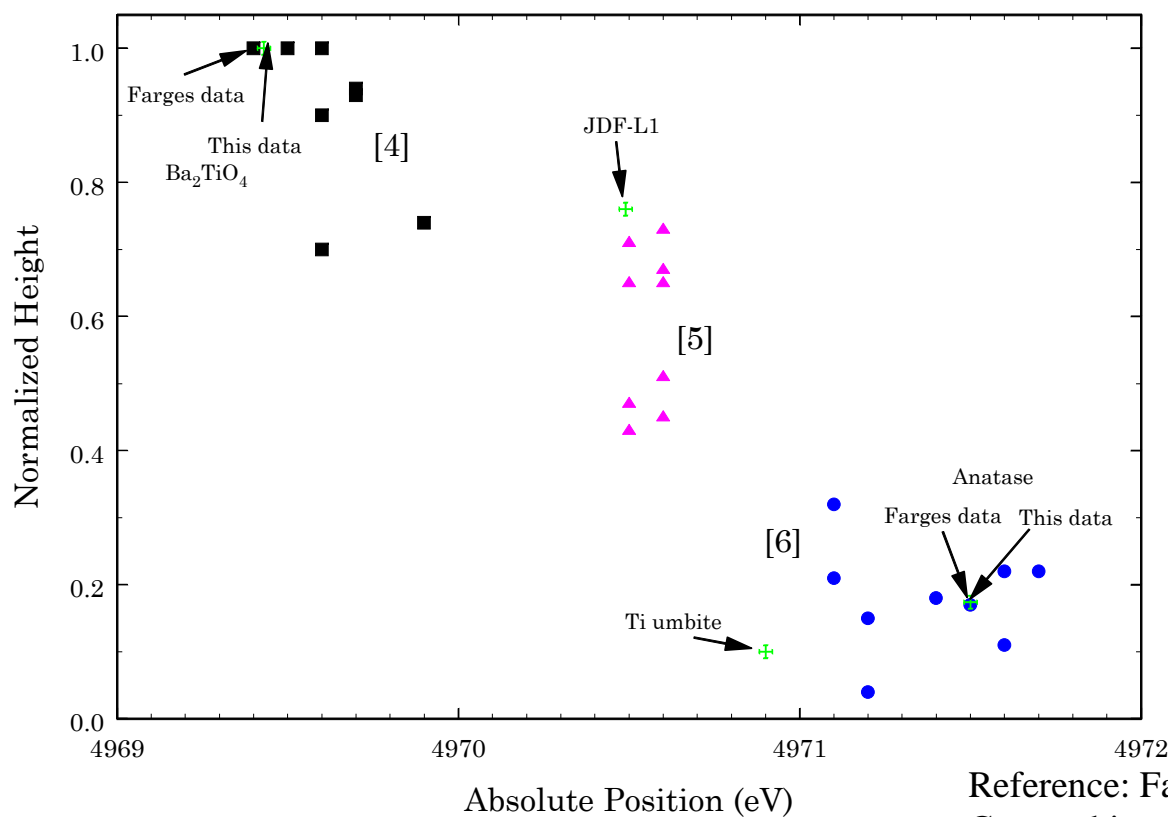
Ti\_refs1.axg

Anatase  
3d split by mixing with O2p into  $t_{2g}$  and  $e_g$  like orbitals.  
3<sup>rd</sup> peak is quadrupolar in nature

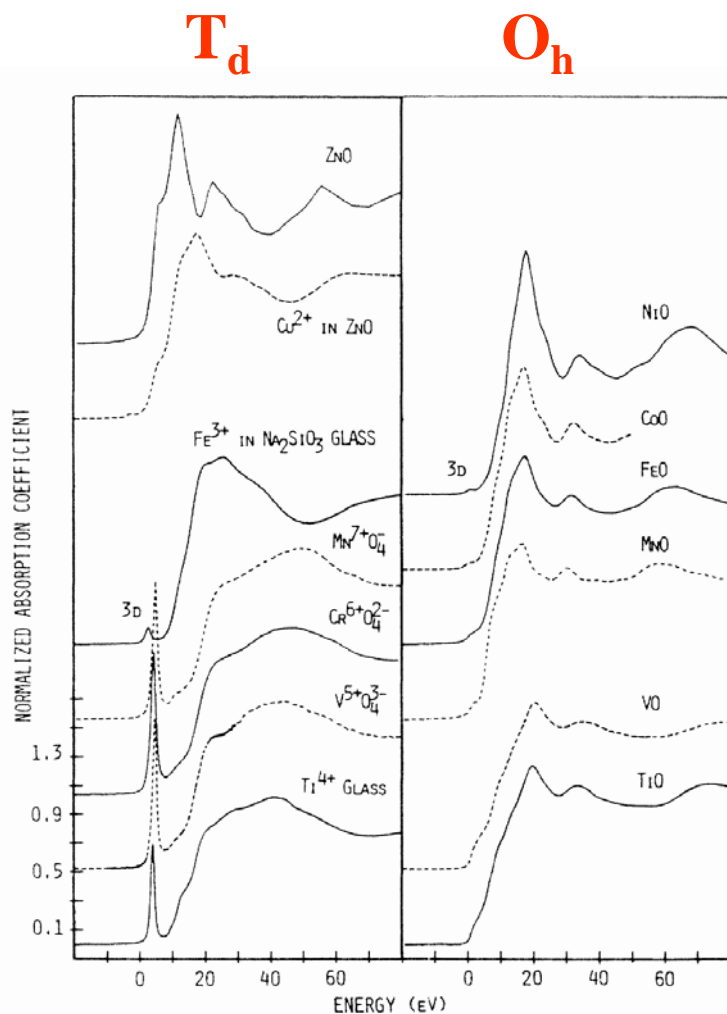
- Symmetry around absorbing atom strongly affects pre-edge transition: ability to differentiate 4, 5, 6-fold coordination.

# 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*

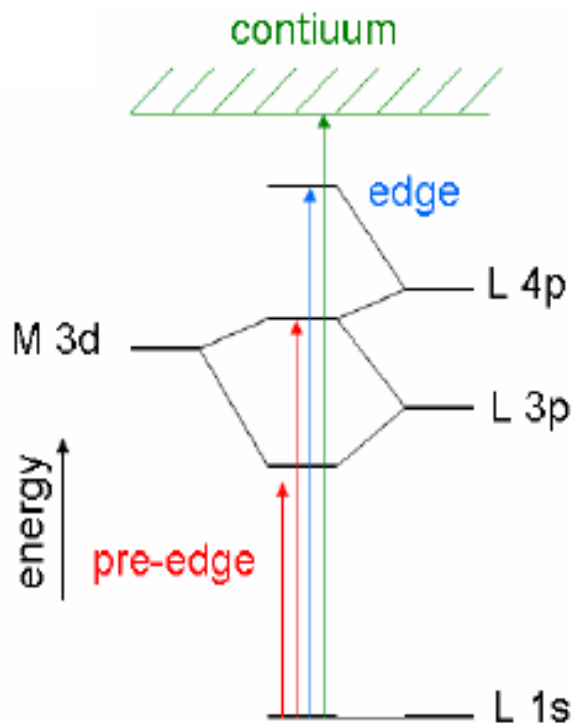


- For T<sub>d</sub> symmetry 1s to 3d pre-edge peak sharp and intense from Ti→Mn, decreases Fe → Cu, absent for Zn.
- Decrease in intensity due to progressive filling of the 3d band.
- O<sub>h</sub> symmetry shows only a small pre-edge peak throughout series.

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

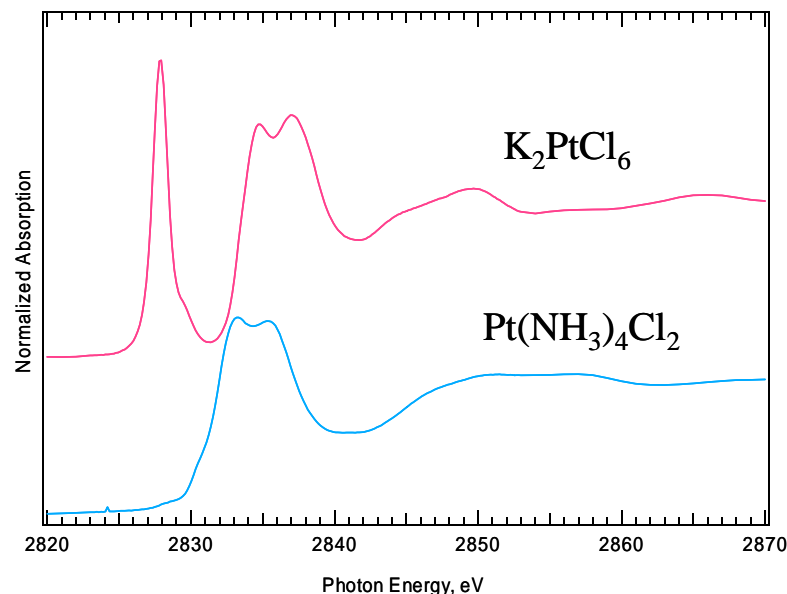
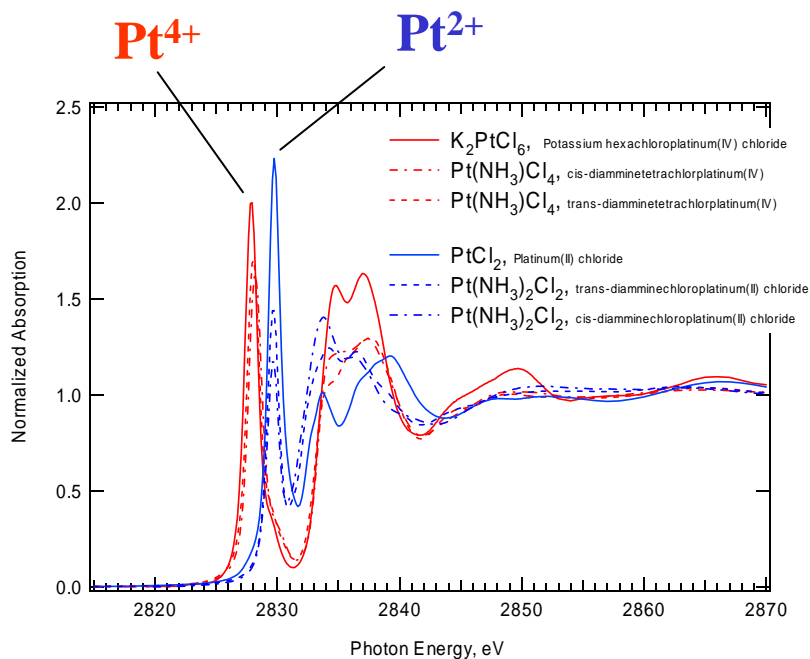
# *Ligand-Metal Binding from Ligand K-edge XANES*

