XANES Measurements and Interpretation

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Acronyms

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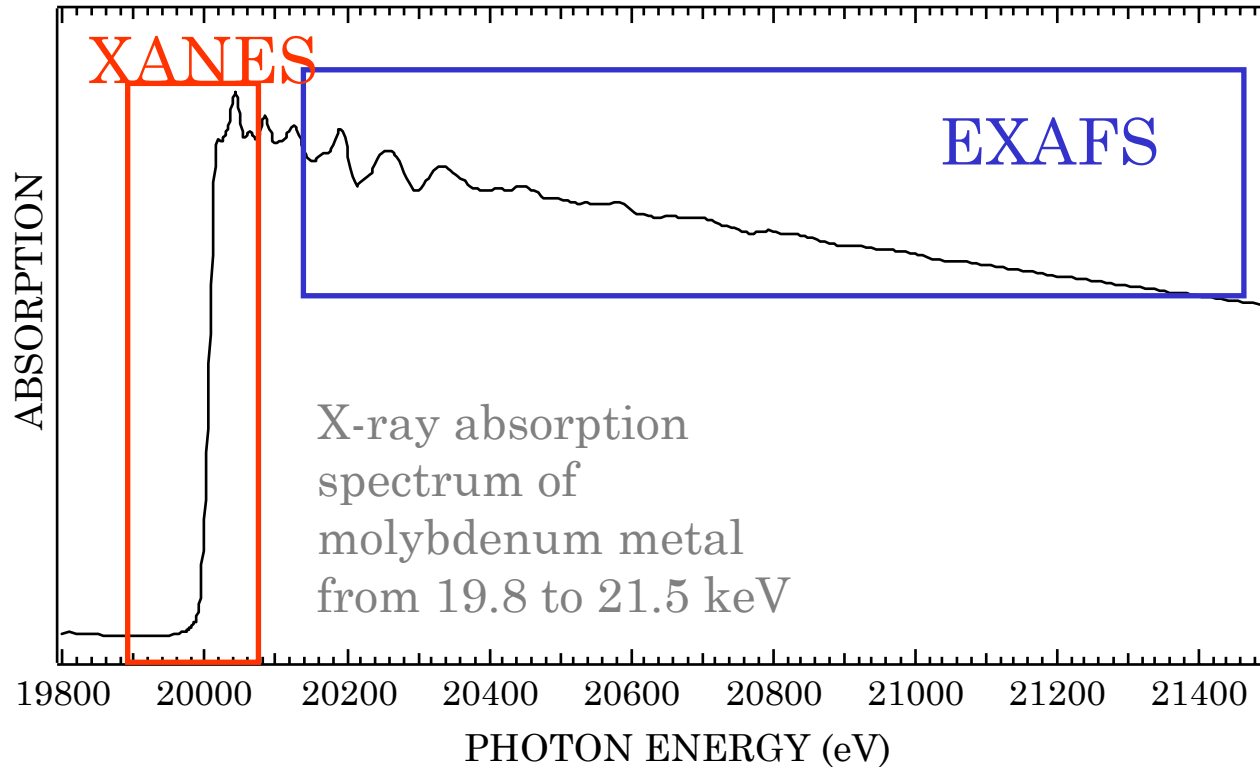
- **X**-ray **A**bsorption **N**ear **E**dge **S**tructure

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...
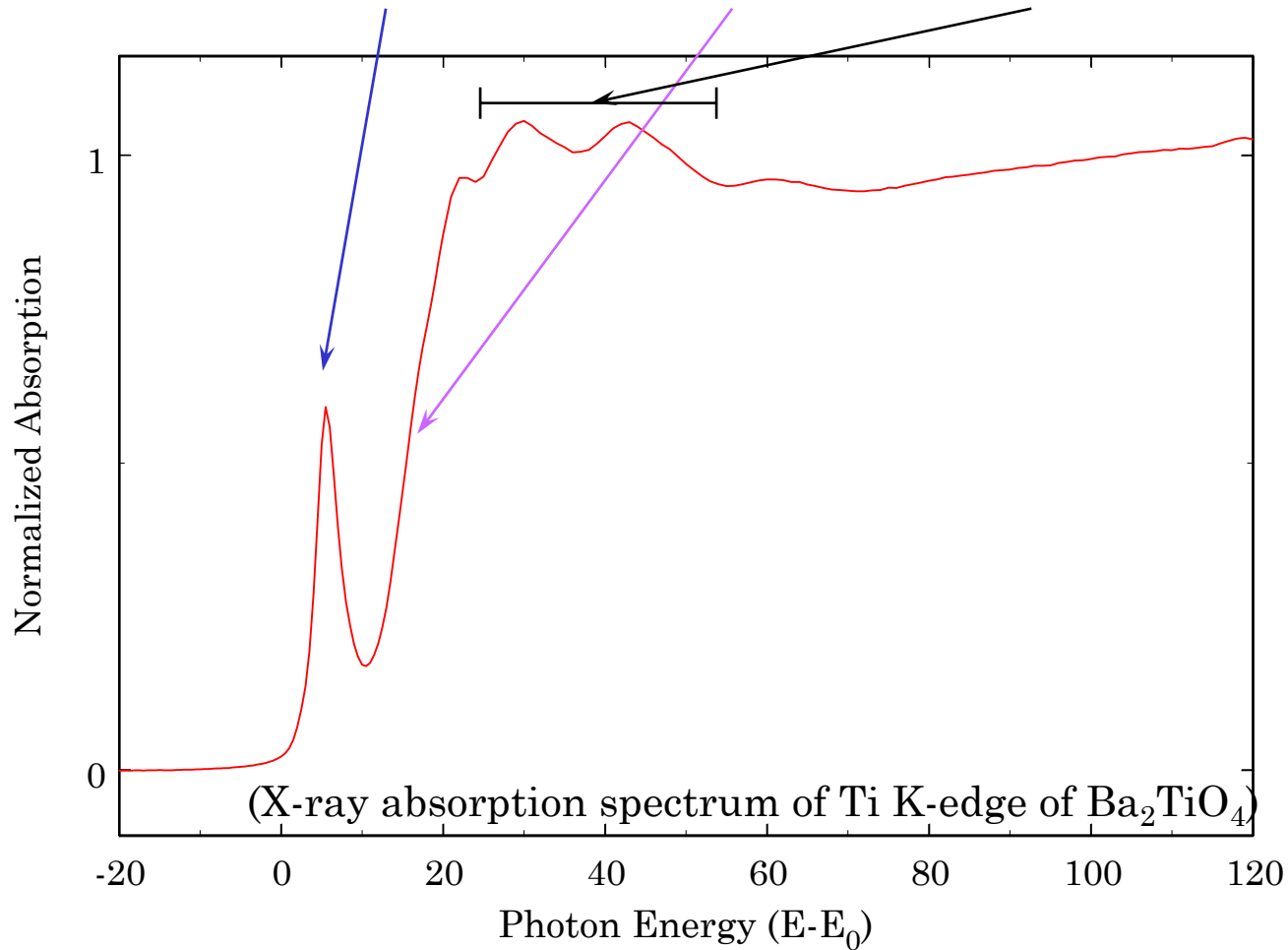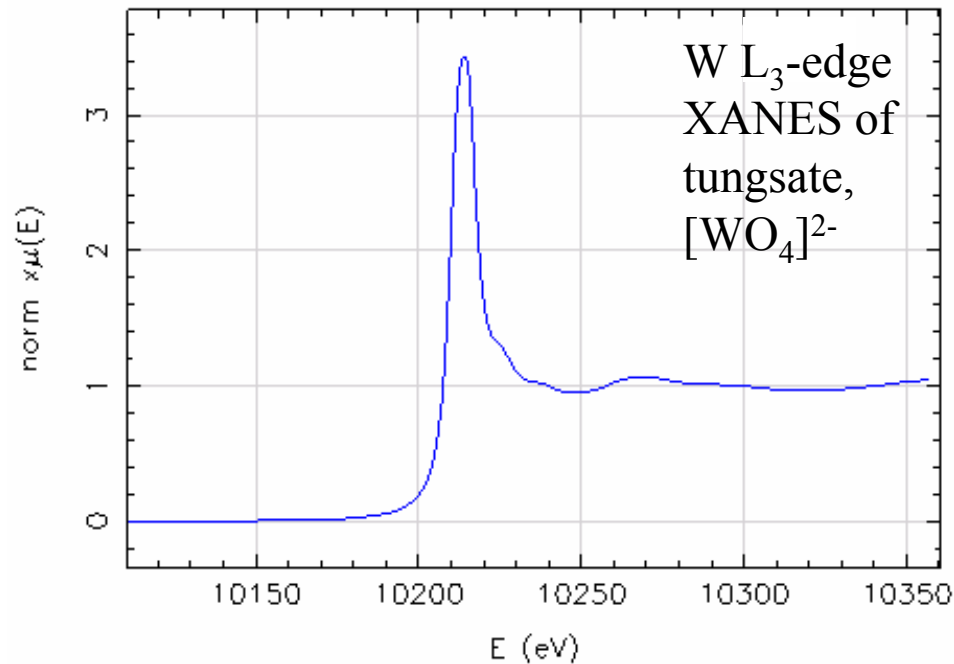
What Is XANES?

XANES

EXAFS

ABSORPTION

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

PHOTON ENERGY (eV)

- **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 Ba_2TiO_4)
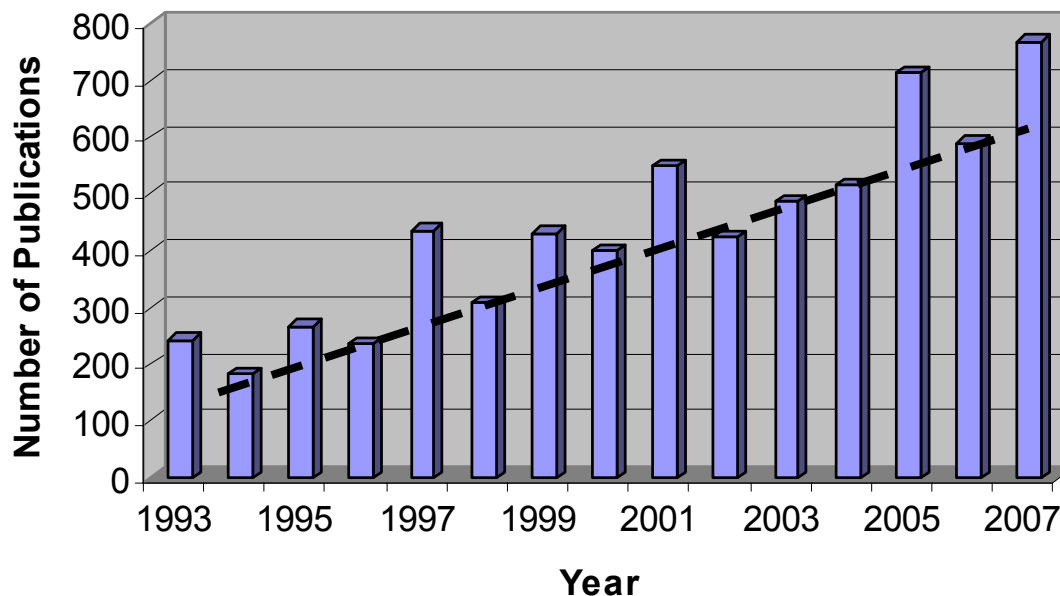
"White line"

W L_3-edge XANES of tungsate, $[WO_4]^{2-}$

- 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

- Increasing number of publications per year.

Representative Publications (2007)

- **Microstructure and ion exchange properties for nanotubular titanate,** Kubo, T. et al.,   Journal of Ion Exchange (2007), 18(4), 310-315.

- **New 100-Hz repetition rate soft x-ray laser plasma source for ultrafast XANES applications,** Fourmaux, S. et al., Proceedings of SPIE (2007), 6703(Ultrafast X-Ray Sources and Detectors), 67030D-67030D-9.

- **Coordination of Sr and Mg in calcite and aragonite,** Finch, A. et al., Mineralogical Magazine (2007), 71(5), 539-552.

- **In situ imaging of organic sulfur in 700-800 My-old Neoproterozoic microfossils using X-ray spectromicroscopy at the S K-edge,** Lemelle, L., et al., Organic Geochemistry (2007), Volume Date 2008, 39(2), 188-202.

