Introduction to X-ray Absorption Spectroscopy

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Introduction

Acronyms

EXAFS – Extended **X**-ray **A**bsorption **F**ine **S**tructure

XAS – X-ray **A**bsorption **S**pectroscopy

XAFS – X-ray **A**bsorption **F**ine **S**tructure

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

NEXAFS- Near-**E**dge **X**-ray **A**bsorption **F**ine **S**tructure

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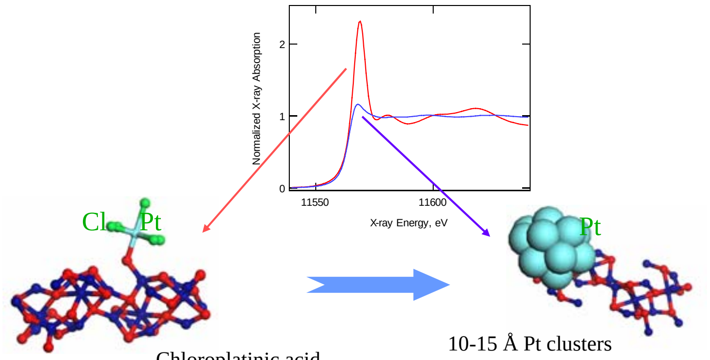
Why are we Interested in XAFS?

- **XAFS gives detailed element-specific information on oxidation state and local atomic structure.**

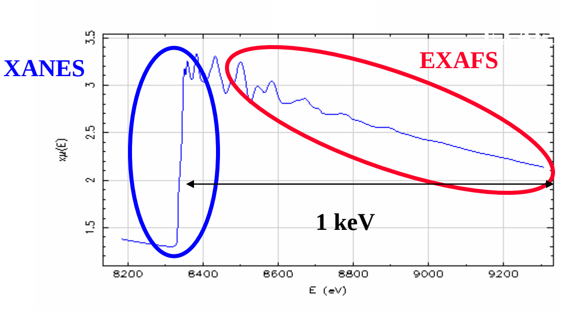


Chloroplatinic acid complex on Al_2O_3

10-15 Å Pt clusters on Al_2O_3

What is XAFS?

- X-ray absorption fine structure is the modulation of the x-ray absorption coefficient (μ) at energies near and above an x-ray absorption edge.
- Commonly broken into two regimes:
  - XANES X-ray absorption near edge structure
  - EXAFS Extended x-ray absorption fine structure



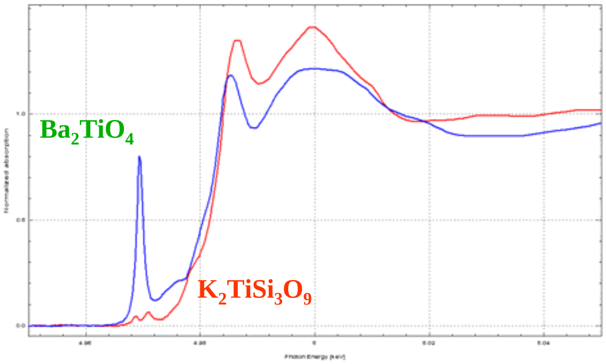
Ni K-edge XAFS of Ni metal

X-ray Absorption Near Edge Structure (XANES)

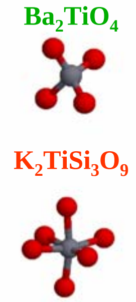
- Provides quantitative information on:
  - Average oxidation state
  - Local coordination environment
  - Electronic structure (empty density of states)

Chemistry!

XANES: Local Coordination Environment

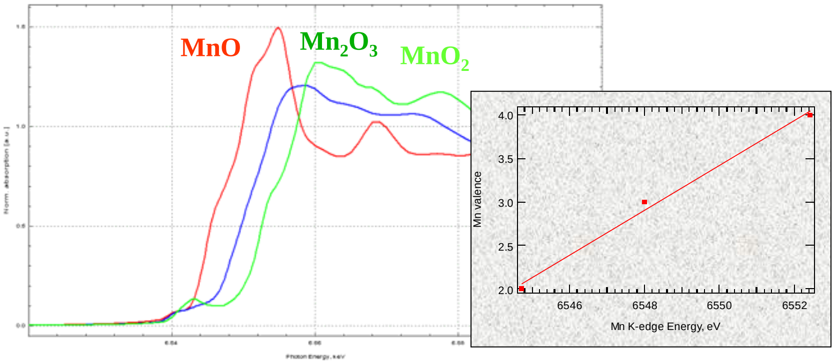


Both Ti^{4+}



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

XANES: Oxidation State



- **Many edges of many elements show significant, easily measurable, 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)