- Provides direct experimental measurement of the ligand 3p character in the highest occupied molecular orbital (HOMO).
- Allows study of “spectator” ligand effects.



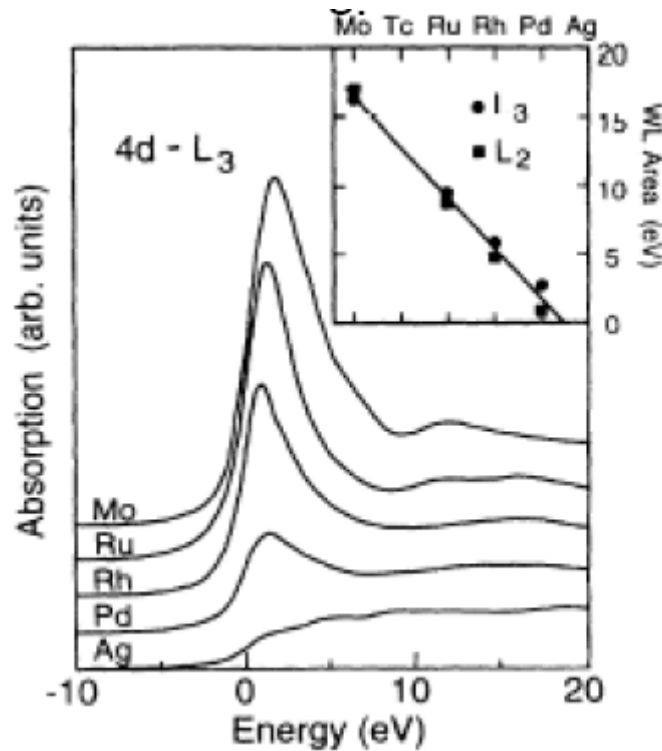


# Ligand-Metal Binding: Cl K-edge XANES



- 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  $Pt(NH_3)_3Cl_2$  there is no direct M-Cl bonding: Cl is a “spectator” ligand – so no pre-edge peak.

## “White line” Intensity of 4d Metals

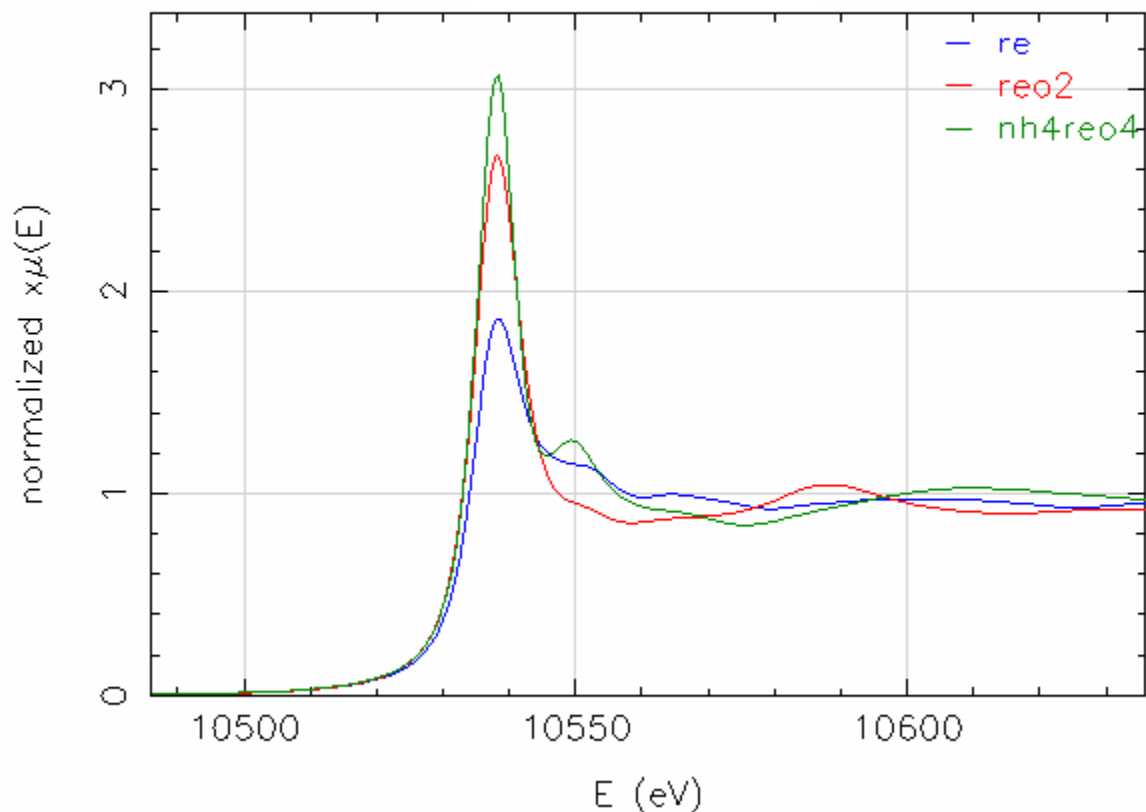


### L<sub>3</sub> edge XANES for 4d metals

- Linear correlation between white line area and number of 4d-holes for Mo to Ag
- 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.

# “White Line” Intensity: Oxides

Re L<sub>3</sub>-edge - Transition from 2p<sub>3/2</sub> to 5d states.



**Re metal (Re<sup>0</sup>) - 5d<sup>5</sup>**

**ReO<sub>2</sub> (Re<sup>4+</sup>) - 5d<sup>1</sup>**

**NH<sub>4</sub>ReO<sub>4</sub> (Re<sup>7+</sup>) - 5d<sup>0</sup>**

- Intensity of Re L<sub>3</sub> white line probes Re LDOS

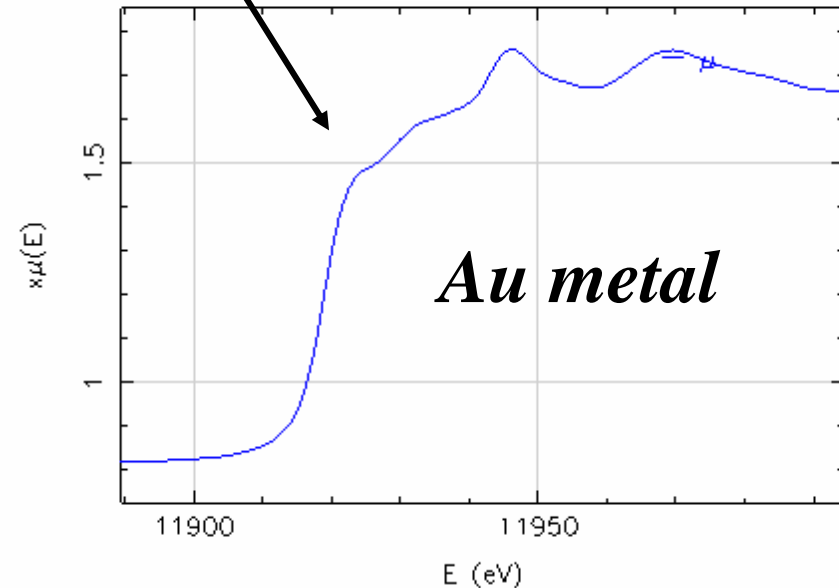
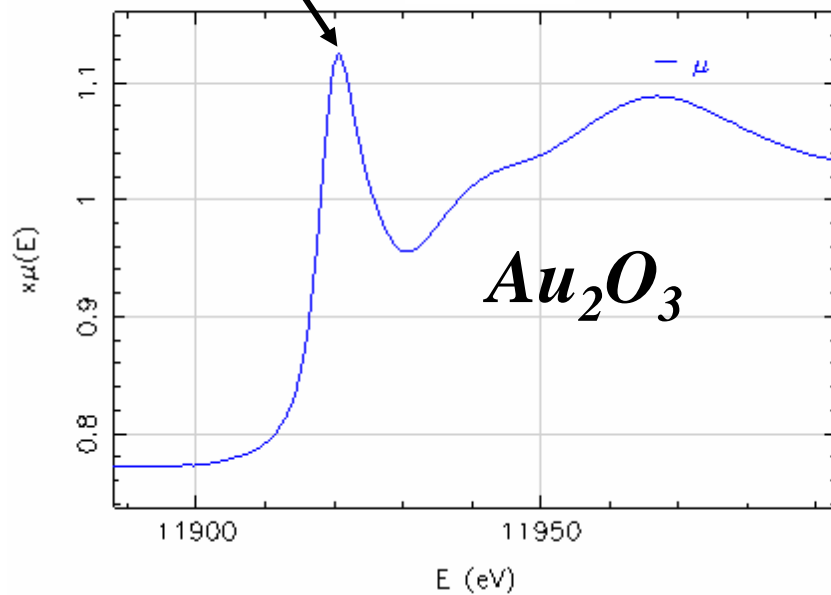
\*Spectra aligned in energy