- **Real-time observation of platinum redispersion on ceria-based oxide by in-situ Turbo-XAS,** Nagai, Y. et al., Studies in Surface Science and Catalysis (2007), 172(Science and Technology in Catalysis 2006), 623-624.
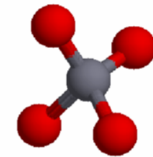
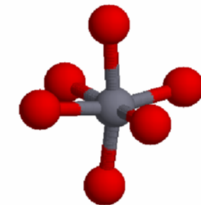# *Why Are We Interested In XANES? Local Coordination Environment*
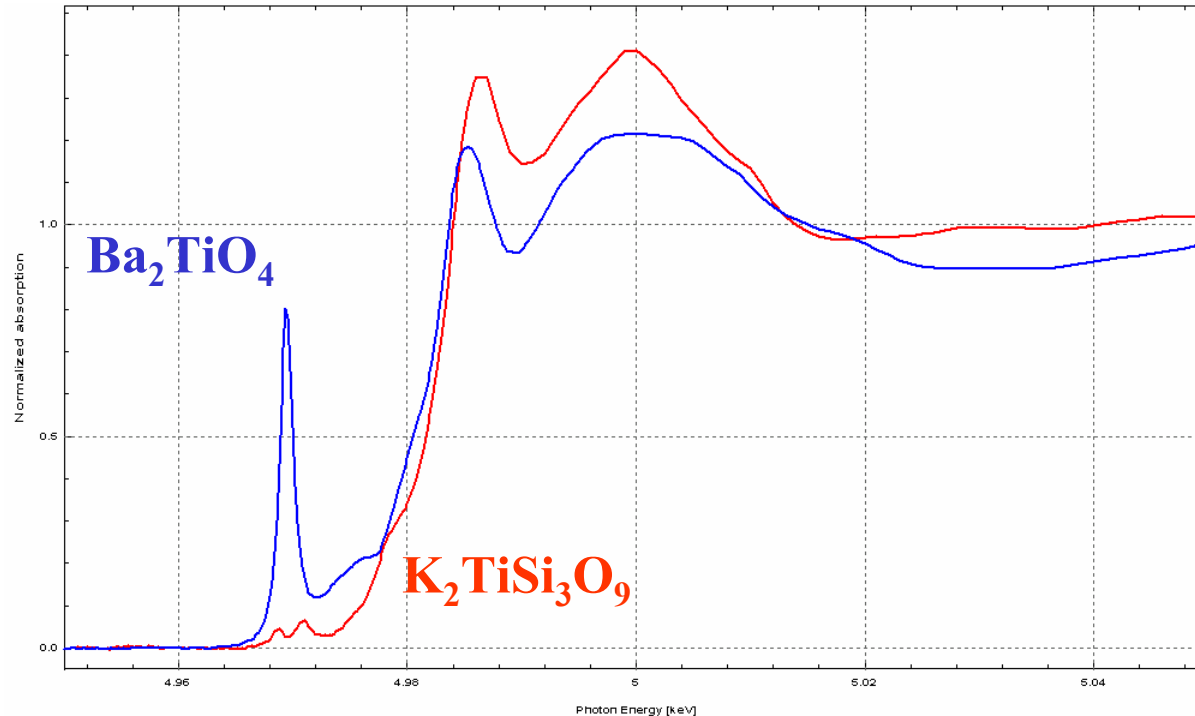
Both Ti^{4+}
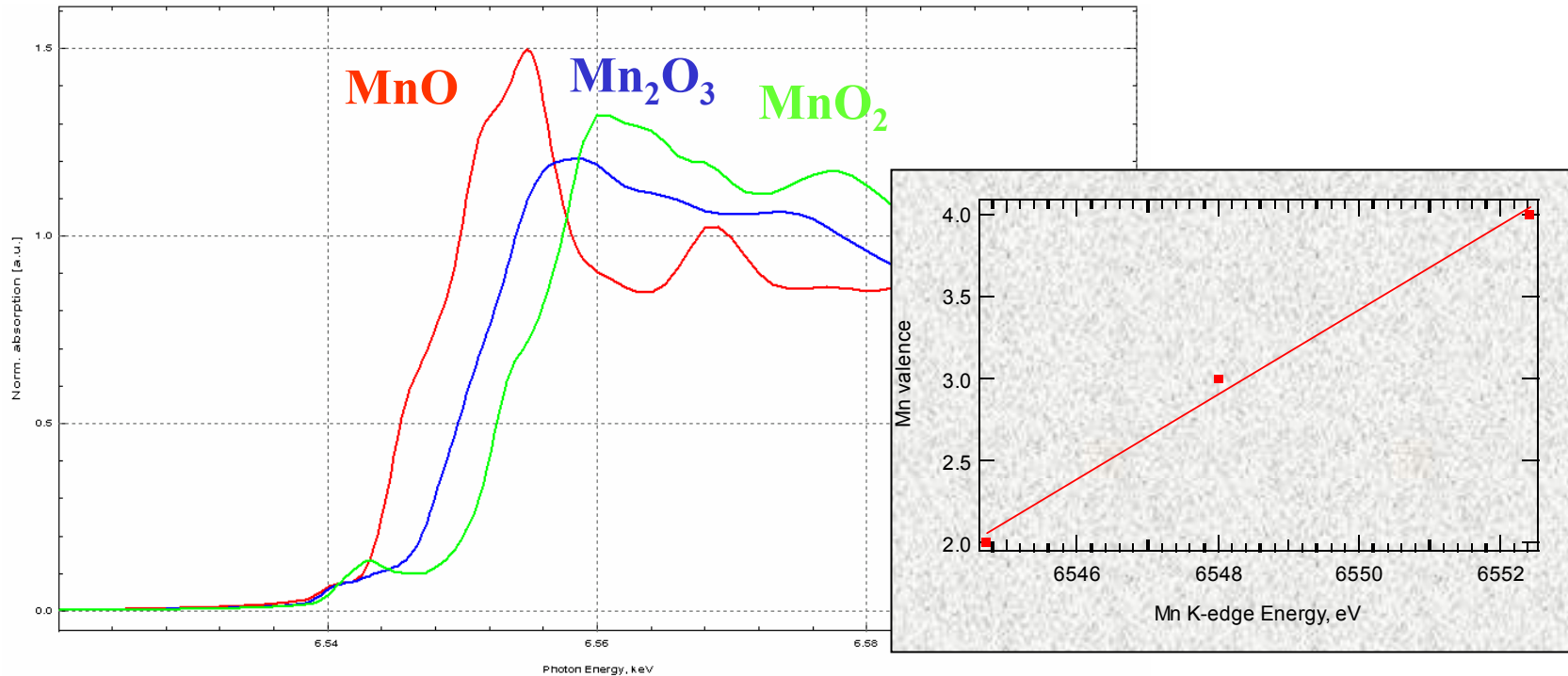
Ba$_2$TiO$_4$

K$_2$TiSi$_3$O$_9$

- 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 unoccupied electronic states.

- Dipole selection rules apply*: Δl *(orbital angular momentum)* $= \pm 1$, Δj (total) $= \pm 1$.

- Primary transition will be:

  - s ($l=0$) $\rightarrow$ p ($l=1$) for K ($1s$ core electron) and L_1 ($2s$ core electron initial state) edges

  - *p ($l=1$) $\rightarrow$ d ($l=2$)* 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 formal EXAFS equation breaks down at low-k, which complicates XANES interpretation.

- **It is not straightforward to calculate the 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 unoccupied 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 (Disorder, Debye-Waller-like term), so spectra can be recorded at reaction temperature (*in situ*):

  - $\text{Exp}(-2k^2\sigma^2) = \exp(-2(2.56)^2 \times 0.005) \sim 1$

  - 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.

$k = 2.56 = 25 \text{ eV}$

XANES Data Collection

- Data collection for XANES no different to EXAFS but need to think about:
  - energy resolution
  - number of data points
- If trying to determine the edge position to 0.1 eV, then don't use step size of 1 eV!
- Energy resolution determined by the energy bandpass of the monochromator: this should be matched to at least the core-hole lifetime of the transition of interest – either by white beam slits or by a collimating mirror.

XANES Data Collection

- Comparison of pre-edge peak at Co K-edge: 0.1 eV/point vs 0.5 eV/point

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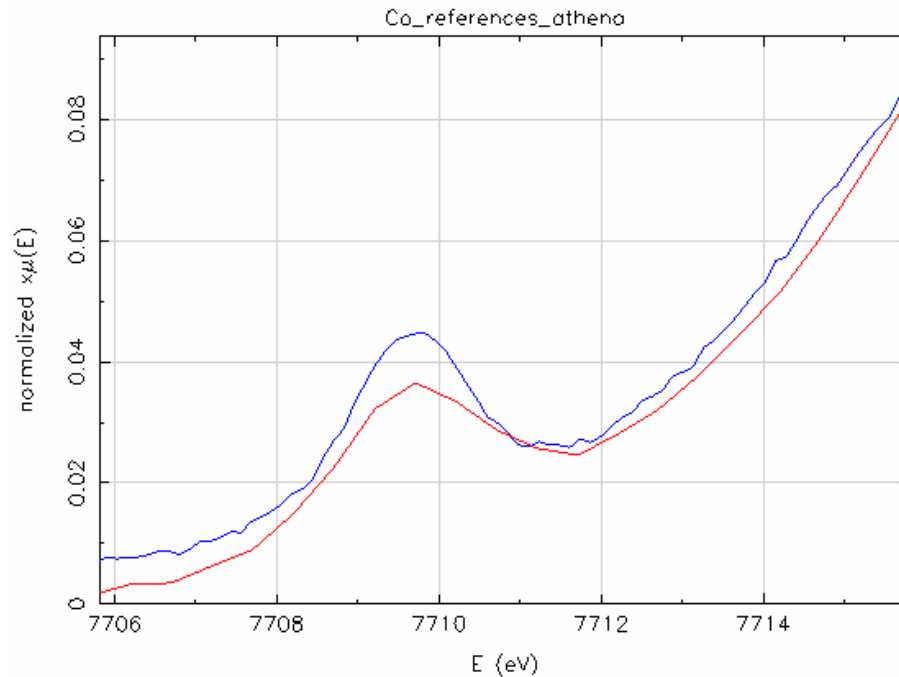
XANES Analysis: Oxidation State Sulfur
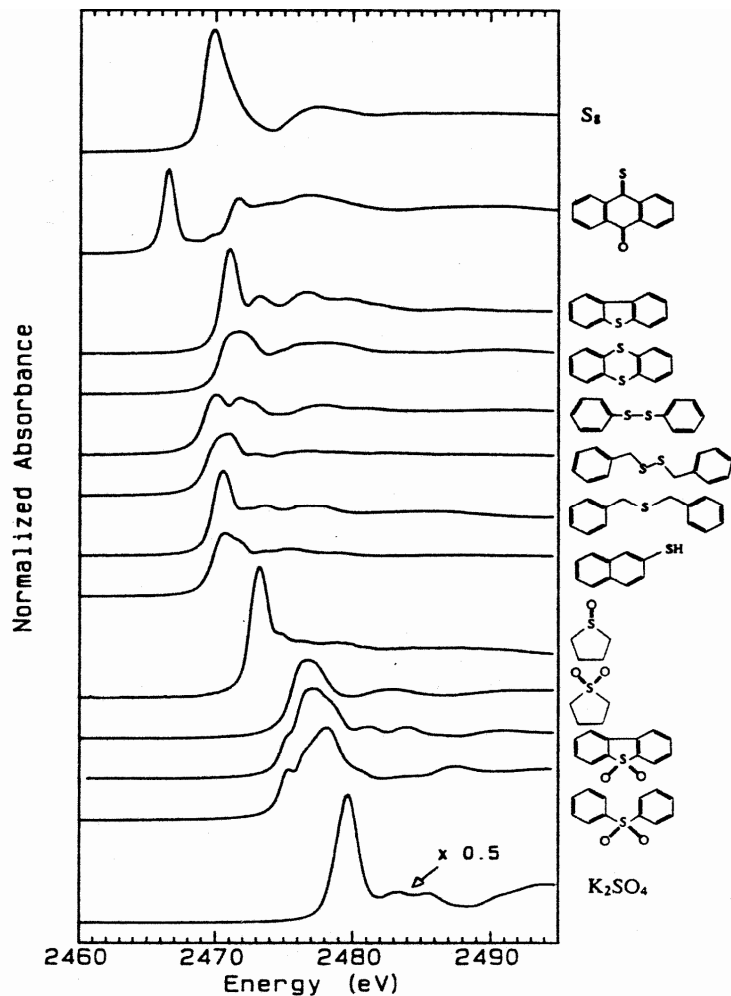
- Sulfur K-edge XANES used to identify and quantify the form of sulfur in petroleum, coals, soils, catalysts, etc.

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

- XANES of S in similar environments is similar: classes of compounds, e.g. thiophene, 2-methylthiophene, 2,5-dimethylthiophene, etc..
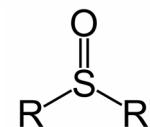
- Can be used as fingerprint.

Reference: George and Gorbaty, J. Am. Chem. Soc. 111 (1989) 3182

XANES Analysis: Oxidation State Sulfur
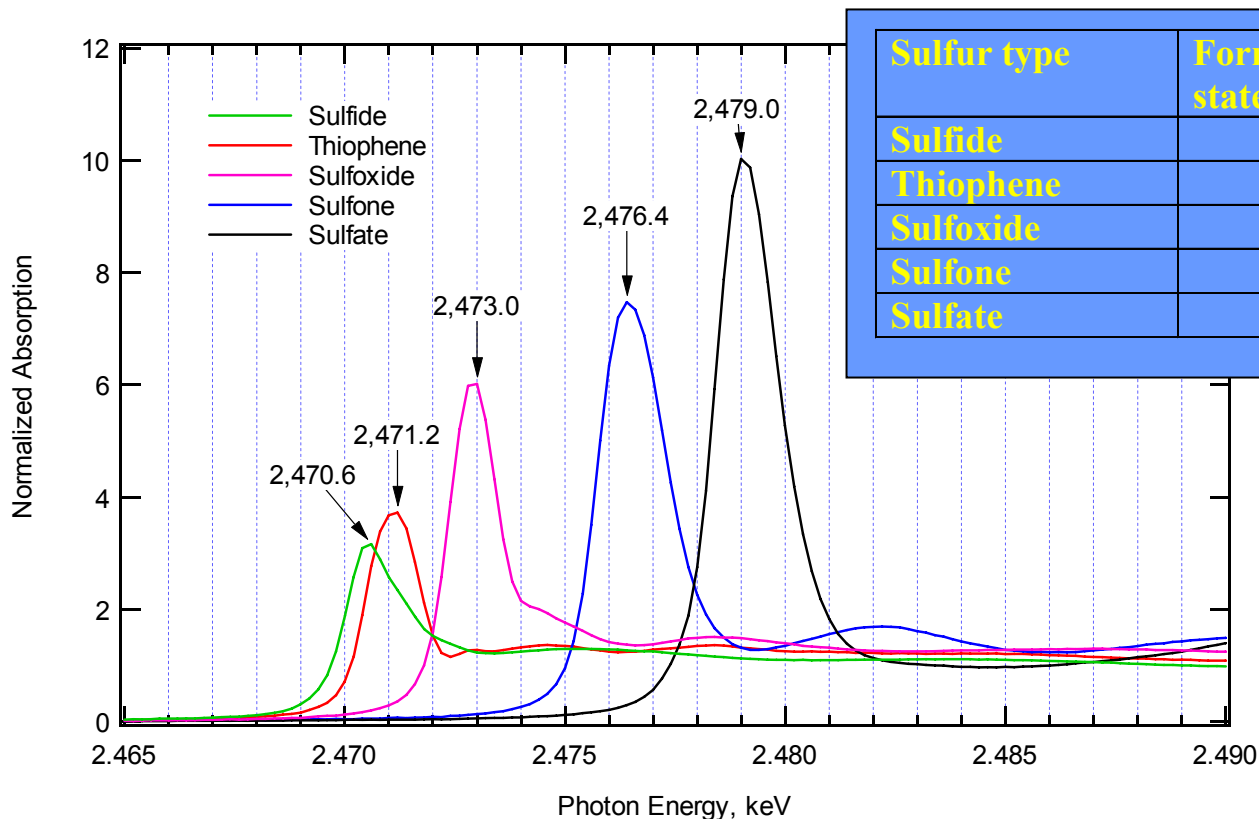
Sulfur type	Formal oxidation state
Sulfide	2-
Thiophene	1+
Sulfoxide	2+
Sulfone	4+
Sulfate	6+
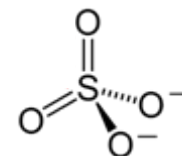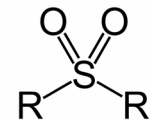
Dodecyl sulfide, thiophene, tetramethylene sulfoxide, tetramethylene sulfone, sulfate(aq)

XANES Analysis: Oxidation State

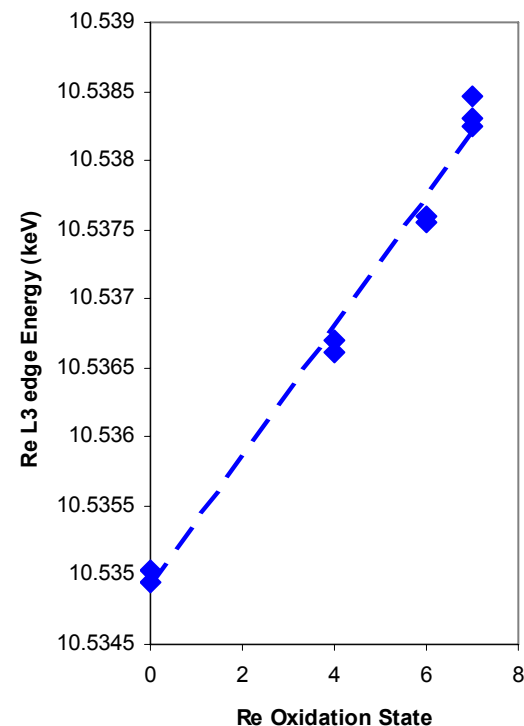Many, many examples in the literature…...