Extended X-ray Absorption Fine Structure (EXAFS)

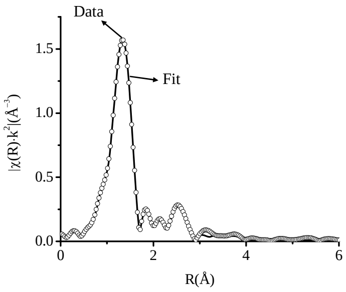
- Provides quantitative information on:
  - Distance to neighboring atoms (average bond length, R_j)
  - Coordination number and type of the neighboring atoms (N_j)
  - Mean-square disorder of bond length (σ_j^2)

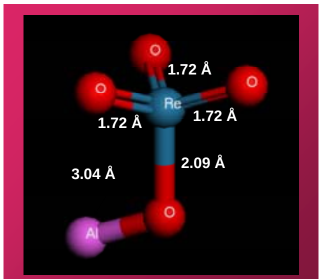
EXAFS Equation

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^{\,2}} \sin[2kR_j + \delta_j(k)]$$

EXAFS: Structure Determination

- Heterogeneous catalyst: rhenium oxide dispersed on a high surface area alumina support: what is the structure of the rhenium oxide species?





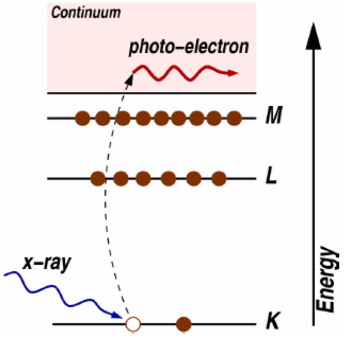
Implied structure of *in situ* dried calcined catalyst

- Four O atoms in distorted tetrahedral arrangement (3 short, 1 long)
- $[ReO_4]$ is anchored to the alumina surface through Re-O-Al linkage.

X-ray Absorption

- X-rays are absorbed by all matter through the photo-electric effect.

- An x-ray is absorbed by an atom when the energy of the x-ray is transferred to a core-level electron (K, L or M shell) which is ejected from the atom.
- The atom is left in an excited state with an empty electronic level (a core hole). Any excess energy from the x-ray is given to the ejected photo-electron.

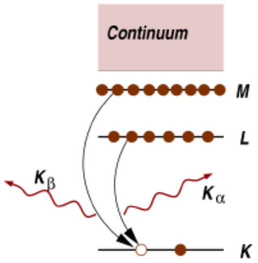


Absorption Edges: Nomenclature

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

X-ray Fluorescence

- **When x-rays are absorbed via photo-electric effect, the excited core-hole will relax back to a ground state of the atom. A higher level core electron drops into core hole and a fluorescent x-ray (or Auger electron) is emitted.**



$K_\alpha: L \longrightarrow K$, $K_\beta: M \longrightarrow K$.

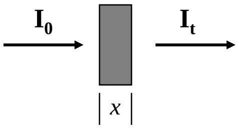
X-ray Fluorescence: An x-ray with energy equal to the difference in core-levels is emitted.

XRF occurs at discrete energies that are characteristic of the absorbing atom, and can be used to identify the absorbing atom.

The X-ray Absorption Coefficient: μ

- **Intensity of x-ray beam passing through a material of thickness *x* is given by the absorption coefficient μ:**

$$I_t = I_0 e^{-\mu x}$$



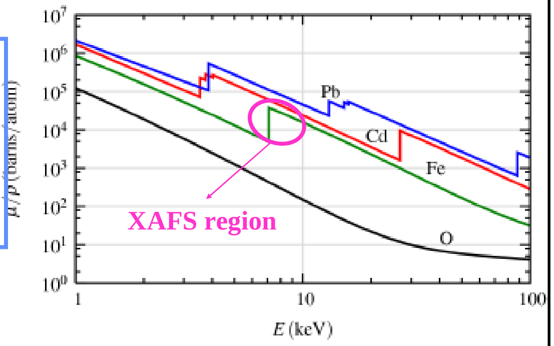
Where I_0 is the x-ray intensity impinging on the material and I_t is the intensity transmitted through the material.