# Metals & Oxides

## *Au L<sub>3</sub>-edge XANES*

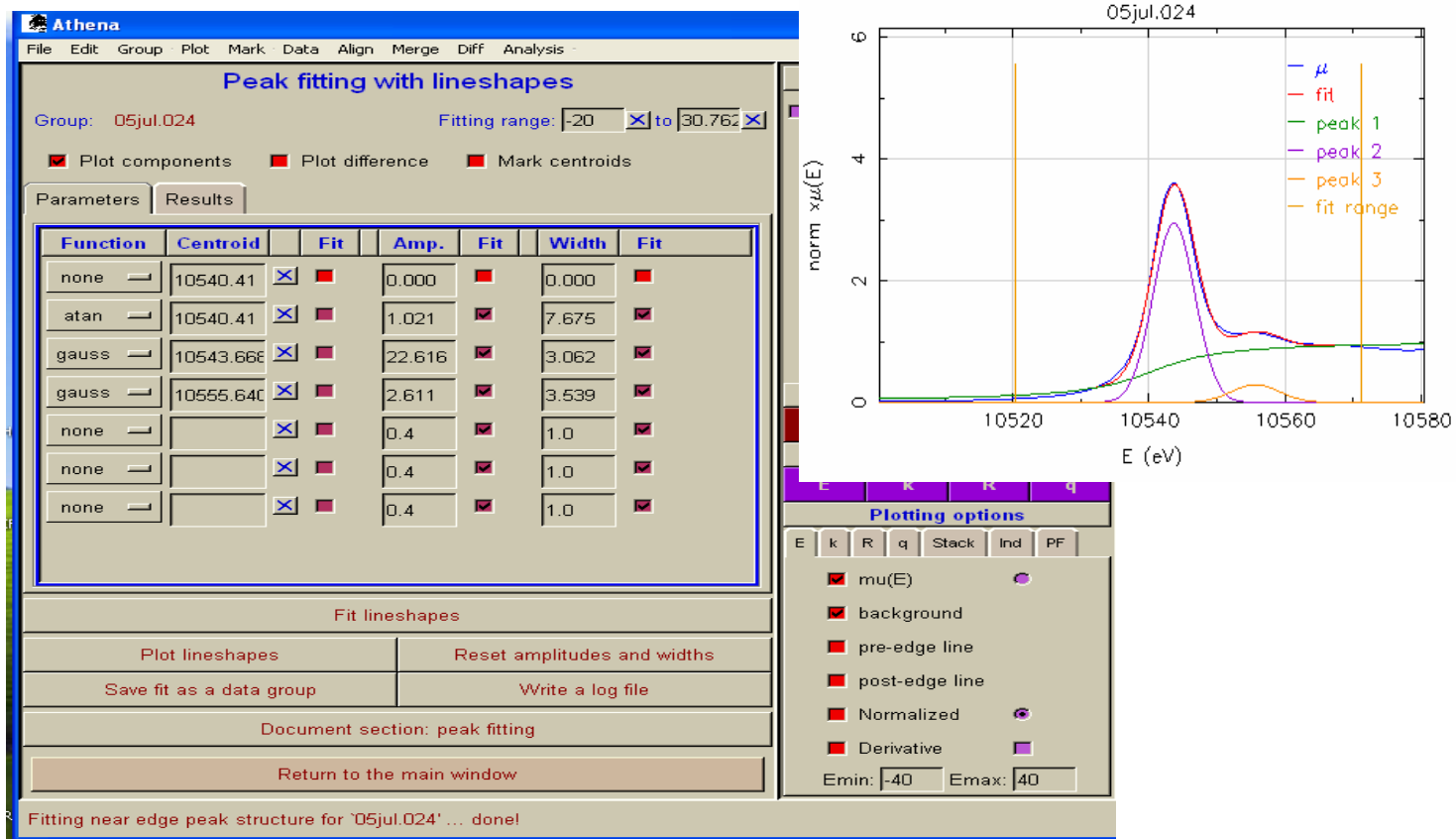
White line  
reflects holes in  
d-band

No white line



- Overall shape of spectrum also different.

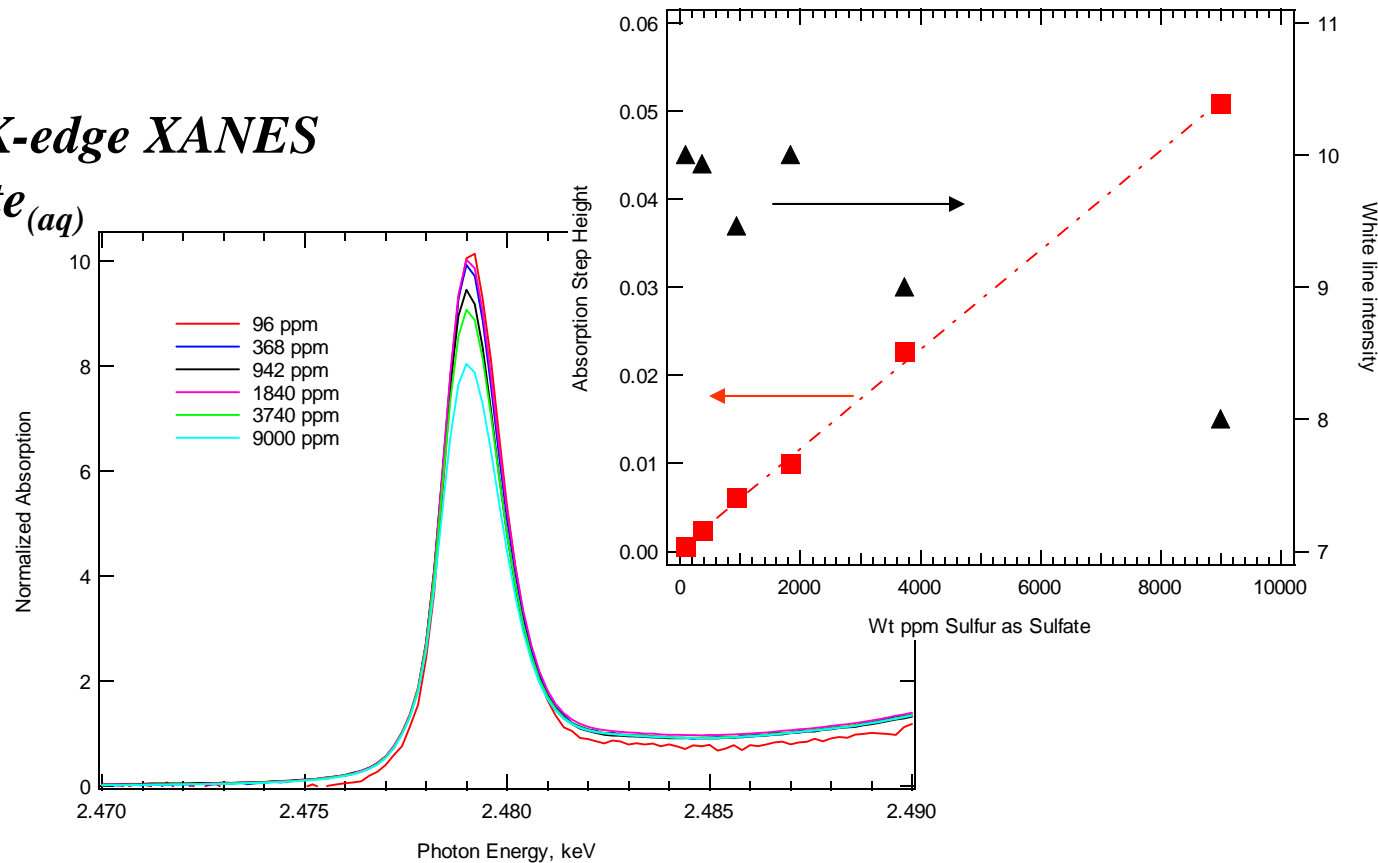
# XANES Peak Fitting in Athena



- Useful for quantification of areas, etc.