Mo K-edge
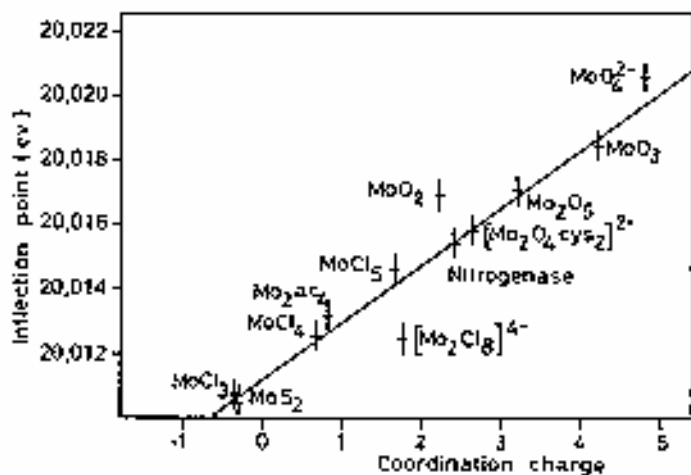
V K-edge

Re L₃-edge

Ref: Cramer et al., JACS, 98 (1976) 1287
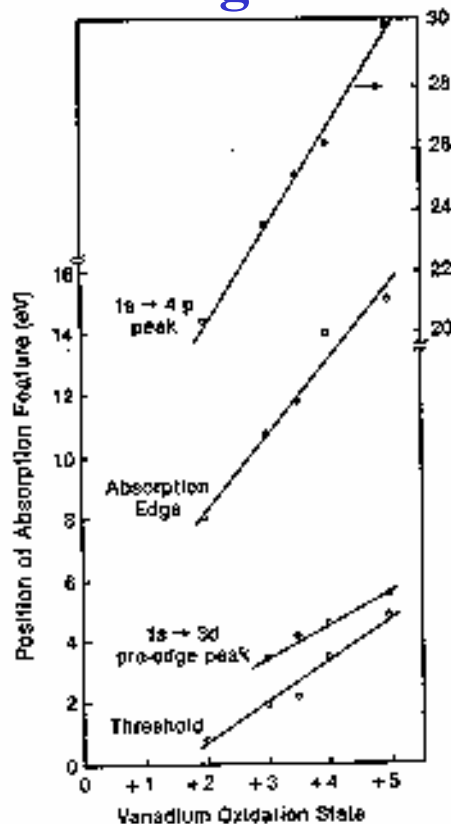
Ref: Wong et al., Phys Rev. B 30 (1984) 5596

S.R.Bare, unpublished
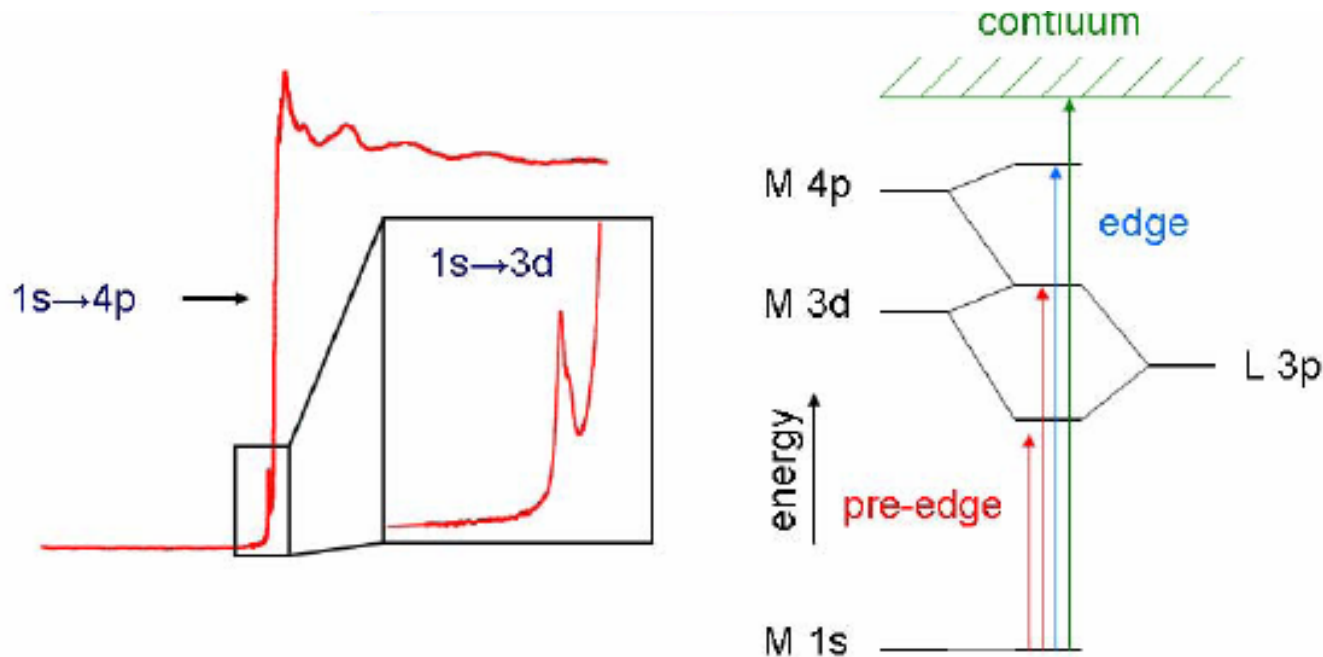
XANES Analysis: Oxidation State

Mo K-edge XANES of Mo oxides
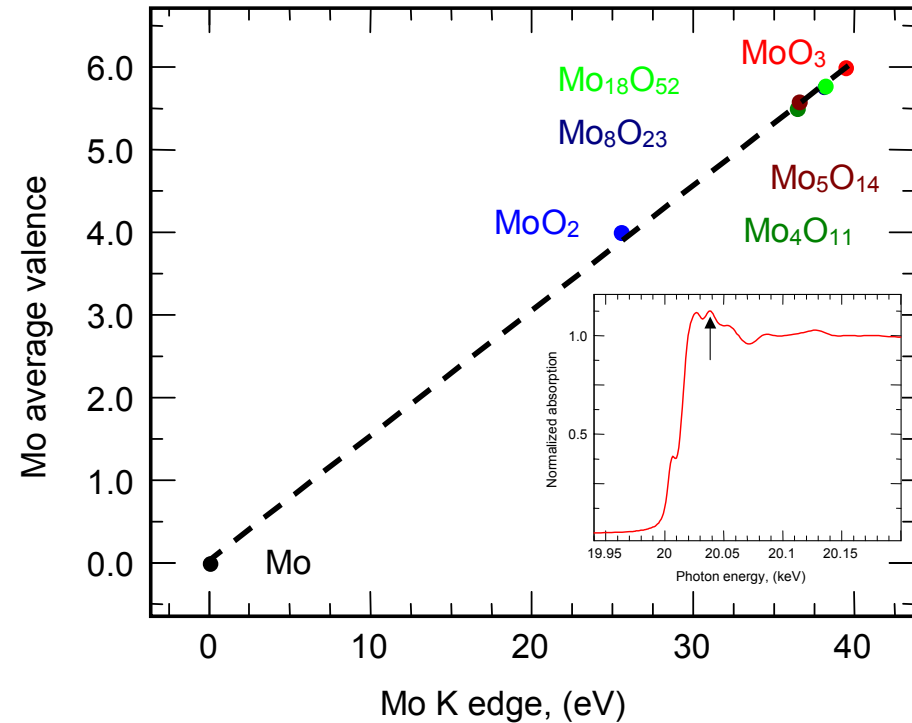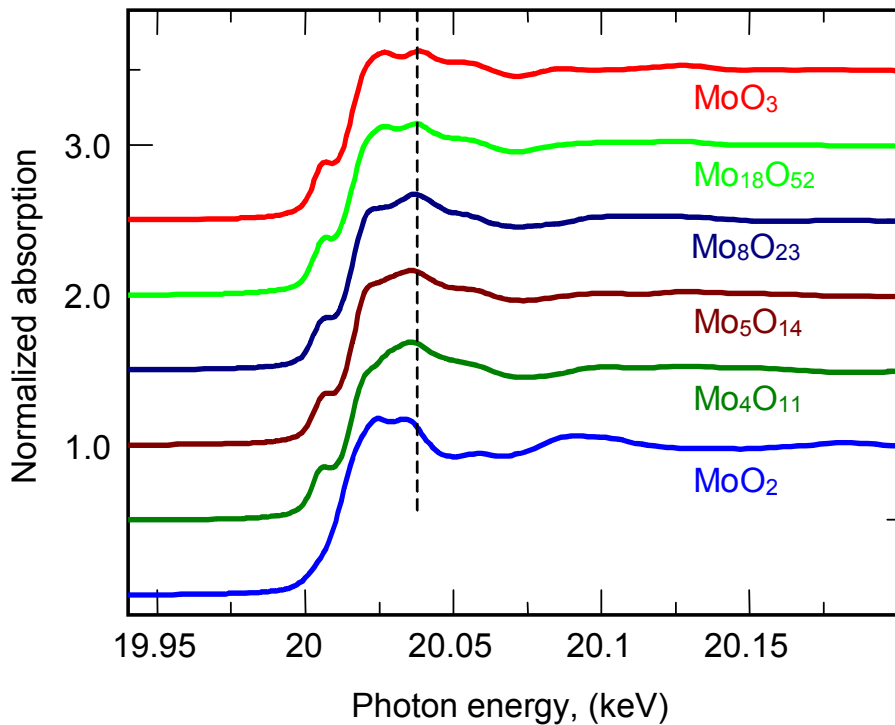
- Linear fit of Mo valence with K-edge position only obtained using a feature above the absorption edge!
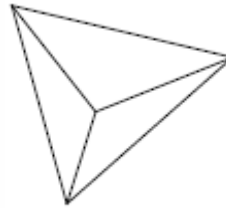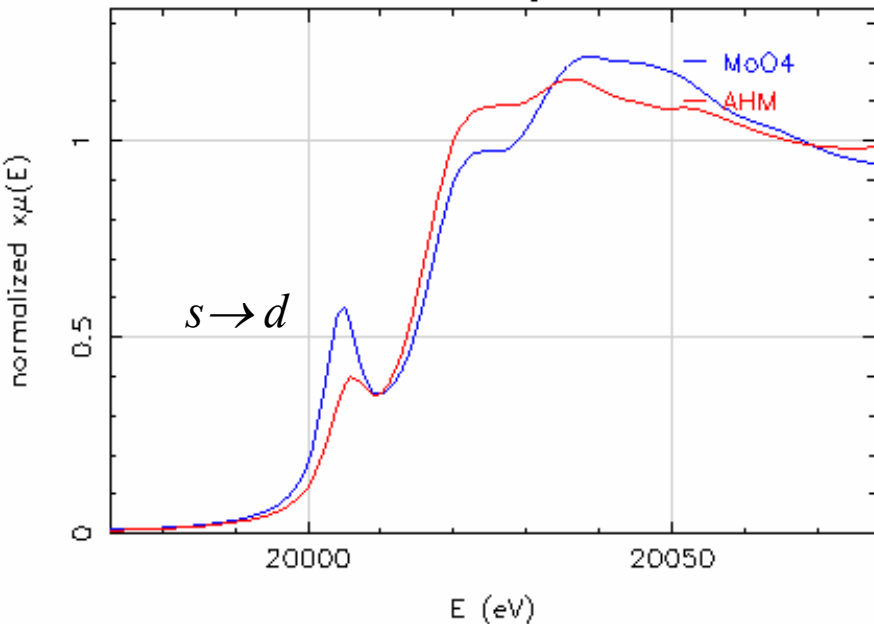
T. Ressler et al. J. Cat 210 (2002) 67
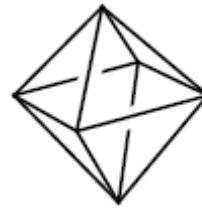
Metal K-edge XANES

- 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

Na$_2$MoO$_4$

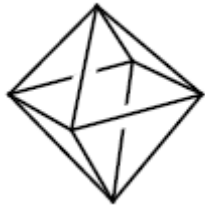**Tetrahedral coordination**

(NH$_4$)$_6$Mo$_7$O$_{24}$

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.
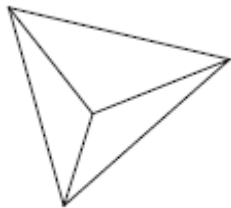
Transition Metal K-edge Pre-edge Peaks