The X-ray Absorption Coefficient: μ

μ has sharp absorption edges corresponding to the characteristic core-level energies of the atom.

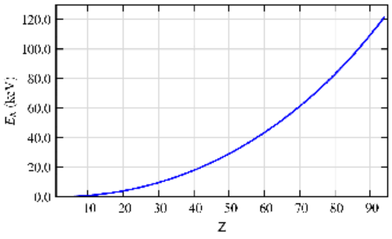
μ depends strongly on x-ray energy E and atomic number Z, and on the density ρ, and atomic mass A:

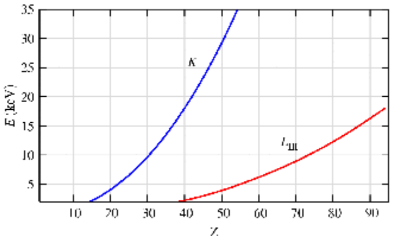
$$\mu \approx \frac{\rho Z^4}{AE^3}$$



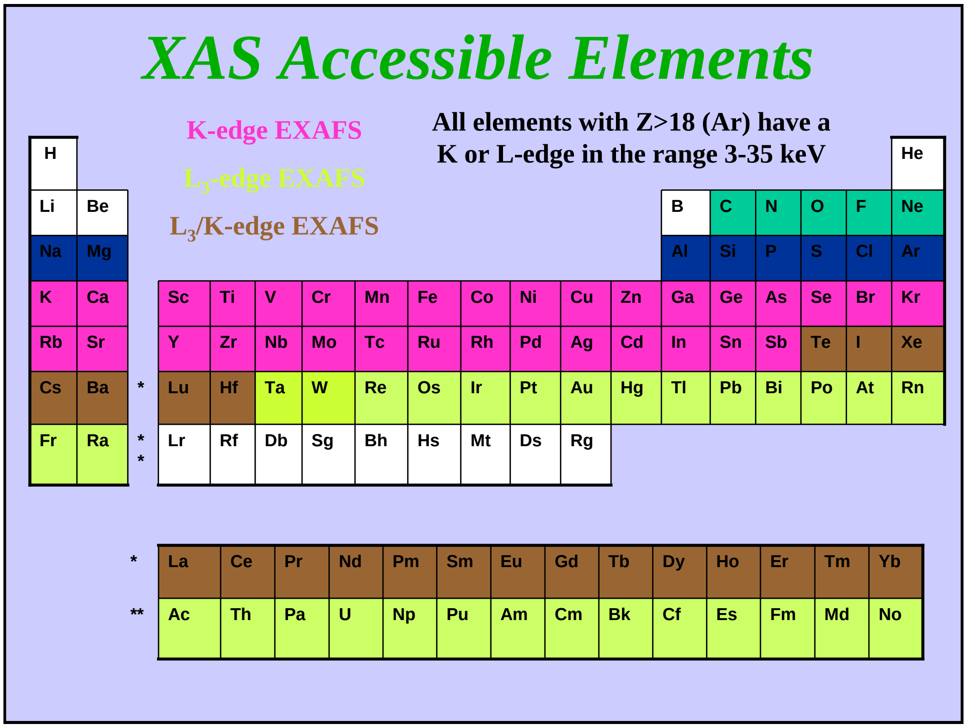
Absorption Edge Energies

- **The energy of the K-edge scales roughly as Z^2**





- **All elements with Z >18 (Ar) have either a K or L-edge between 3 - 35 keV – a convenient energy range for most synchrotron sources.**



XAS Accessible Elements

K-edge EXAFS

L_3-edge EXAFS

L_3/K-edge EXAFS

All elements with Z>18 (Ar) have a
K or L-edge in the range 3-35 keV

H																		He
Li	Be													B	C	N	O	F	Ne
Na	Mg													Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

X-ray Absorption Spectroscopy

A Honeywell Company

- XAS measures the energy dependence of the x-ray absorption coefficient $\mu(E)$ above the absorption edge of a particular element.