# “White Lines”: large change in absorption coefficient

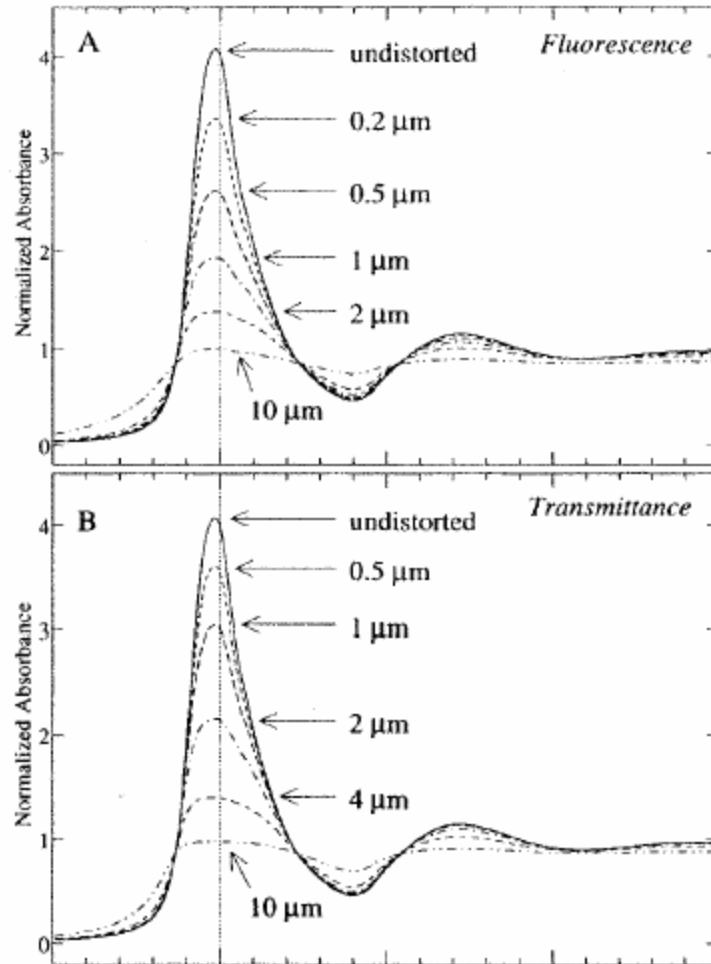
## Sulfur K-edge XANES of sulfate<sub>(aq)</sub>



- 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<sub>8</sub>



Pickering et al. Biochem 40 92001) 8138

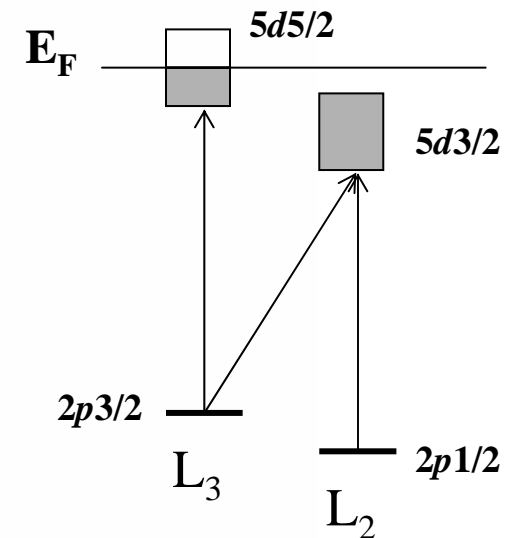
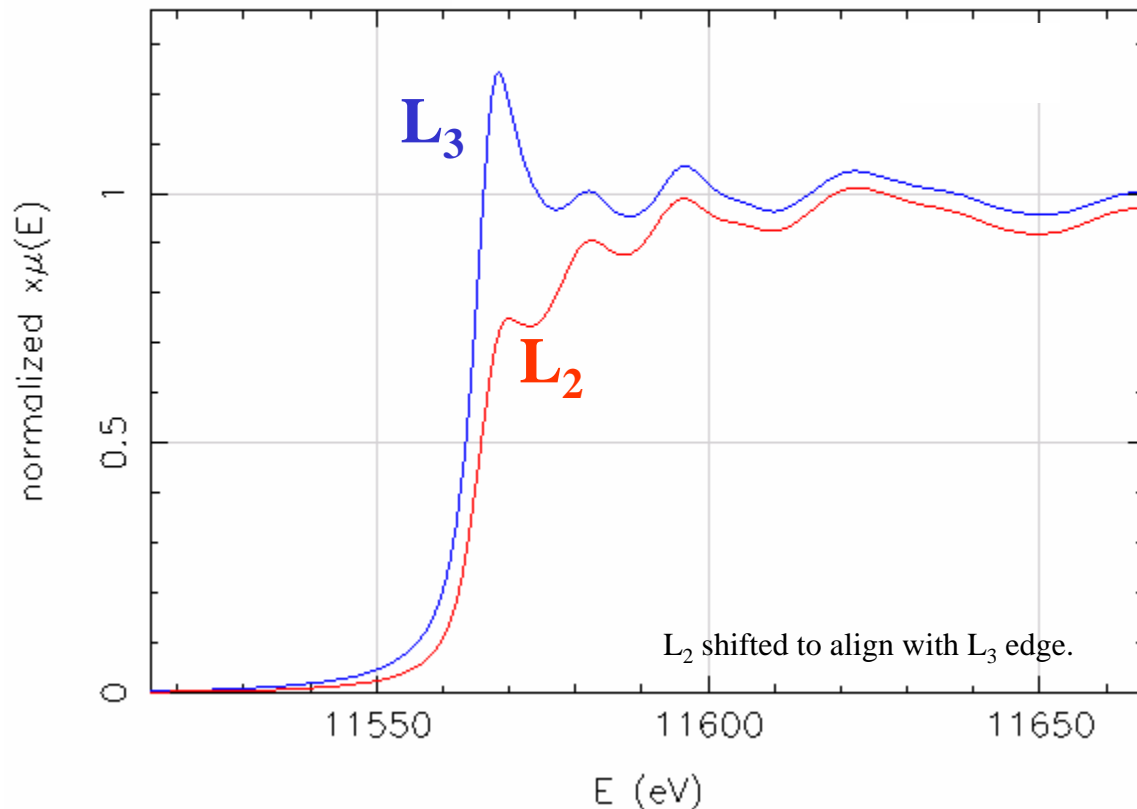
- Calculation of sulfur K-edge XANES (2.47 keV) for different spherical particles of sulfur.
- Severe distortion of the spectrum for particles 1 μm radius! One absorption length is ~ 2 μm.

*Quotation from a recent publication on sulfur XANES:*

*“Due to their relatively high sulfur concentrations, all standards were powdered and sieved to particles sizes  $\leq 10\mu\text{m}$  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.



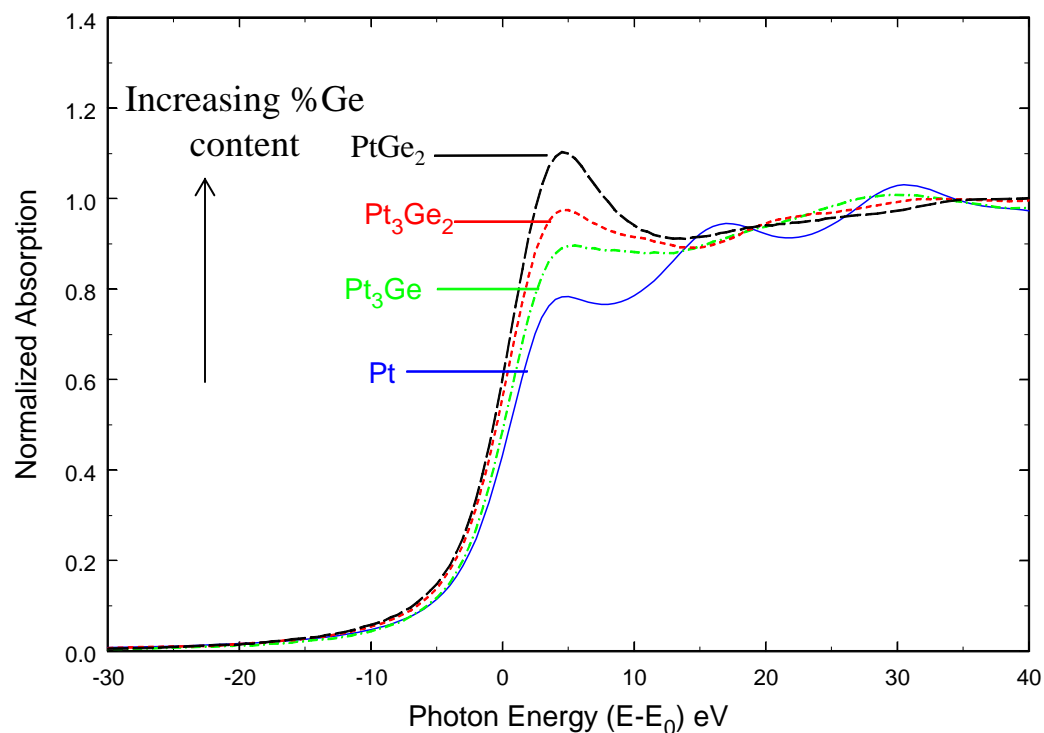
- Pt  $5d3/2$  filled, so no white line.

- Same  $l=2$  final density of states but because of selection rule,  $\Delta j = \pm 1$ , different total quantum number probed.
- Only  $j=3/2$  probed by  $L_2$ -edge, both  $j = 3/2$  and  $j = 5/2$  probed by  $L_3$ -edge.