Pure octahedral case

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

Distortion from octahedral

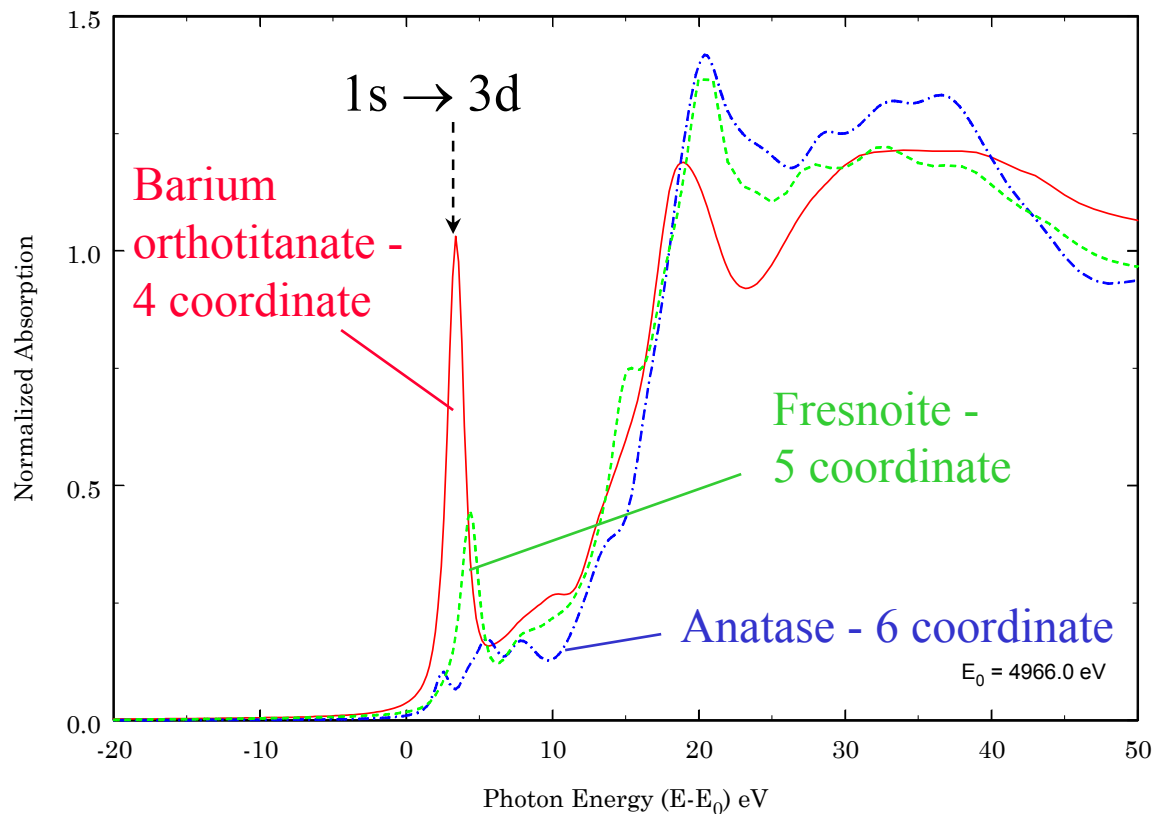> p-d mixing allowed: dipole transition in pre-edge – increasingly larger intensity.

Pure tetrahedral

> Largest pre-edge intensity.

Local Site Symmetry in Ti-containing Compounds

Ti K-edge XANES: Reference Compounds

$1s \rightarrow 3d$

Barium orthotitanate - 4 coordinate

Fresnoite - 5 coordinate

Anatase - 6 coordinate

$E_0 = 4966.0$ eV

Normalized Absorption

Photon Energy (E-E$_0$) eV

Ti_refs1.axg

Anatase

3d split by mixing with O2p into t_{2g} and e_g like orbitals.

3rd 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.
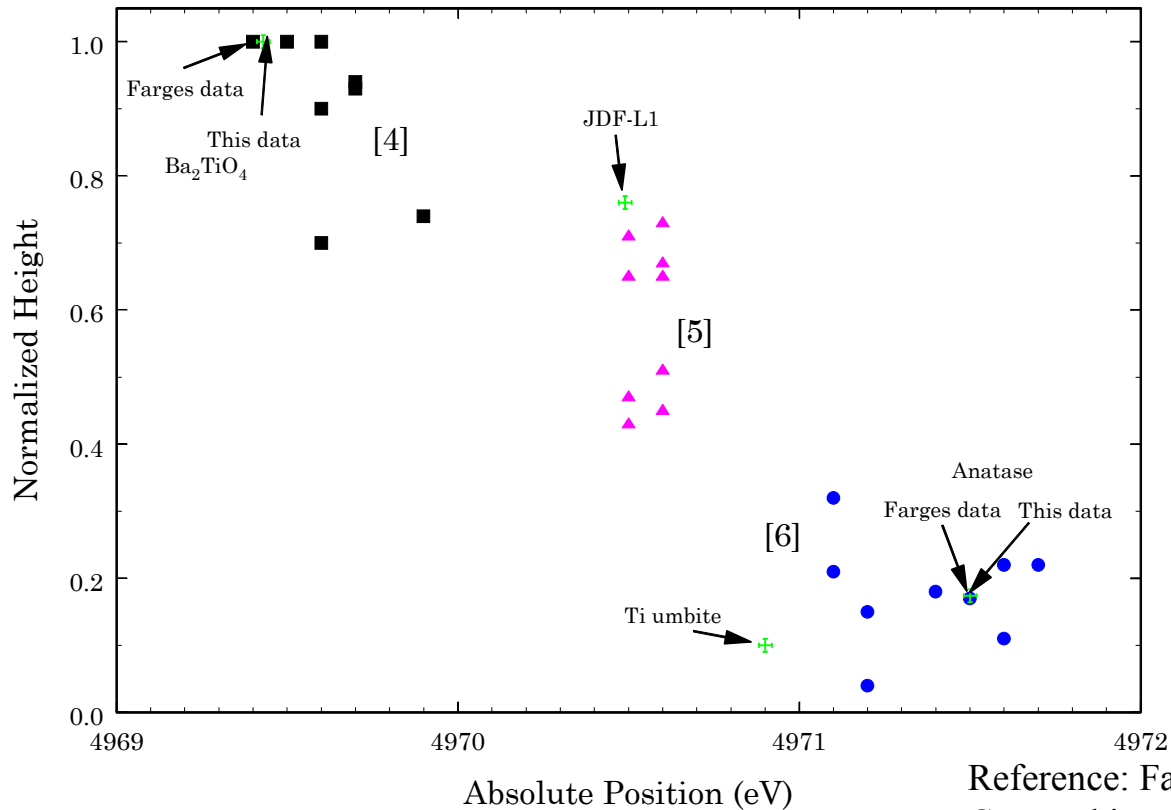
Reference: Farges et al., Geochim. Cosmochim. 60 (1996) 3023

XANES of 3d Transition Metals: Coordination

T$_d$ **O$_h$**
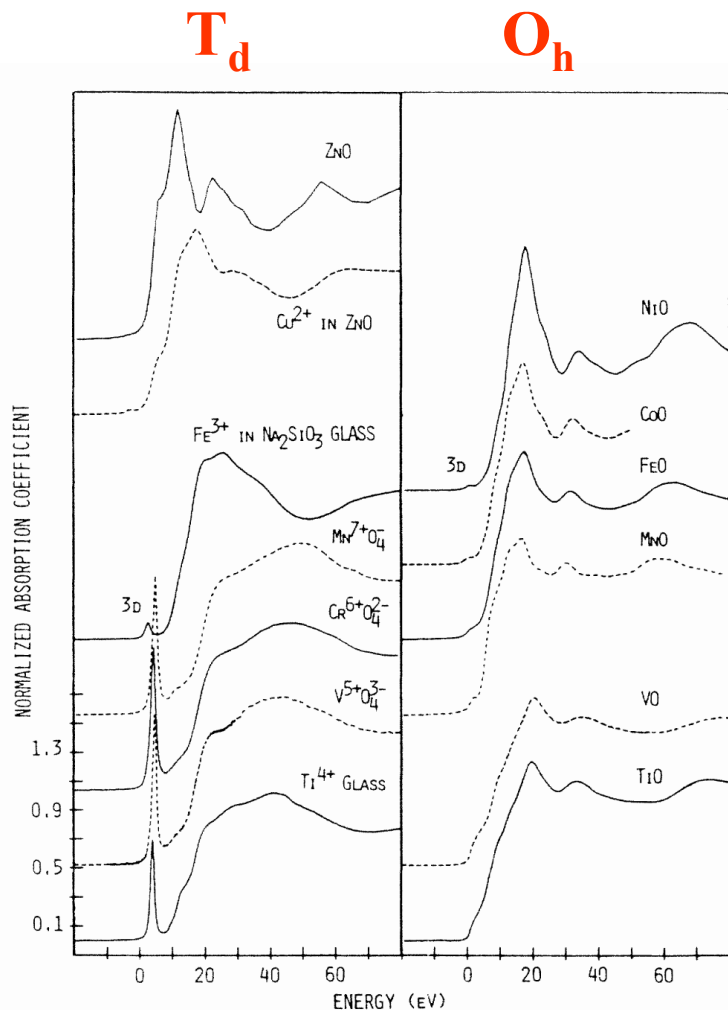
- For T$_d$ symmetry 1s to 3d pre-edge peak sharp and intense from Ti$\rightarrow$Mn, decreases Fe $\rightarrow$ Cu, absent for Zn.

- Decrease in intensity due to progressive filling of the 3d band.

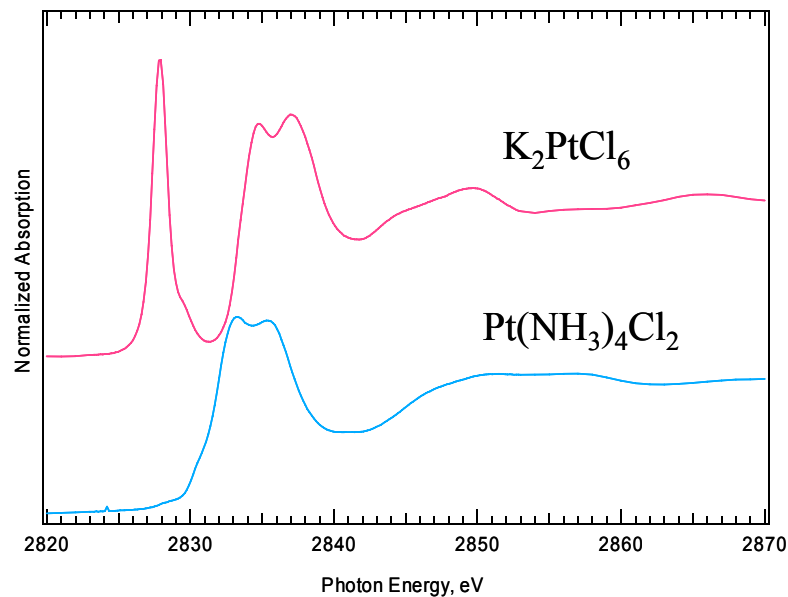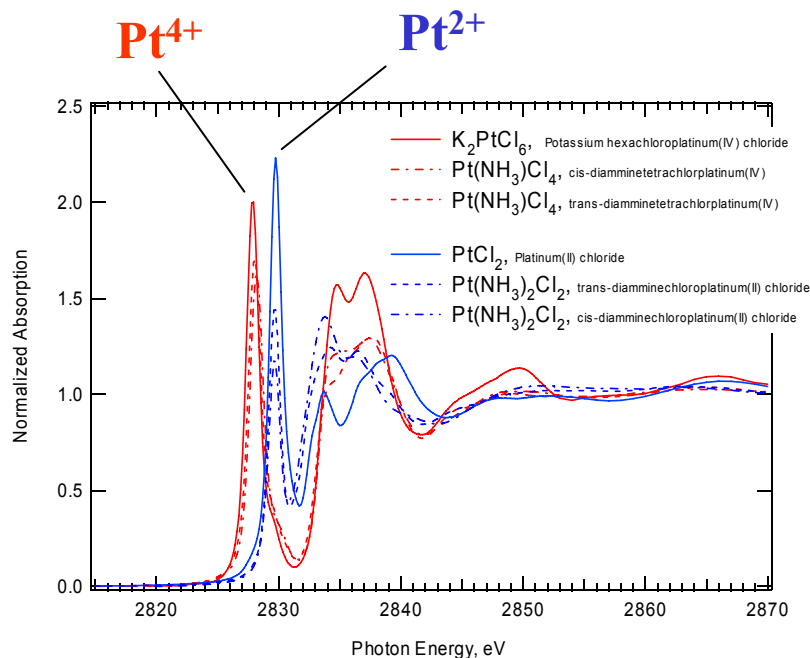- O$_h$ symmetry shows only a small pre-edge peak throughout series.

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

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.
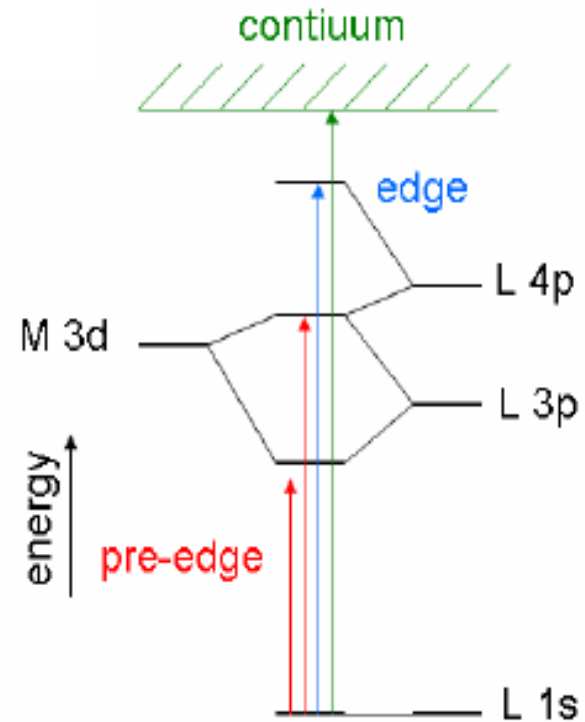
Ligand-Metal Binding: Cl K-edge XANES