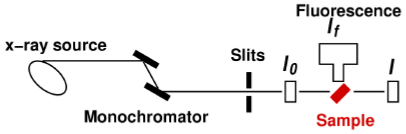
  $\mu(E)$ is measured in one of two ways:

  - **Transmission**: the absorption is measured by detecting the transmitted x-ray flux through the sample:

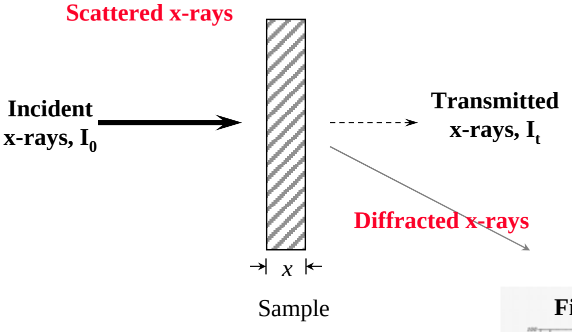
    $$I = I_0 e^{-\mu(E)x}$$
    $$\mu(E)x = \ln(I/I_0)$$

  - **Fluorescence**: the refilling of the deep core hole is detected. Usually the fluorescent x-ray is measured:

    $$\mu(E) \propto I_f/I_0$$



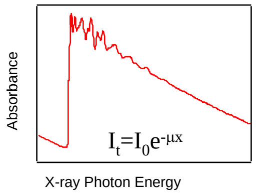
XAFS vs. XRD



X-ray Absorption

Incident Energy Varied

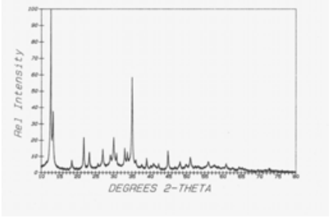
Short range order



Long range order

X-ray Diffraction

Fixed Incident Energy

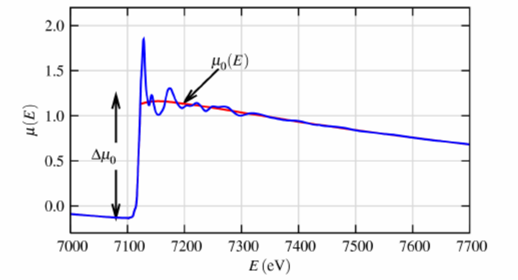


XAFS in Practice

- **We are interested in the energy dependent oscillations μ(E) as these tell us something about the neighboring atoms, so we define EXAFS as:**

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

  - **The "bare atom" background μ_0(E) is subtracted from the spectrum, and divided by the "edge step" Δu_0(E) to give the EXAFS oscillations normalized to one absorption event:**

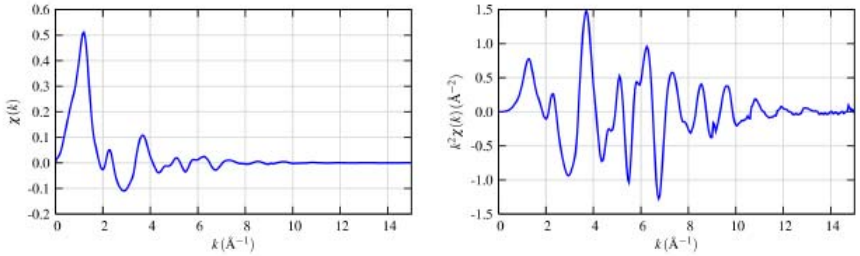


EXAFS: χ(k)

- **XAFS is an interference effect that depends on the wave nature of the photoelectron. It is therefore convenient to think of XAFS in terms of the photoelectron wavenumber, *k*, rather than x-ray energy:**

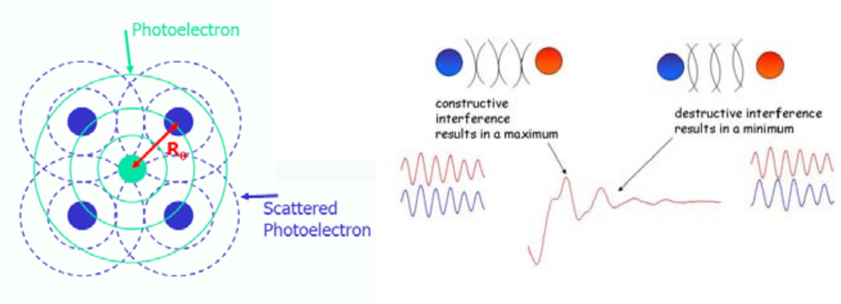
$$k=\sqrt{\frac{2m(E-E_0)}{\hbar^2}}$$

χ(k) is often weighted (multiplied) by k^2 or k^3 to amplify the oscillations at high-k