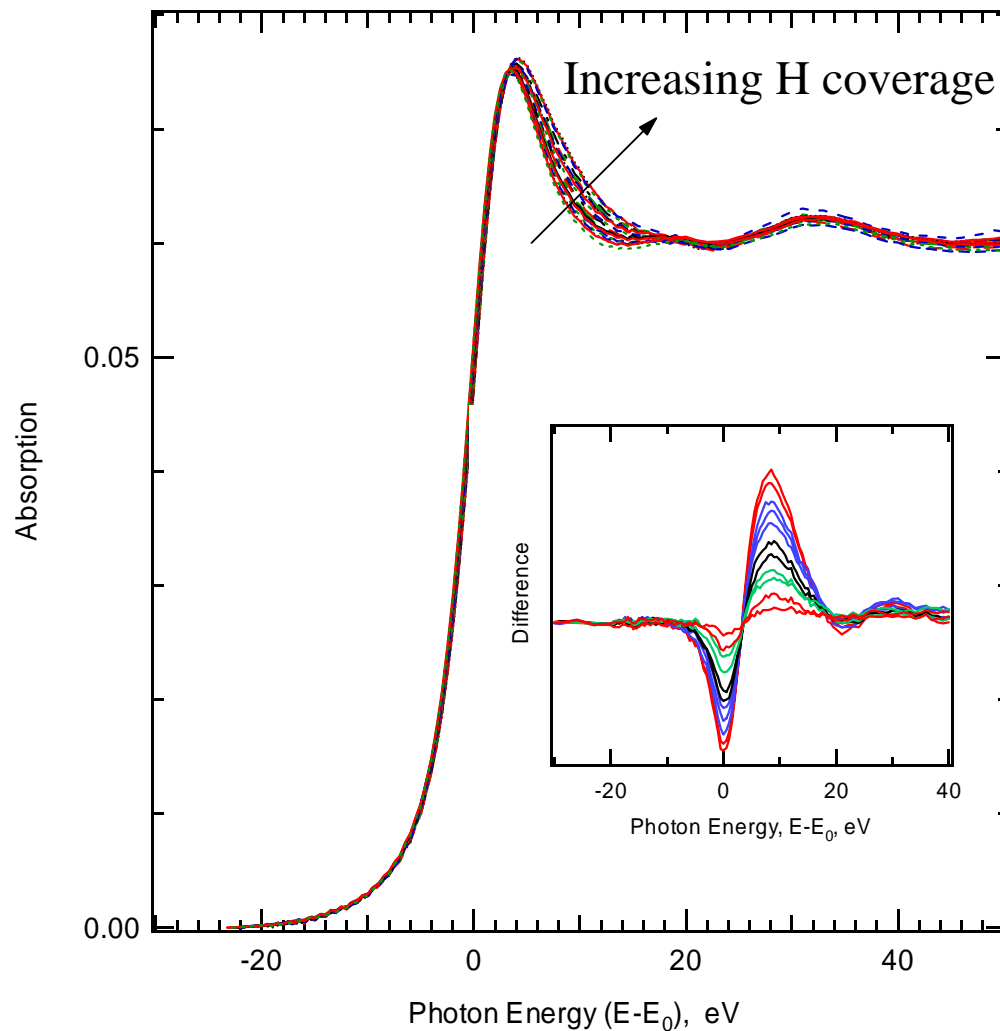
# XANES to Probe Charge Transfer in Alloys

## Platinum L<sub>2</sub>-edge XANES: Pt<sub>x</sub>Ge<sub>y</sub> Intermetallics



- 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.

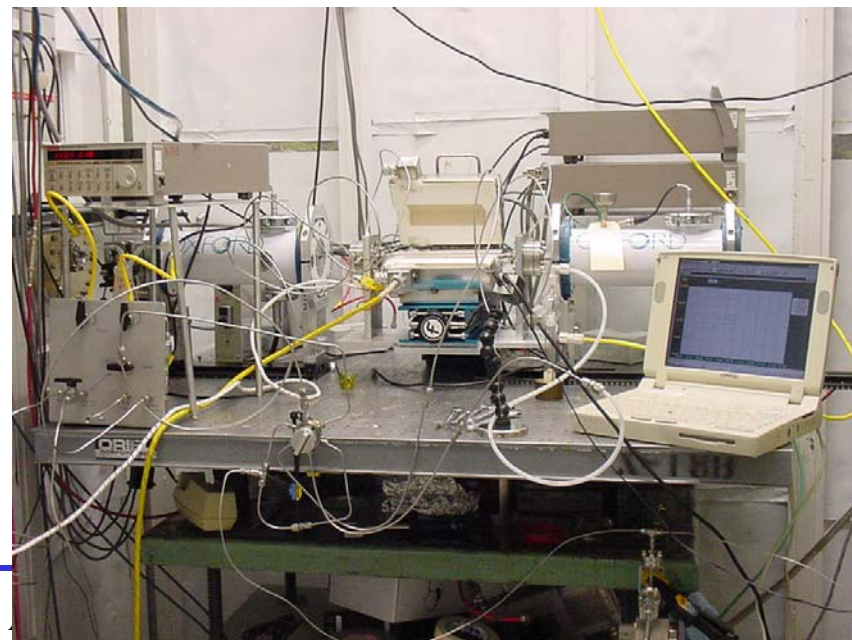
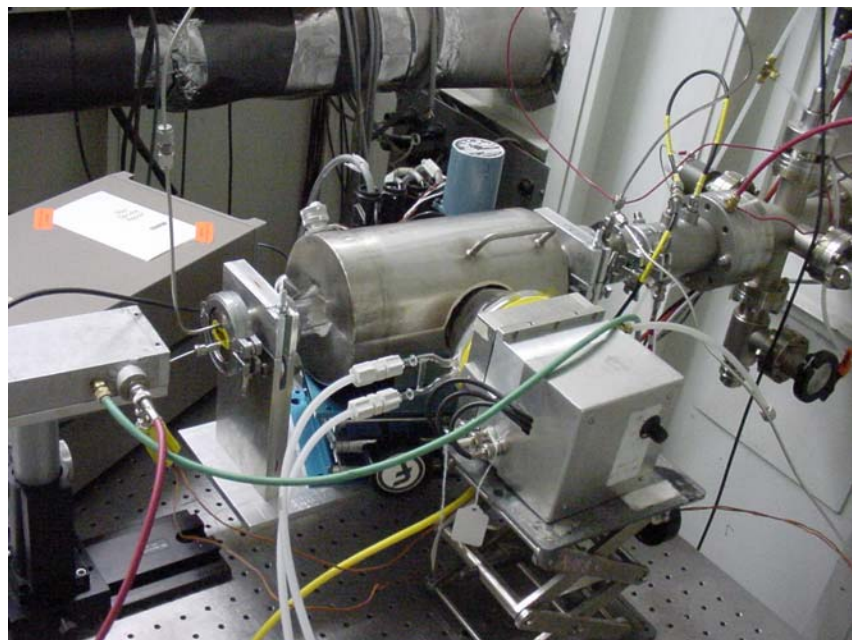
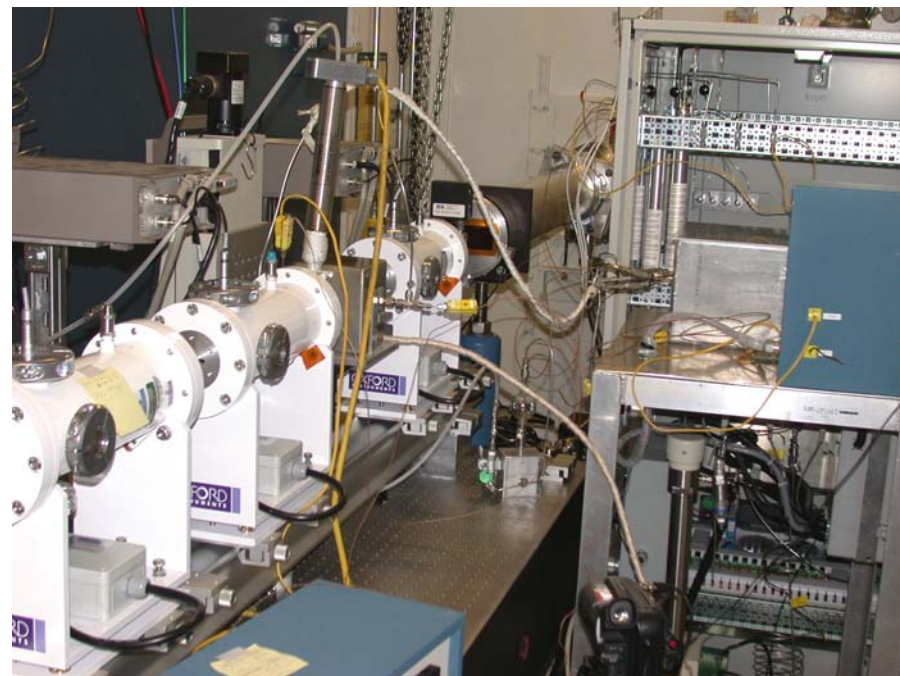
# Effect of Adsorbed Hydrogen on Pt $L_3$ XANES