- 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.
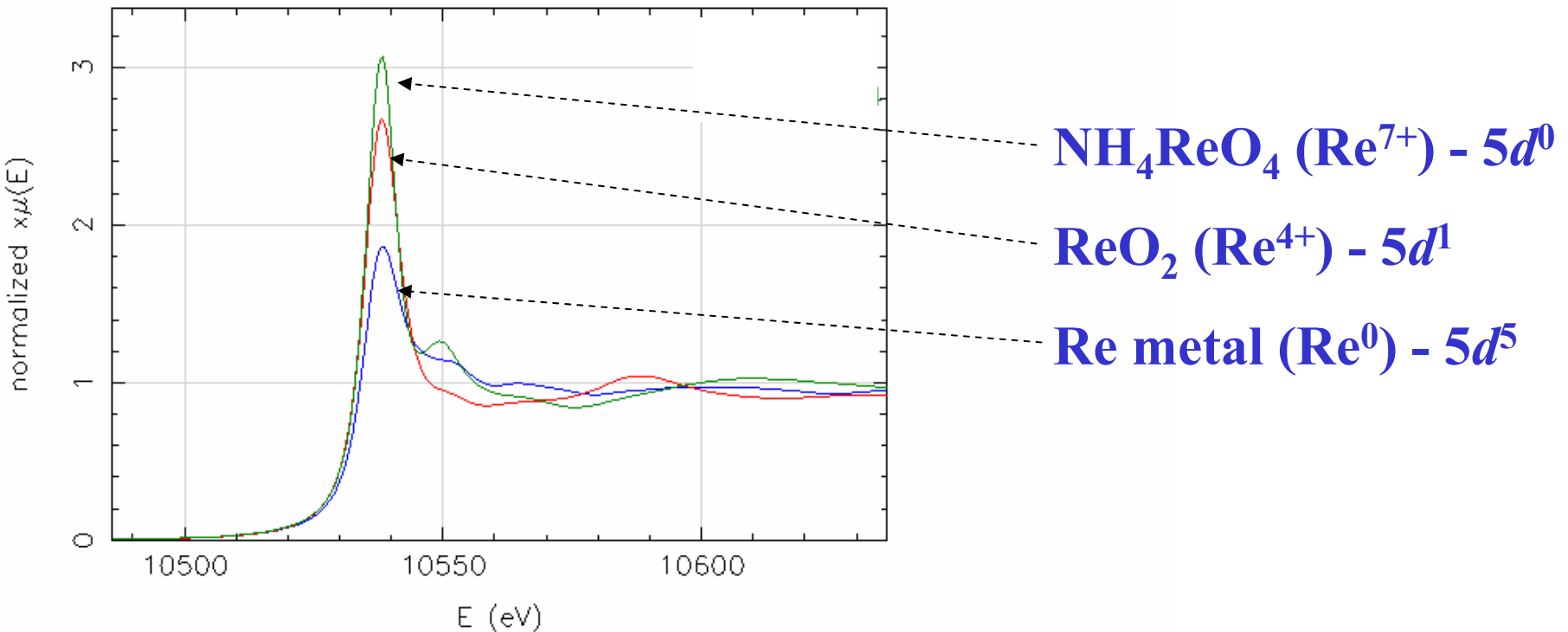
"White line" Intensity of 4d Metals
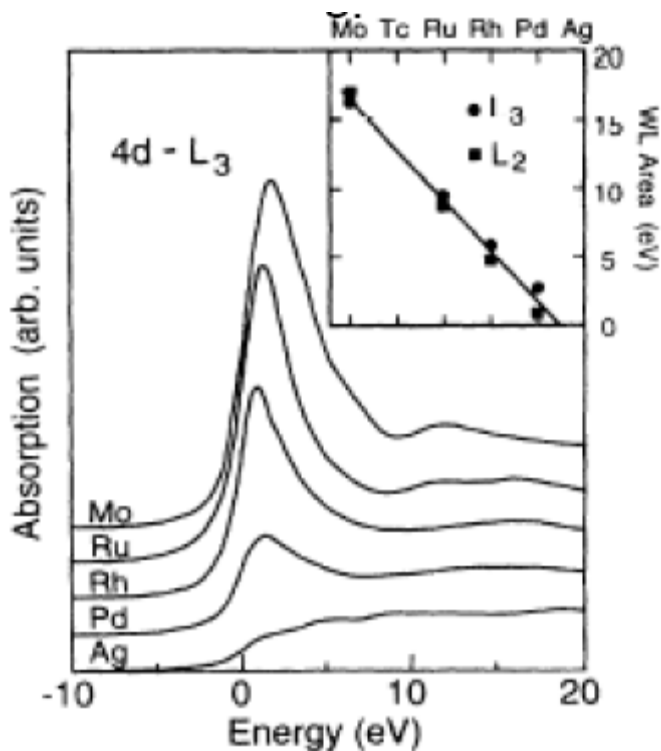
L$_3$ edge XANES
for $4d$ metals

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

- Transition from $2p3/2$ 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_3-edge - Transition from $2p3/2$ to $5d$ states.

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

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

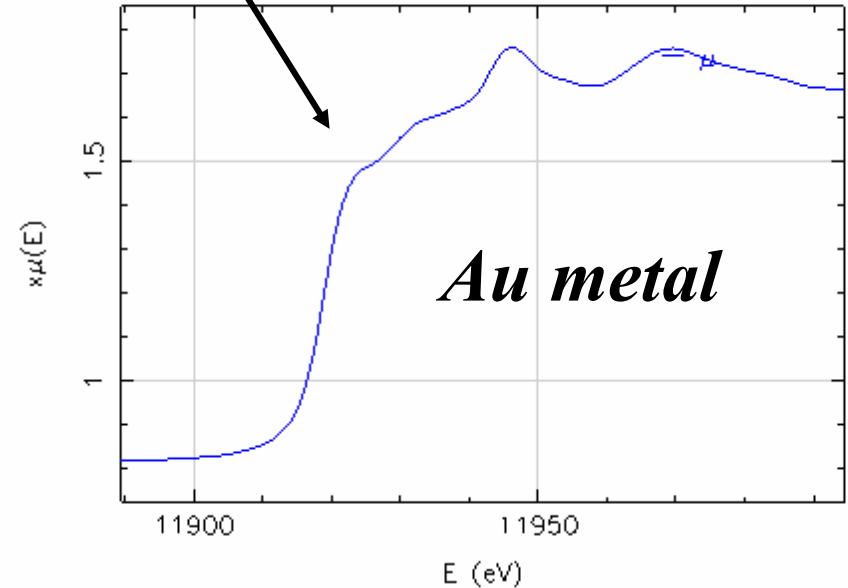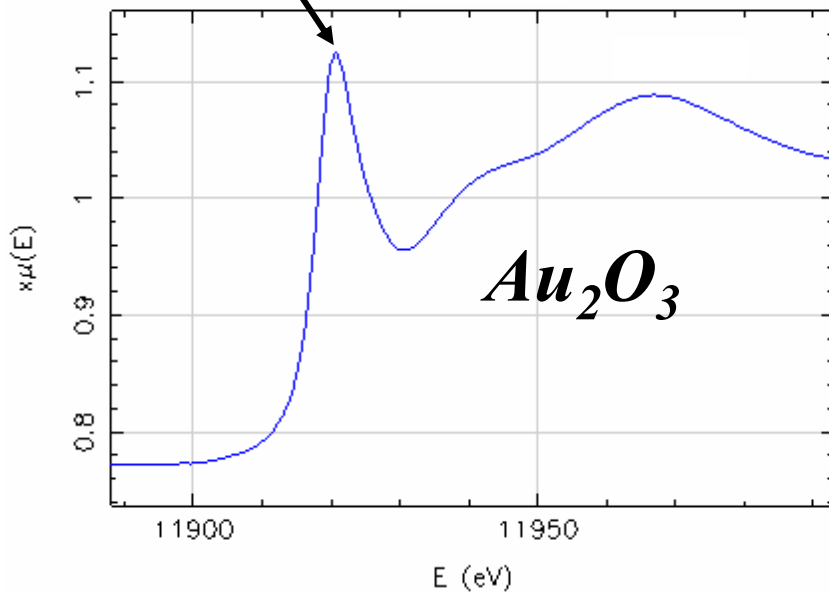**Re metal (Re^0) - $5d^5$**

- Intensity of Re L_3 white line probes Re LDOS

*Spectra aligned in energy

Metals & Oxides

Au L₃-edge XANES

White line reflects holes in d-band

No white line

Au_2O_3

$Au\ metal$

- Overall shape of spectrum also different.

XANES Peak Fitting in Athena
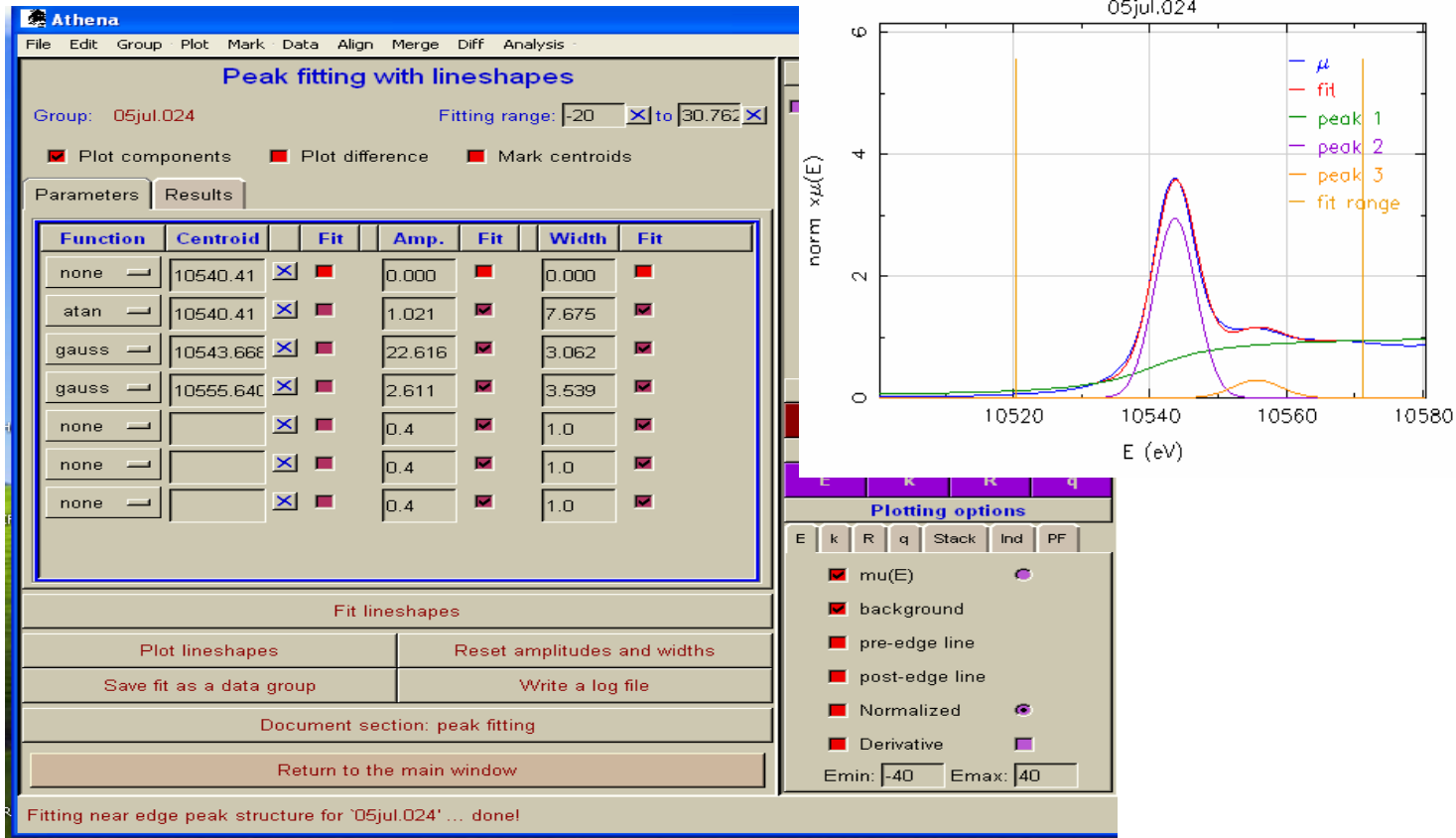
- Useful for quantification of areas, etc.

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"White Lines": large change in absorption coefficient
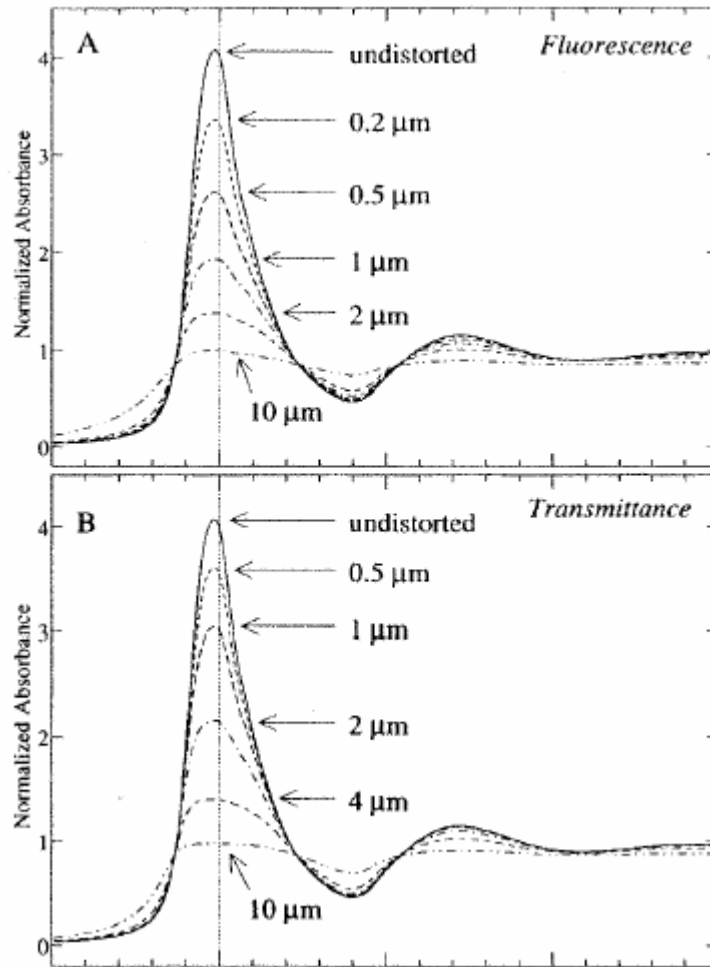
Sulfur K-edge XANES
of sulfate$_{(aq)}$
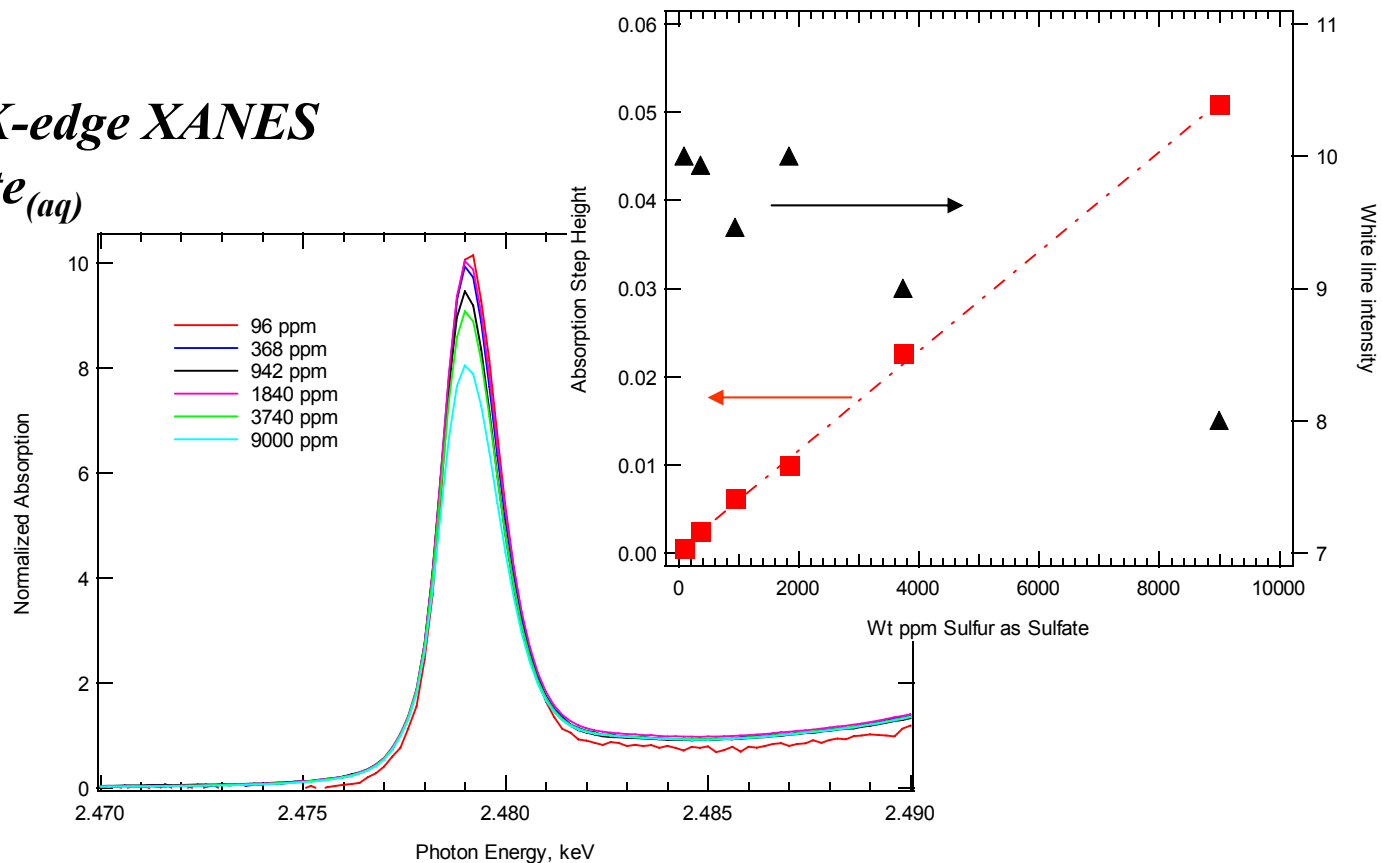
- Step height linear with concentration from 100-10,000 ppm S - but relative white line intensity constant only for <2000 ppm.