EXAFS: An interference effect

- **Photoelectron waves either constructively or destructively interfere, giving rise to oscillation in the amplitude.**



- **EXAFS spectrum comprised of a series of sine waves of different amplitude representative of the different scattering paths undertaken by the photoelectron wave.**

The EXAFS Equation

- To determine the structure surrounding the absorbing atom we fit the experimental EXAFS data using the EXAFS equation:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^{\,2}} \sin[2kR_j + \delta_j(k)]$$

- Where f(k) and δ(k) are photo-electron scattering properties of the neighboring atom.
- If we know these values then we can determine:
  - R distance to neighboring atoms
  - N coordination number of neighboring atoms
  - σ^2 mean-square disorder of the neighbor distance

- The scattering amplitude f(k) and the phase-shift δ(k) depend on the atomic number Z of the scattering atom, so this allows us to determine the neighboring element.

XAFS

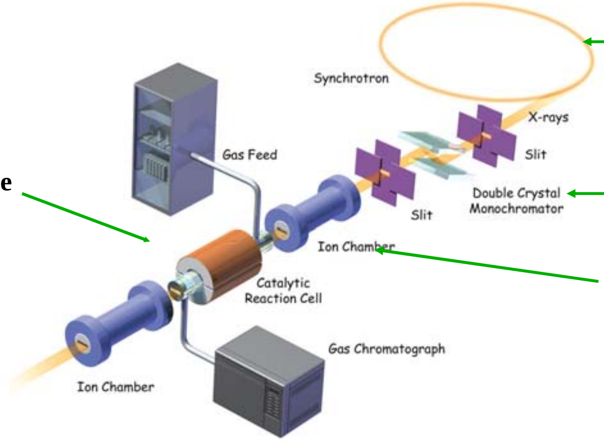
- *Elementally specific*: information around each element in multi-element catalyst can be determined separately.
- X-ray absorption is a *bulk technique* - but if the element of interest if highly dispersed then majority of atoms are surface atoms.
- *Local order only*: due to inelastic mean free path XAFS only probes local order (5-6 Å).
- *All elements* (except hydrogen).
- *Sensitivity*: bulk compounds to sub ppm.
- *All phases can be studied*: solids - both crystalline and amorphous, liquids and gases.
- EXAFS is a photon-in / photon-out spectroscopy so data can be collected under extreme conditions.
- *Spatial information* - with specialized experiments.

EXAFS Measurement

Important Considerations

- **Monochromatic x-rays**: need x-rays with small energy spread $\Delta E \sim 1$ eV at 10 keV
- **Linear Detectors**: the XAFS signal is small ($\chi(k) \sim 10^{-2}$ of total signal), so lots of photons needed and detectors that are linear in x-ray intensity
- **Well-aligned Beam**: the x-ray beam hitting the detectors should be the same as that hitting the sample
- **Homogeneous Sample**: uniform and of appropriate thickness, free of pinholes
- **Counting Statistics**: good $\mu(E)$ data should have a noise level of $\sim 10^{-3}$, so need to collect at least $\sim 10^6$ photons

Elements of an XAFS Experiment



X-ray source

Sample

Beam line

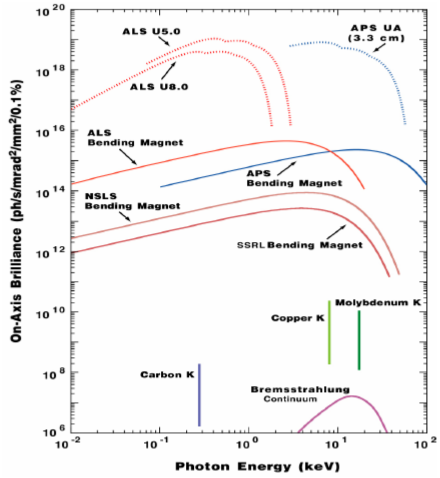
X-ray detectors

X-ray Source: Synchrotron

- Electrons at near relativistic energies are confined to an orbit by a series of magnets. As electrons are deflected through a magnetic field they give off electromagnetic radiation.
- Synchrotron light:
  - Tunable
  - High Intensity
  - Collimated
  - Polarized
  - Time structure

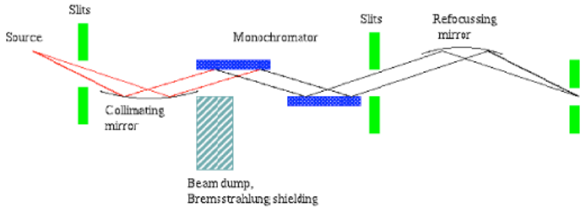
Synchrotron Radiation

- Broad spectrum of radiation: from UV to hard X-rays.