## *10-15Å Pt clusters supported on $Al_2O_3$*

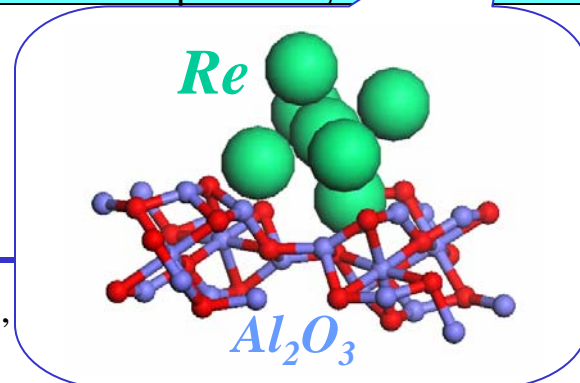
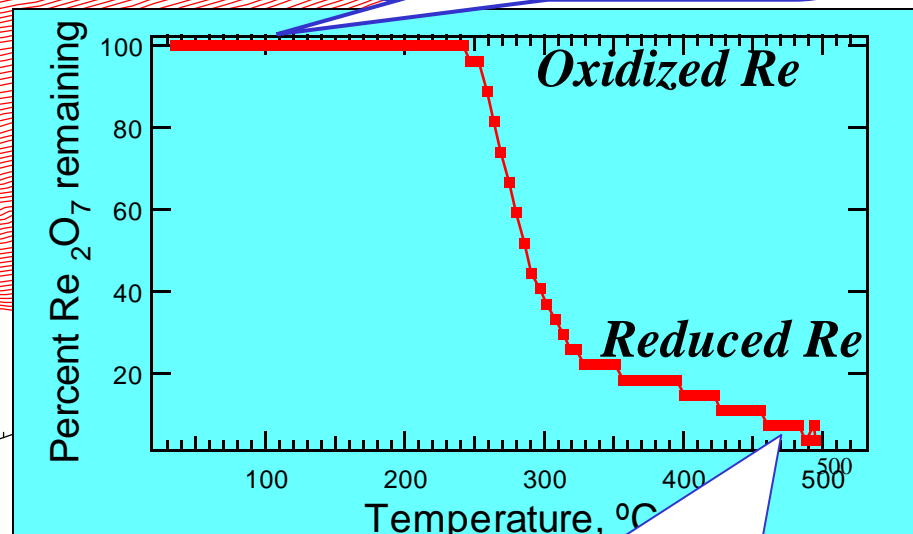
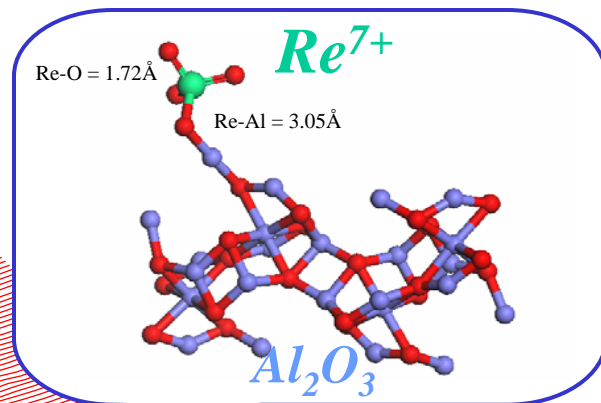
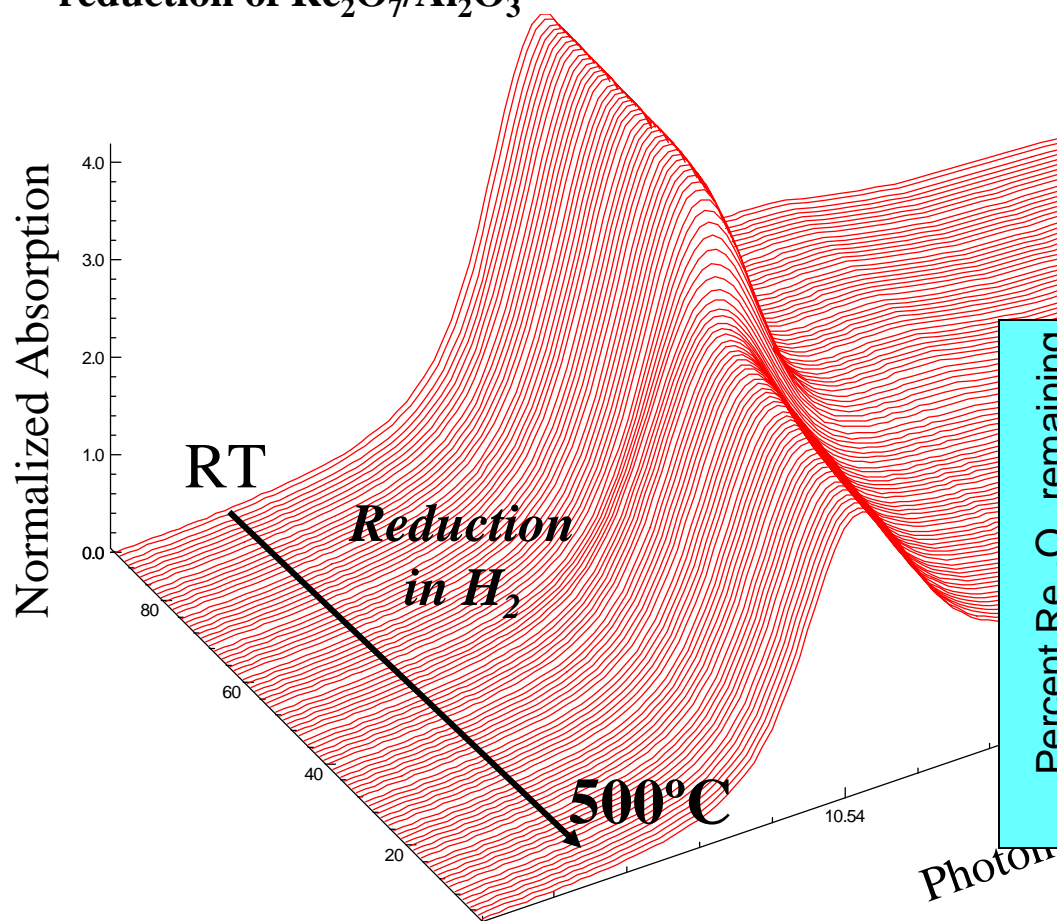
- White-line intensity decreases and spectra broaden to higher energies as H is added.
- Difference signal typically leads to broad structure  $\sim 8$  eV above absorption edge.
- Several different interpretations in the literature.

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



# Time Evolution of XANES: Kinetics

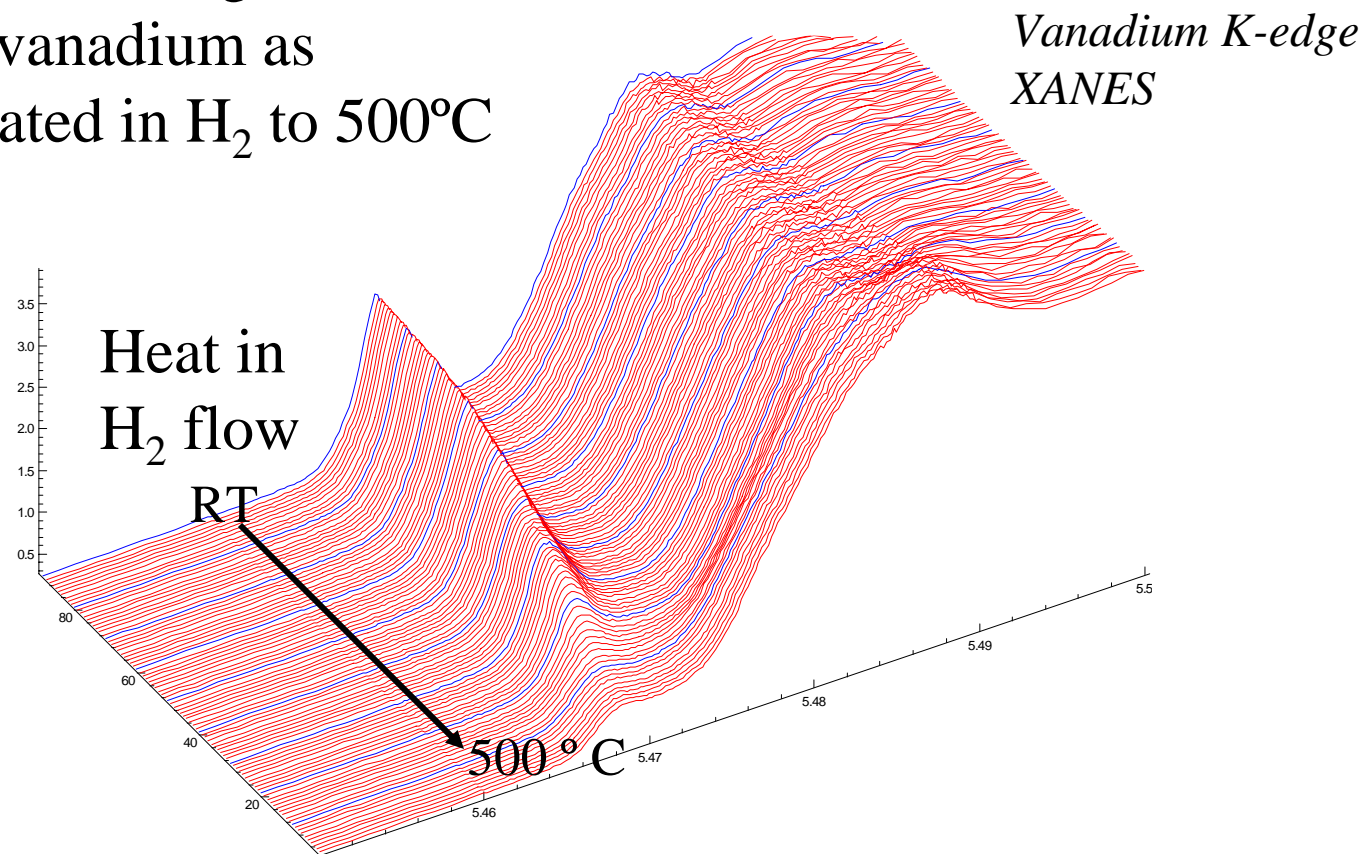
In situ temperature programmed reduction of  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$