- Important if using a "reference" spectrum for fitting or fingerprinting.

Caution about use of absolute intensity of "white line"

Solid sulfur, S_8

A — Fluorescence
- undistorted
- 0.2 μm
- 0.5 μm
- 1 μm
- 2 μm
- 10 μm

B — Transmittance
- undistorted
- 0.5 μm
- 1 μm
- 2 μm
- 4 μm
- 10 μm

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 ≤10μm in diameter to minimize self-absorption effects at the sulfur K-edge"

Pt L₃ and L₂ Edge XANES

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

L_3

L_2

L_2 shifted to align with L_3 edge.
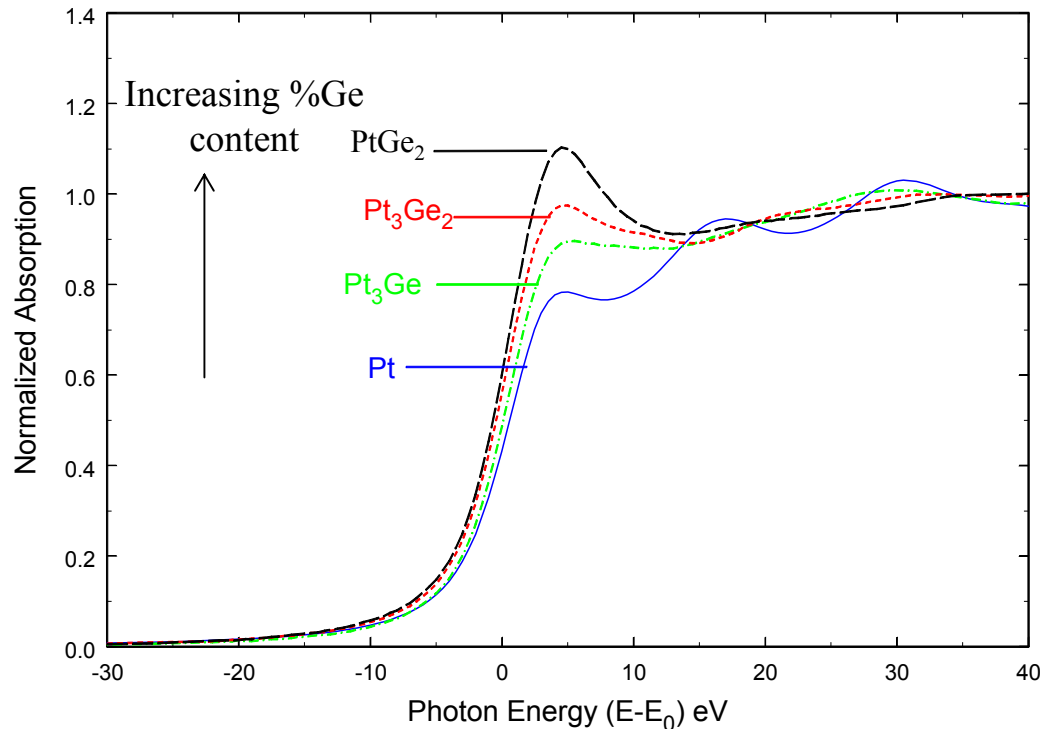
E_F — 5d5/2

5d3/2

2p3/2

L_3

2p1/2

L_2
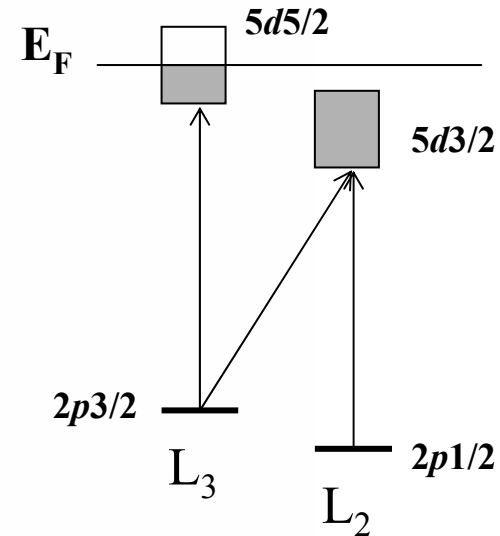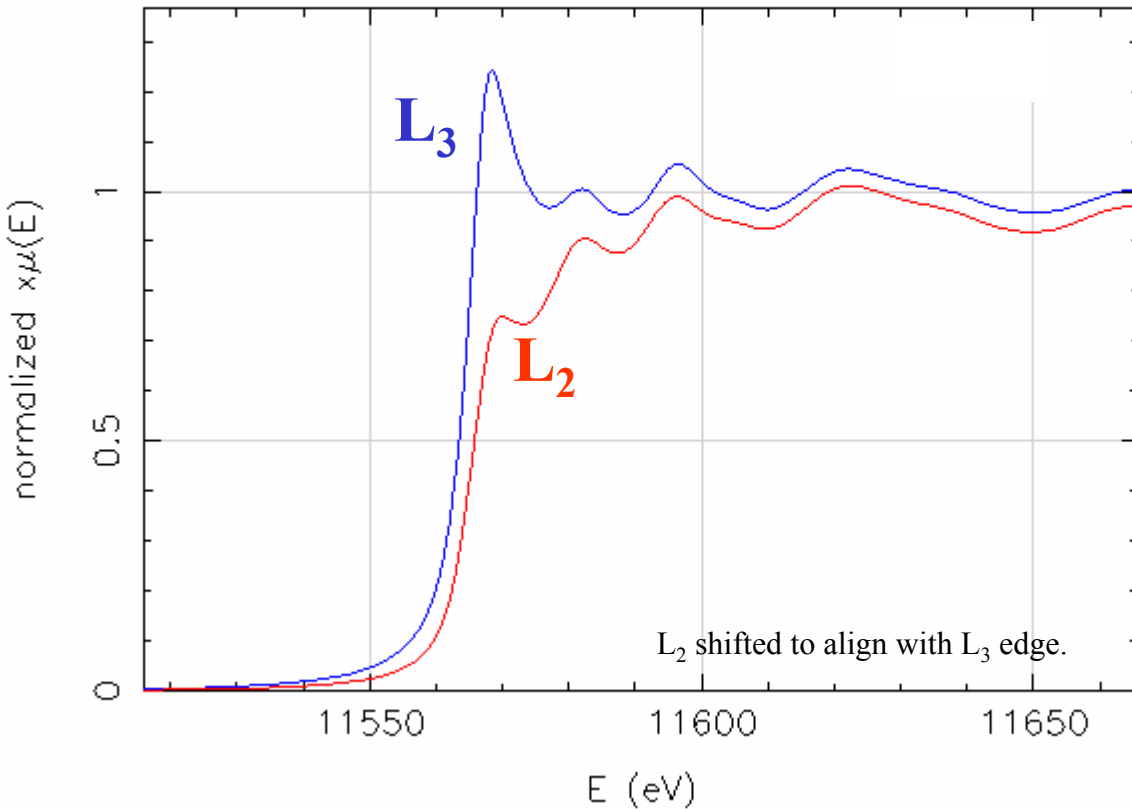
- Pt $5d3/2$ filled, so no white line.

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

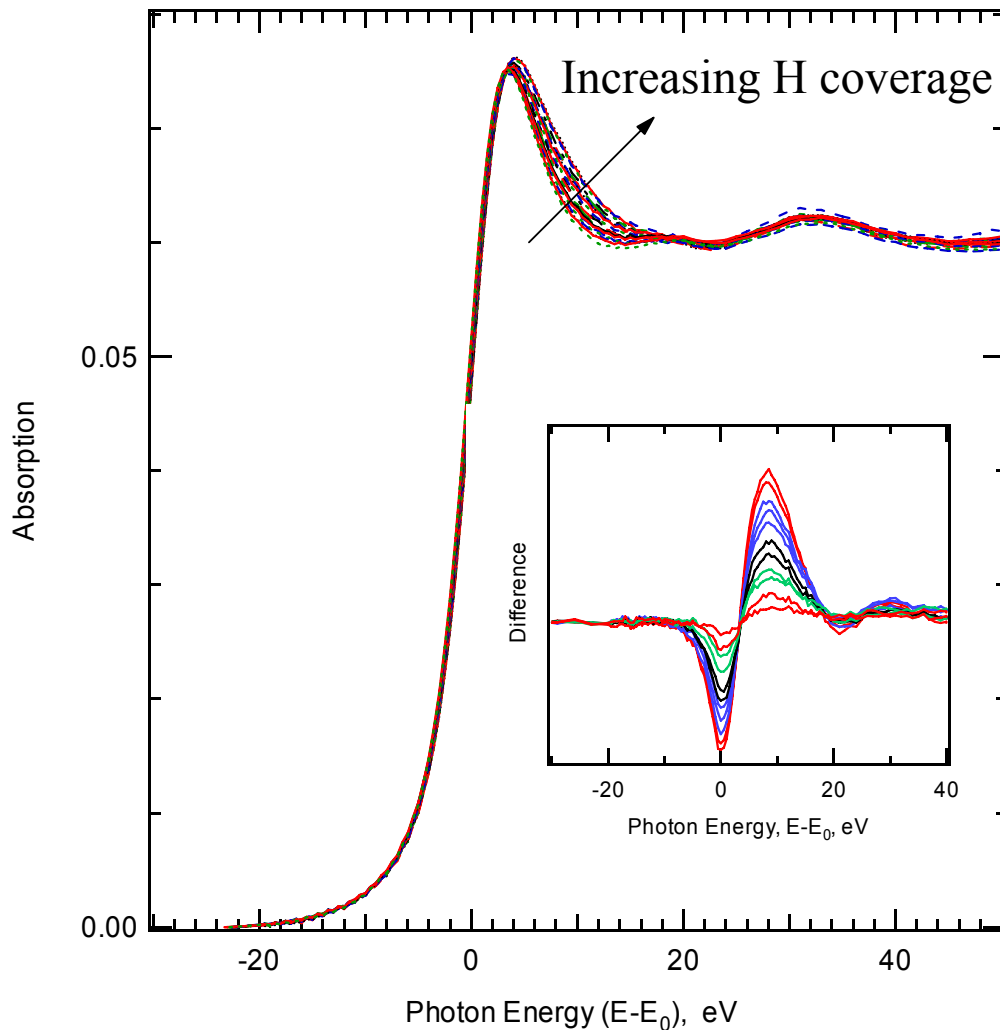- Only $j=3/2$ probed by L_2-edge, both $j = 3/2$ and $j = 5/2$ probed by L_3-edge.