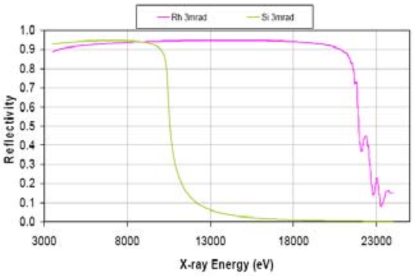
Beamline

- Used to “transport” and condition the synchrotron radiation (x-rays) for the XAFS experiment.
- Slits, mirrors, monochromator, shutter – similar to any other electromagnetic radiation source e.g. FTIR – only on a larger scale.



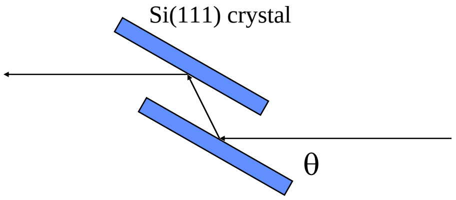
X-ray Mirrors

- Glancing incidence needed for reflectivity in x-ray energy range.
- Ultra-smooth surfaces needed (<1nm rms roughness).
- Small angles mean mirrors need to be long.
- Mirrors used to collimate and focus the beam by bending.
- Also used for harmonic rejection.



Monochromator

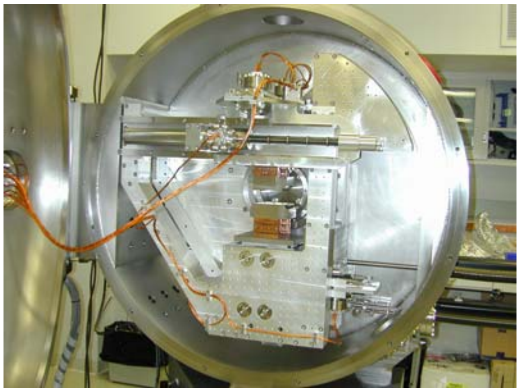
- Used to select energy (wavelength) of interest: For EXAFS need x-rays with small energy spread: ΔE ~1 eV at 10 keV
- Must be able to scan the energy for XAFS.
- Must be very stable.



Si double crystal monochromator – energy scanned by rotating θ

- White beam impinges on perfect single crystal of Si of specific orientation.
- Photons that meet the Bragg diffraction condition $n\lambda = 2d_{hkl}\sin(\theta)$ are diffracted.
- Second crystal simply redirects the beam parallel to incident beam.

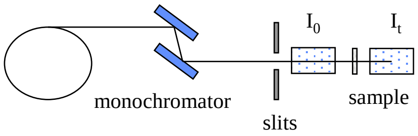
Monochromator



33-BM Monochromator at APS

Transmission XAFS Experiment

- Used for concentrated samples (>1wt%)



- Use ionization chamber to detect incident and transmitted x-rays.

Photon is absorbed by gas atom (He, N_2, Ar -dependent on energy)

Photoelectrons emitted (ionization)

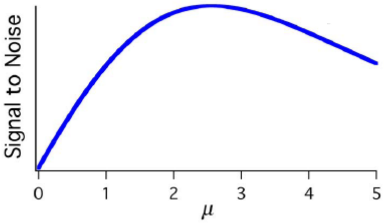
These electron initiate more ionization

High voltage bias across plates causes electron and ions to drift in opposite directions.

Charges collected result in current flow which is proportional to the incident x-ray intensity

Transmission XAFS Experiment

- Need to get enough transmission through the sample to get a decent signal with I_t ion chamber.
- Sample thickness is adjusted so that $\mu(E)x \approx 2.5$ above the absorption edge, and/or edge step $\Delta\mu(E)x \approx 1$.