# *Time Evolution of XANES: Kinetics*

TPR-XANES showing  
reduction of vanadium as  
catalyst is heated in H<sub>2</sub> to 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  $<1\mu\text{m}$  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

**Linear combination fitting**

Unknown: Unknown  
 Fitting range: -20 to 30  
 Fitting space:  norm(E)  deriv(E)  chi(k)

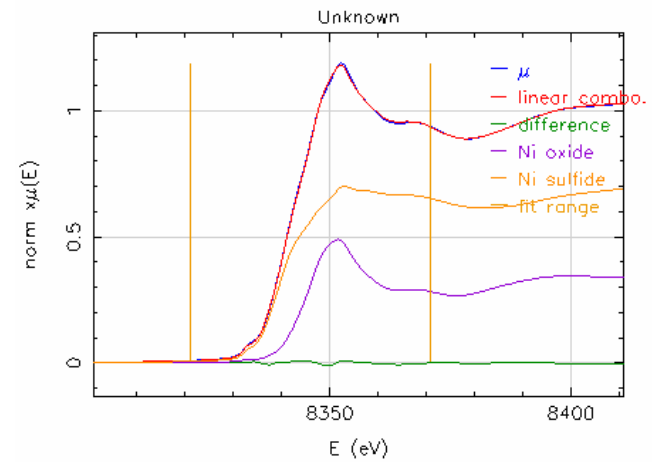
Standards	weight	e0	fit e0?
1 Ni oxide	0.326	0.000	<input checked="" type="checkbox"/>
2 Ni sulfide	0.674	0.000	<input checked="" type="checkbox"/>
3 None	0	0	<input type="checkbox"/>
4 None	0	0	<input type="checkbox"/>

Add a linear term after e0  
 Non-negative weights  
 Force weights to sum to 1

Buttons: Fit, Plot data and sum, Write a report, Save fit as a group, Reset

Data groups (modified): Ni oxide, Unknown, Ni sulfide, FY, Trans

Plotting options:  mu(E),  background,  pre-edge line,  post-edge line,  Normalized,  Derivative



**Linear combination fitting**

Unknown: Unknown  
 Fitting range: -20 to 30  
 Fitting space:  norm(E)  deriv(E)  chi(k)

Fit results:

```

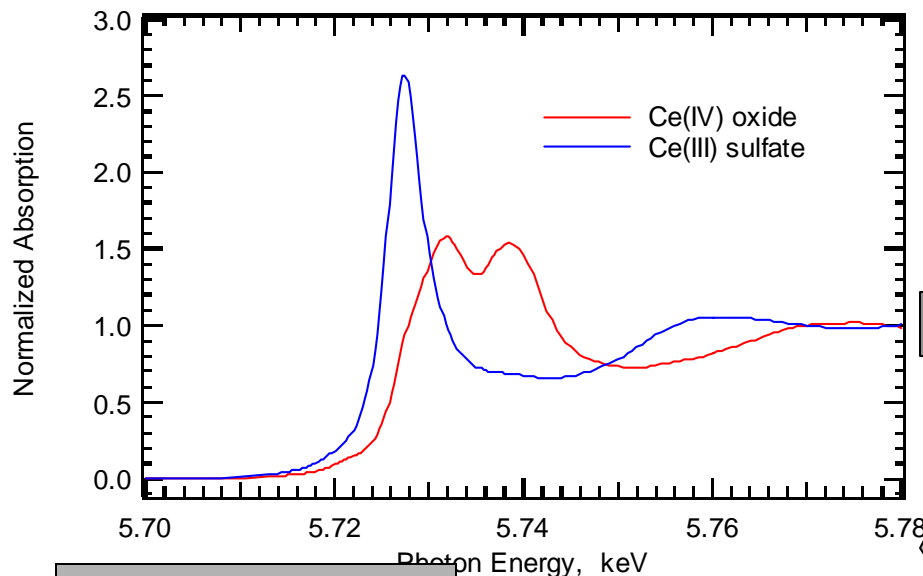
Fitting Unknown as norm(E) from -20.000 to 30.000
Fit included 99 data points and 1 variable
R-factor = 0.000036
chi-square = 0.00210
reduced chi-square = 0.0000210

group      weight
-----
Ni oxide   0.326(0.002)
Ni sulfide 0.674(0.002)

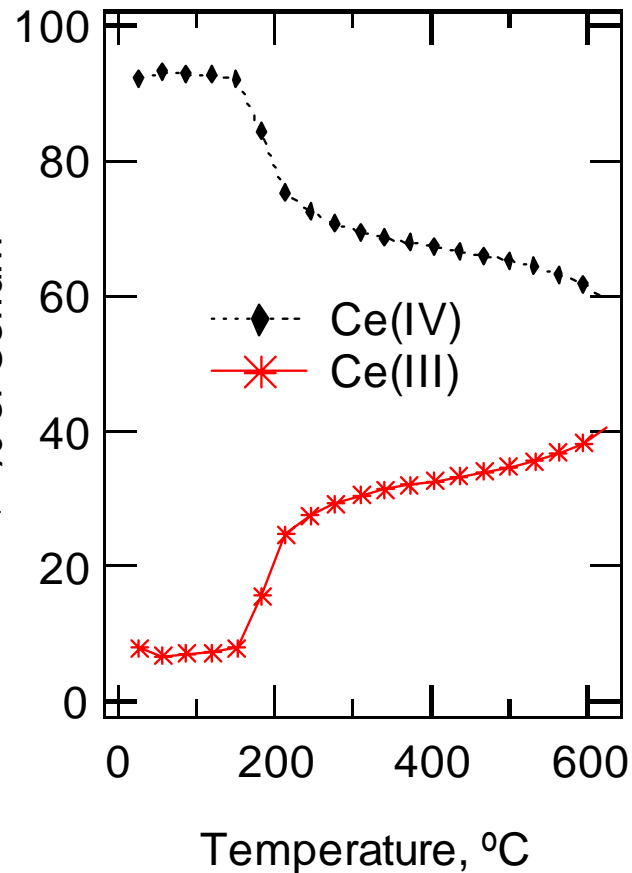
group      e0 shift
-----
Ni oxide   0.000(0.000)
Ni sulfide 0.000(0.000)
  
```

Buttons: Fit, Plot data and sum, Write a report, Save fit as a group, Reset

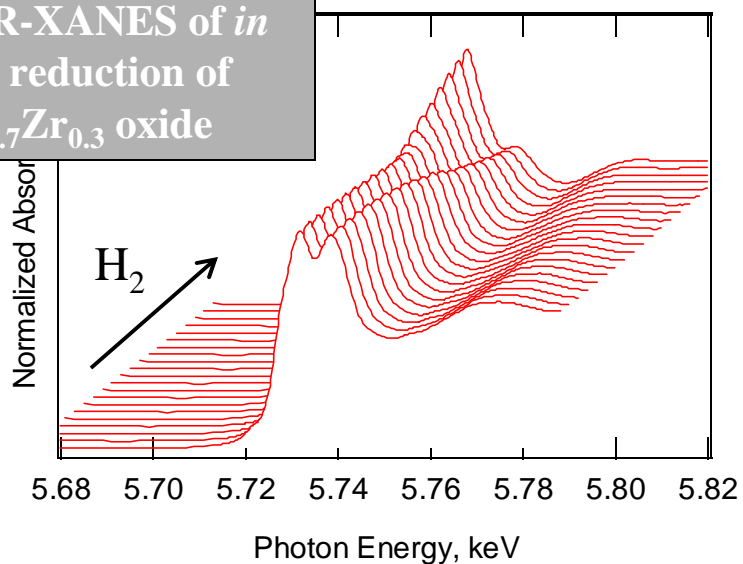
# Linear Combination Fitting



Fit experimental data to linear combination of known reference compounds



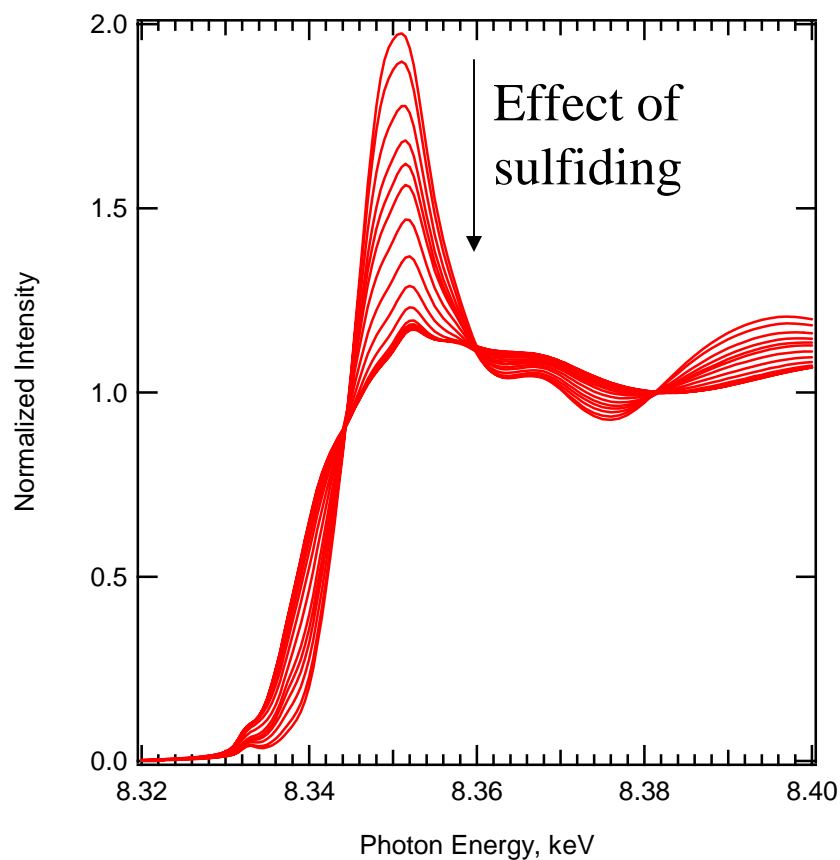
TPR-XANES of *in situ* reduction of  $\text{Ce}_{0.7}\text{Zr}_{0.3}$  oxide