XANES to Probe Charge Transfer in Alloys

Platinum L$_2$-edge XANES: Pt$_x$Ge$_y$ 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.
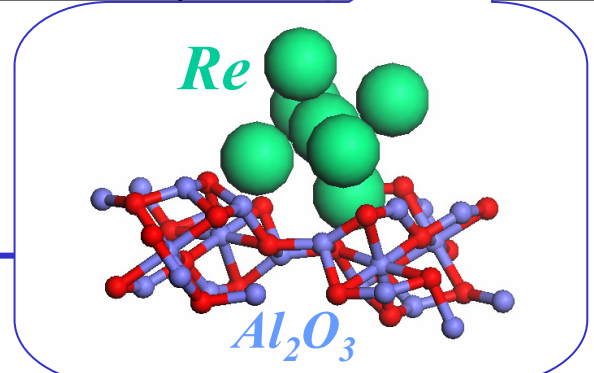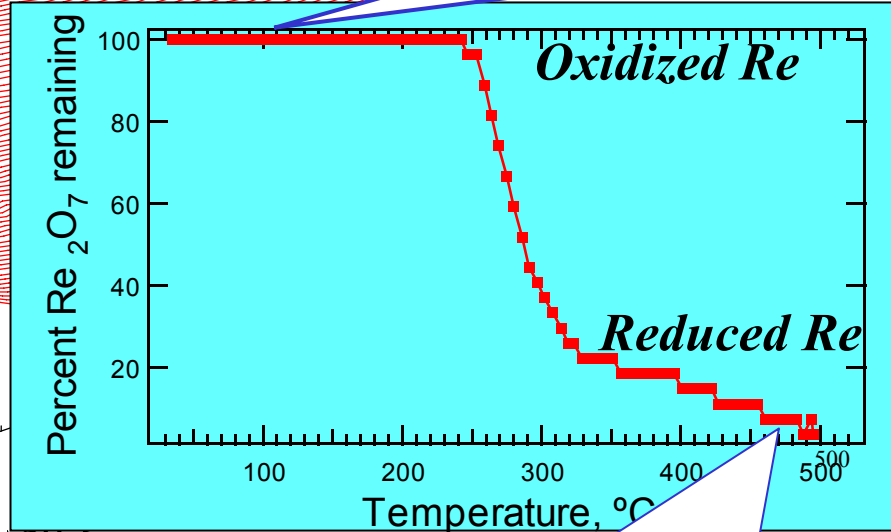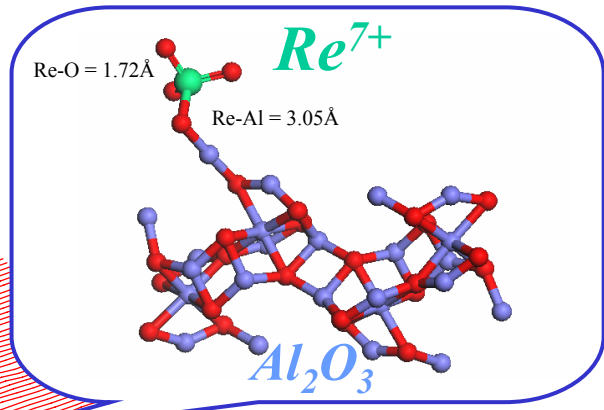
Effect of Adsorbed Hydrogen on Pt L$_3$ XANES

Increasing H coverage

Absorption

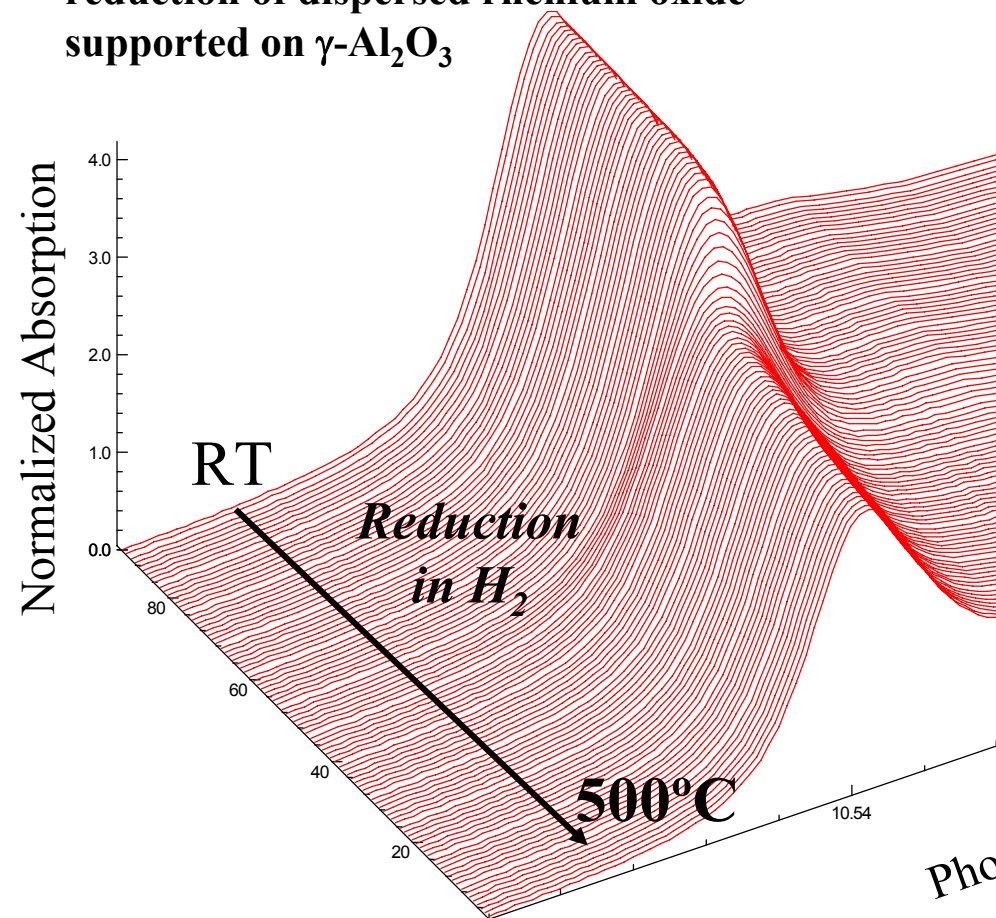Photon Energy (E-E$_0$), eV

Difference

Photon Energy, E-E$_0$, eV

10-15Å diameter nano-Pt clusters supported on γ-Al$_2$O$_3$

· 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.

Time Evolution of XANES: Kinetics

In situ temperature programmed reduction of dispersed rhenium oxide supported on γ-Al$_2$O$_3$

Re^{7+}

Re-O = 1.72Å

Re-Al = 3.05Å

Al_2O_3

Normalized Absorption

RT

Reduction in H$_2$

500°C

10.54

Photon

Percent Re$_2$O$_7$ remaining

Oxidized Re

Reduced Re

Temperature, °C

Re

Al_2O_3

Time Evolution of XANES: Kinetics

TPR-XANES showing
reduction of vanadium as
catalyst is heated in H_2 to 500ºC

*Vanadium K-edge
XANES*

Heat in
H_2 flow
RT

500 º C
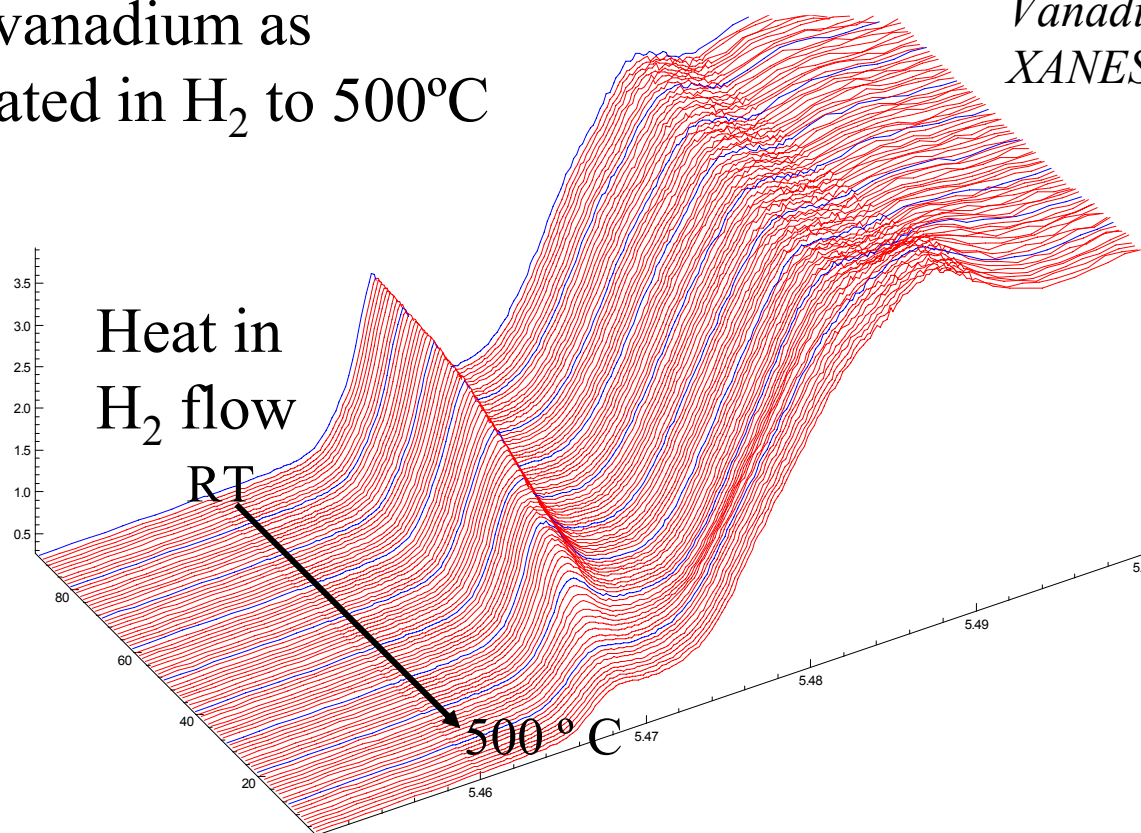
80 sec/scan

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.

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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)

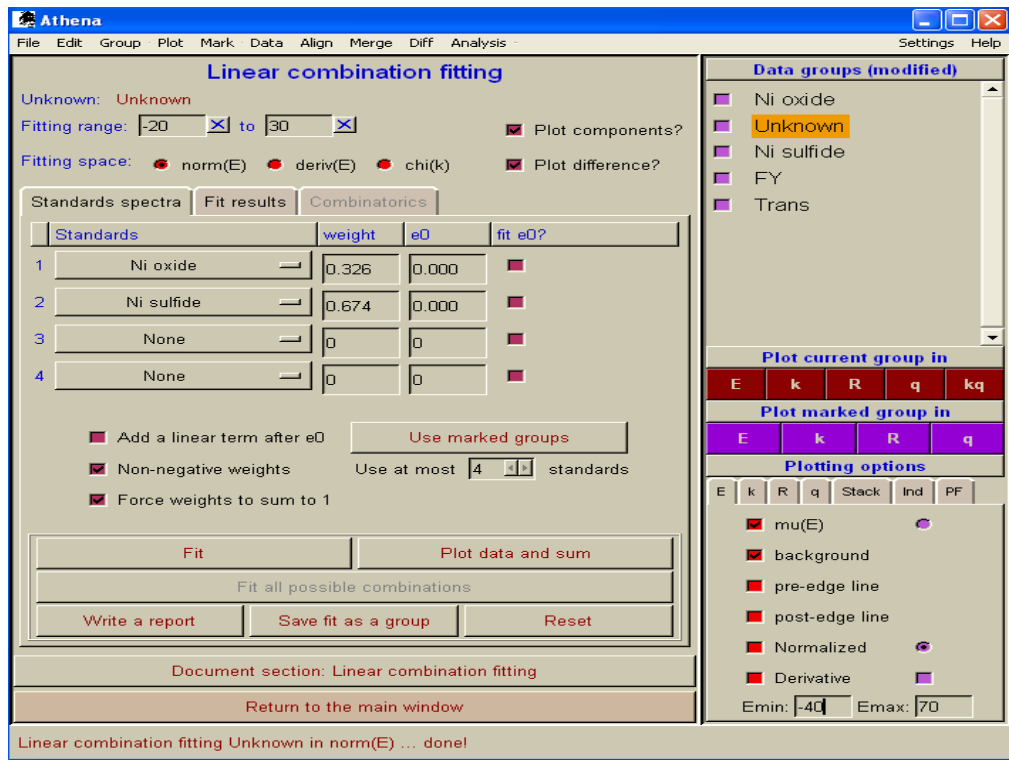http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/Sxm
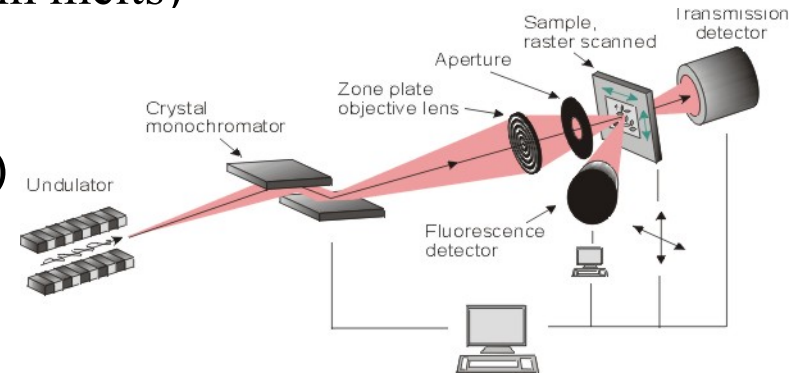
Analysis of Mixtures

- 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
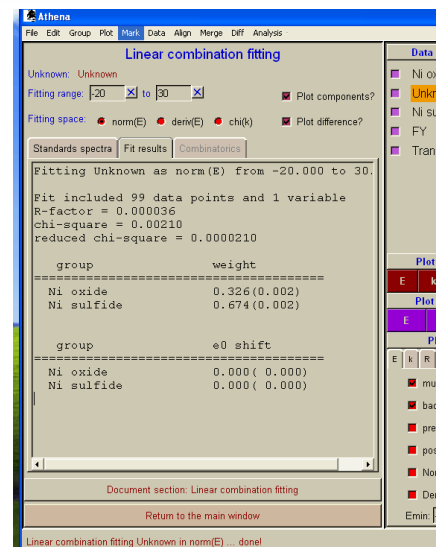
    – Principal component analysis

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
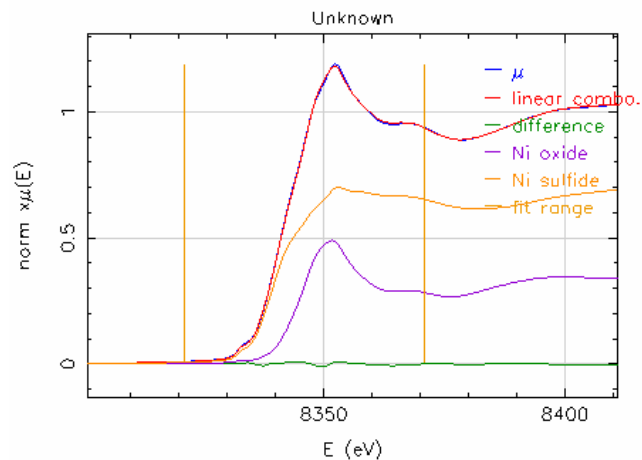
Linear Combination Fitting