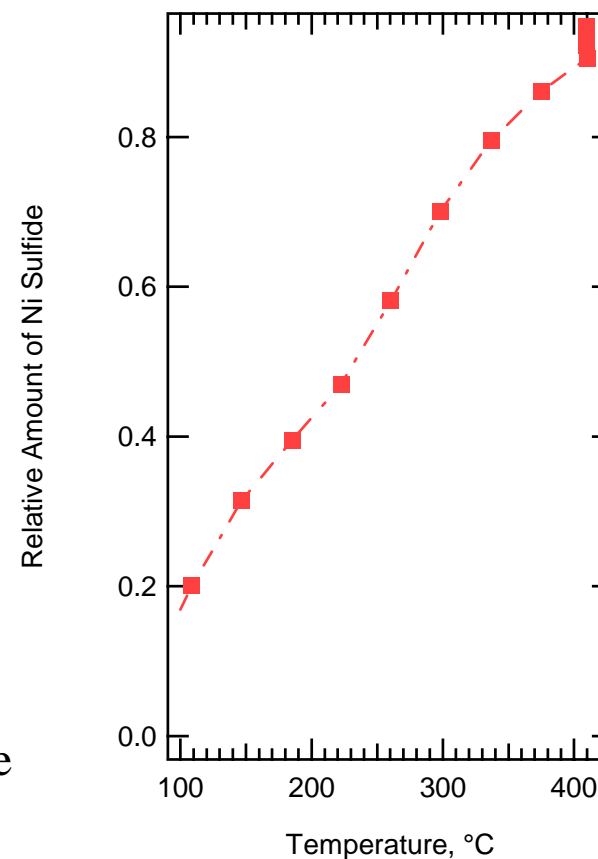
LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature

# Linear Combination Fitting

Ni K-edge XANES of in situ sulfiding of a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst

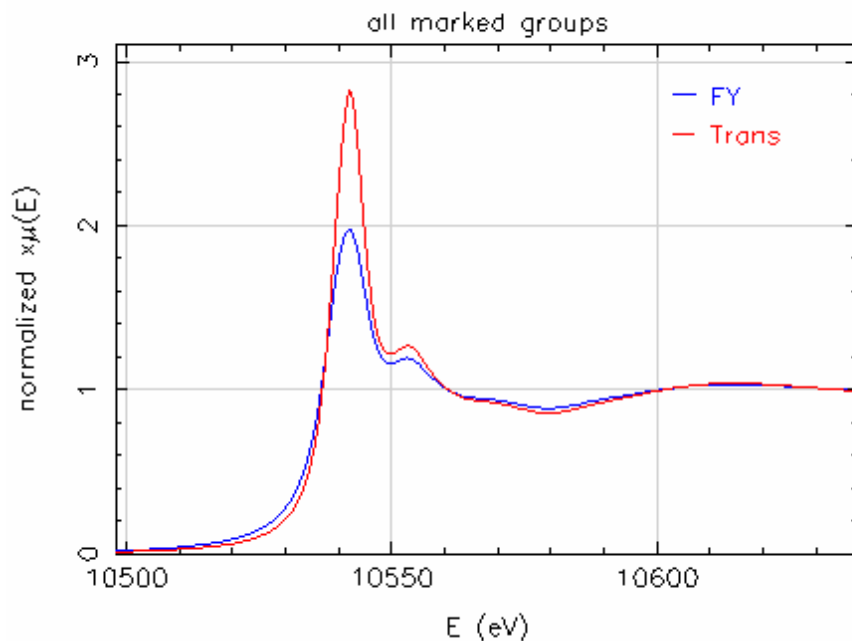


LC-XANES fit to determine amount of oxidized and sulfided Ni present as function of temperature/time



# 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<sub>3</sub>-edge XANES  
spectrum of bulk (NH<sub>4</sub>)ReO<sub>4</sub>*

*White line of spectrum  
collected in  
fluorescence severely  
attenuated.*

# *Principal Component Analysis*

- Used since 1970's in other chemical spectroscopy<sup>†</sup>. 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...

<sup>†</sup>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.
- 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\*.

\*"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<sup>5+</sup> 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”).**

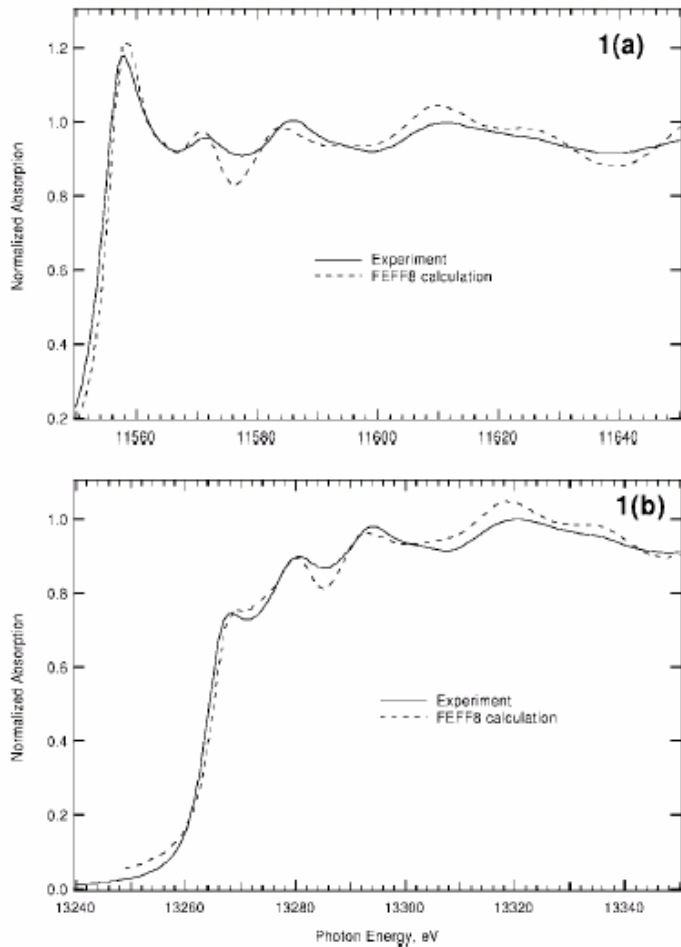


# *Feff8.1 and XANES*

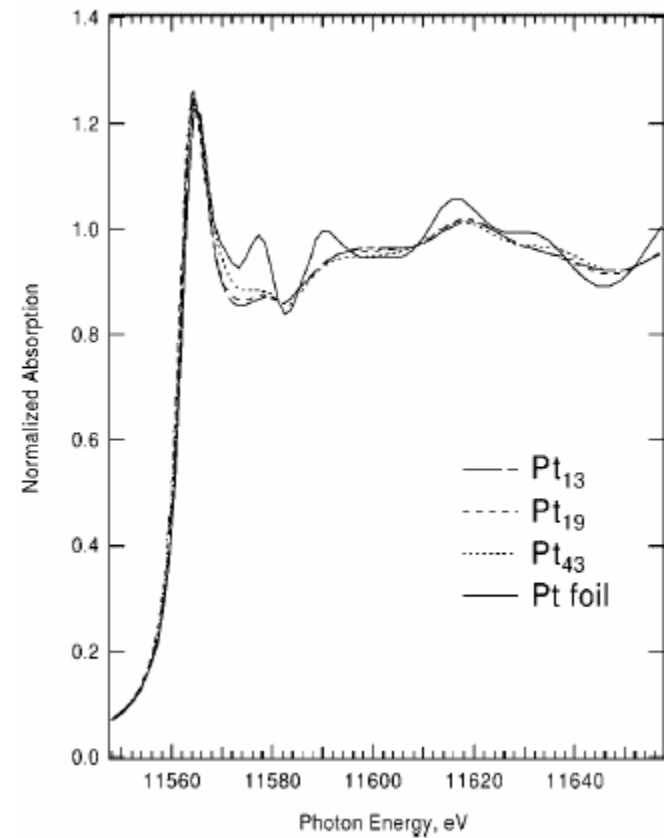
- Dramatic progress in past decade both in theory and *ab initio* calculations.
- Significant progress has been made in understanding XANES.
- Quantitative theory central to quantitative interpretation of XAFS spectra in terms of local geometric and electronic structure.
- For “experts” only at this time.

# *Feff8.1 and XANES: Pt L-edges*

Feff reproduces differences in white line at Pt L<sub>3,2</sub>-edges



Pt L<sub>3</sub>-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.....