Fit experimental data to linear combination of known reference compounds

TPR-XANES of *in situ* reduction of Ce₀.₇Zr₀.₃ oxide
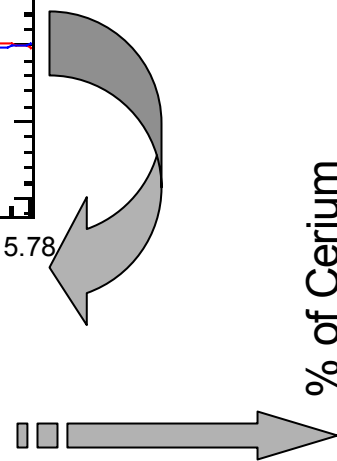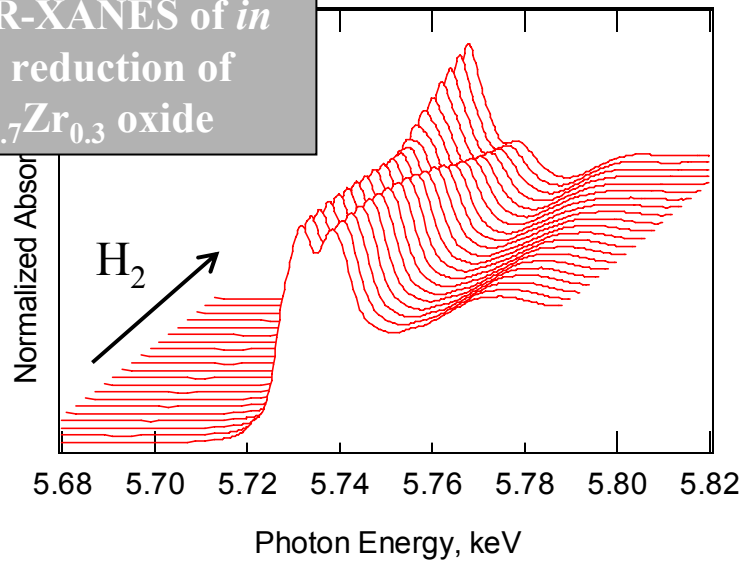
LC-XANES fit to determine amount of Ce(III) and Ce(IV) present as function of temperature
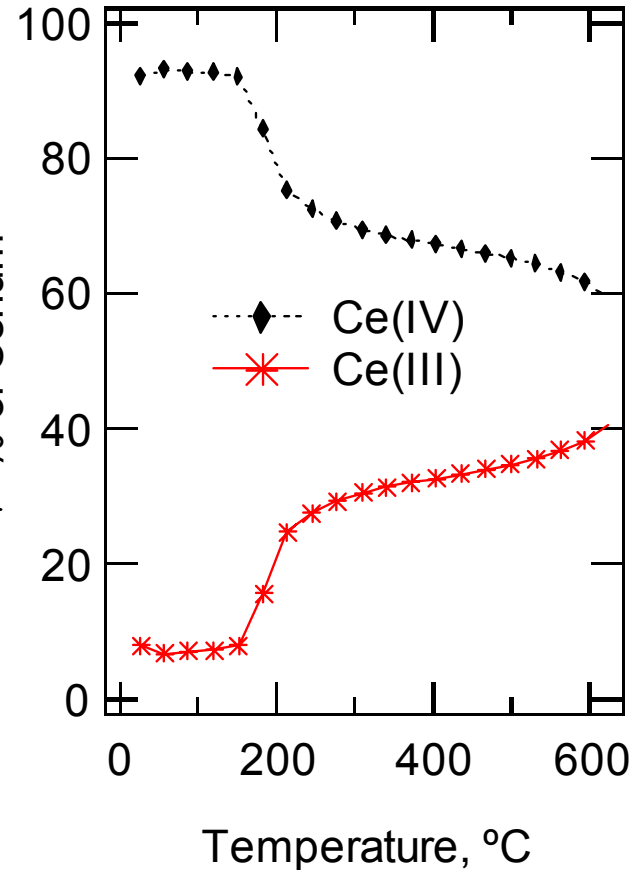
Linear Combination Fitting

Ni K-edge XANES of in situ
sulfiding of a Ni/Al$_2$O$_3$ catalyst

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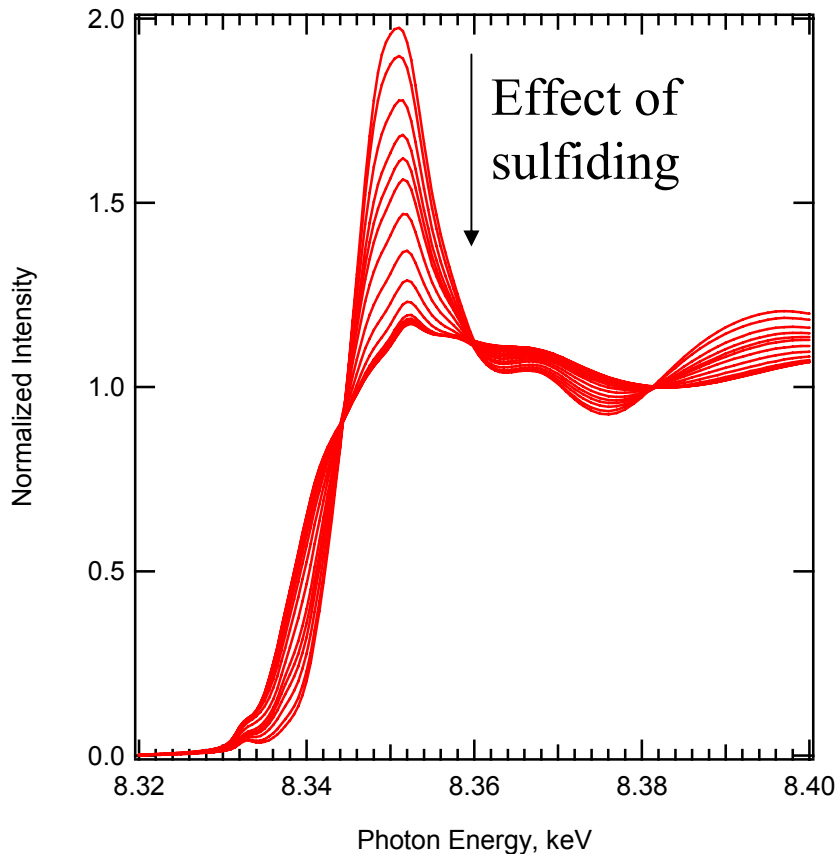
LC-XANES fit
to determine
amount of
oxidized and
sulfided Ni
present as
function of
temperature/time

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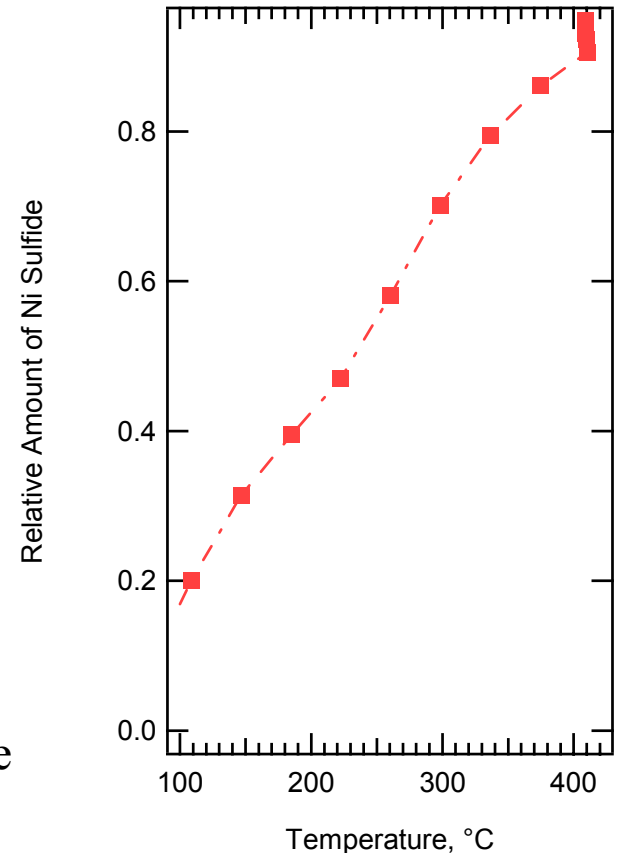
Quantification Using Reference Compounds

- Need to be cautious about collecting XANES data of bulk reference compounds in fluorescence – will get incorrect answer in quantitative fitting!
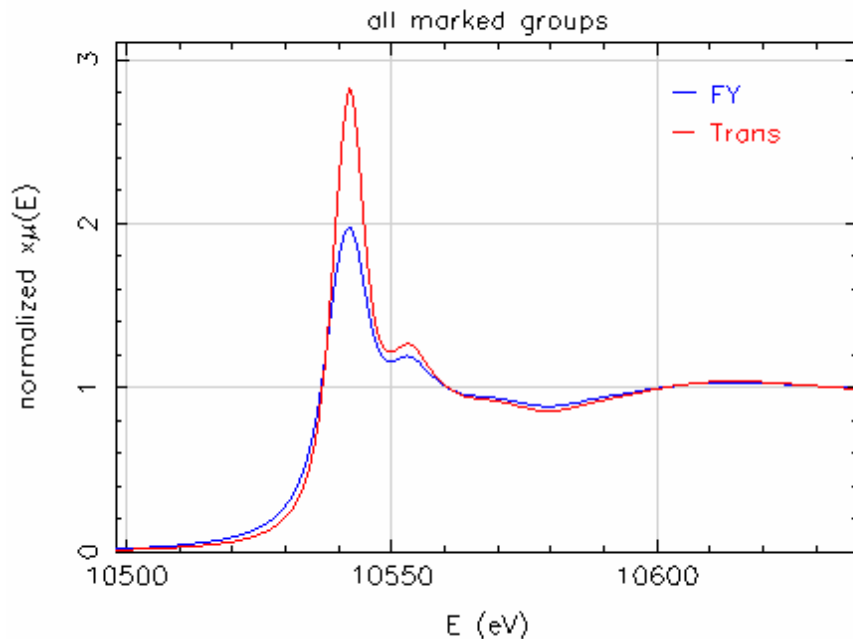
Re L_3-edge XANES spectrum of bulk $(NH_4)ReO_4$

White line of spectrum collected in fluorescence severely attenuated.

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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.

- 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^{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.

- 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
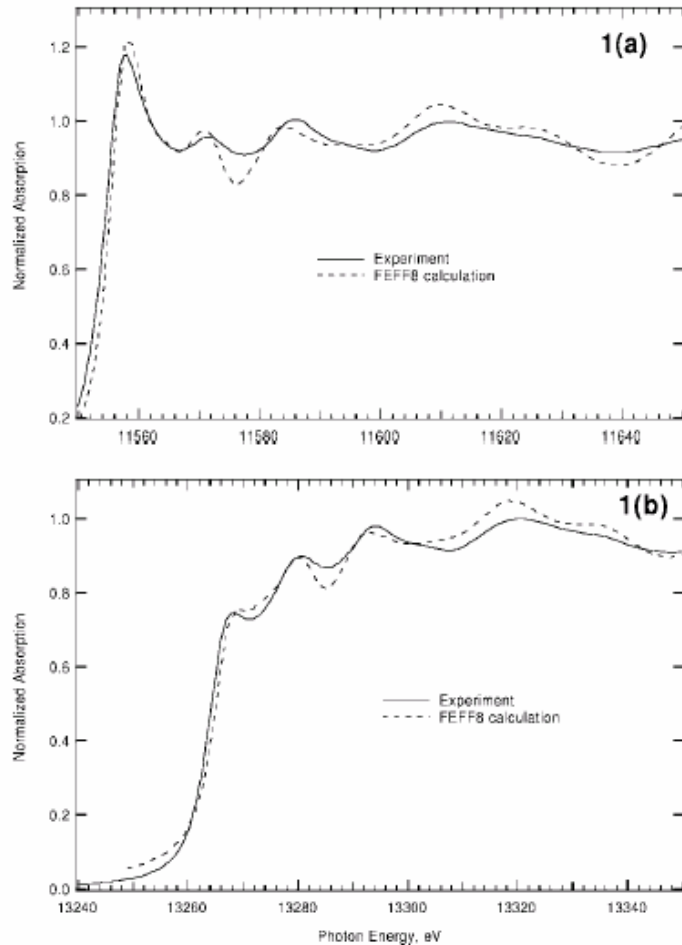
Pt L_3-edge XANES as function of Pt cluster size
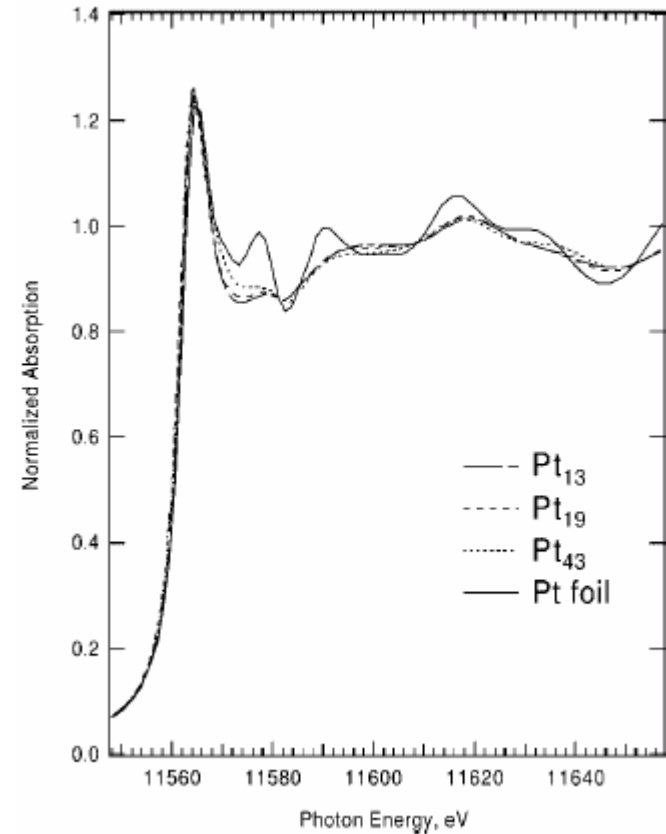
Summary

XANES is a much larger signal than EXAFS

XANES spectra can be collected at lower concentrations, and with less-than-perfect samples / conditions.

XANES is easier to crudely interpret than EXAFS

In many instances the XANES is simply used as a fingerprint.

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

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…..

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