If sample too thick most photons do not get through

If sample too thin most photons do not interact

Ideal: μ ~ 2-3

Transmission XAFS Experiment

- “For transmission measurements the ideal sample is uniform and has a thickness of ~2 absorption lengths. It should be free of pinholes (areas of high x-ray transmission). If a powder the grains should be very fine (<< absorption length) and uniform”.
- Transmission EXAFS experiment relatively easy experiment and should give excellent data – if care is given to experimental details.

Transmission XAFS Experiment : Absorption Length

- **Absorption length should always be calculated before beginning an XAFS measurement.**
  - **Absorption length = 1/μ**

    (distance over which x-ray intensity drops by 1/e = 37%).
  - **For single substance $\mu = \rho.\sigma$**
    - **Where ρ = density (g/cm^3) and σ = cross section (cm^2/g)**
  - **For multi-element substance:** $$\mu = \rho_M \sum_i \frac{m_i}{M}\sigma_i$$
    - **Where ρ_M is the density, m_i/M is the mass fraction of element *i***

Transmission XAFS Experiment : Absorption Length

Fe_3O_4 at 7.2 keV

Density 5.2 g/cm^3

MW = 231.7 g/mol

σ_{Fe} = 393.5 cm^2/g; M_{Fe} = 55.9 g/mol
f_{Fe} = 55.9/231.7 = 0.724

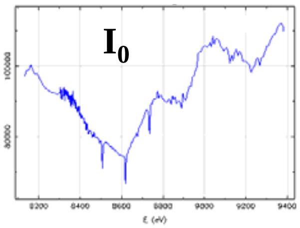
σ_O = 15.0 cm^2/g; M_O = 16.0 g/mol
f_O = 16/231.7 = 0.276

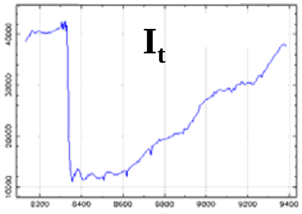
μ = 5.2 g/cm^3 x [(0.724 x 393.5 cm^2/g) + (0.276 x 15.0 cm^2/g)]
= 1503 cm^{-1}
= 0.15 μm

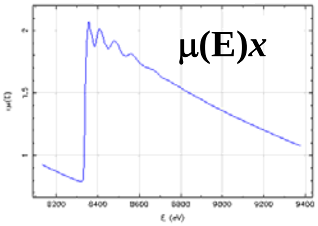
Absorption length = 1/0.15 μm = 6.7 μm

Transmission XAFS Experiment

- The x-ray energy is scanned across the absorption edge of the element of interest. The intensity of the incident beam and transmitted beam through the sample are measured.



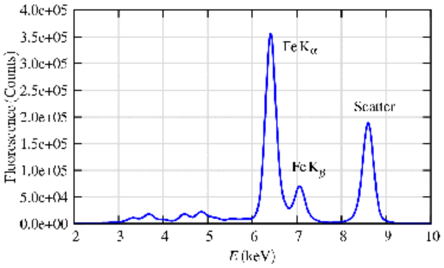




$$\mu(E)x = -\ln(I/I_0)$$

Fluorescence XAFS Experiment

- For thick samples (no transmission) or for low concentration (down to ppm levels) measuring the x-ray fluorescence is the preferred measurement.



- The x-rays emitted by the sample will include the fluorescence line of interest (e.g. Fe Kα and Fe Kβ) as well as scattered x-rays, and other fluorescence lines (Ca, Ti, and V in this sample).

- In many cases the scatter or other fluorescence lines will dominate the fluorescence spectra.

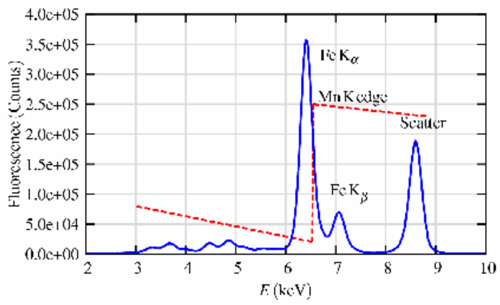
Fluorescence XAFS Experiment

- Two main considerations for getting good quality fluorescence measurement:
- Energy discrimination: It may be helpful to either physically or electronically filter the unwanted portions of the fluorescence/scatter spectrum.
- Solid Angle: The fluorescence is emitted isotropically in all directions so collecting as much of the 4π solid angle as possible is good (large detector, close to sample)

Fluorescence XAFS Experiment

- Fluorescence - filtering

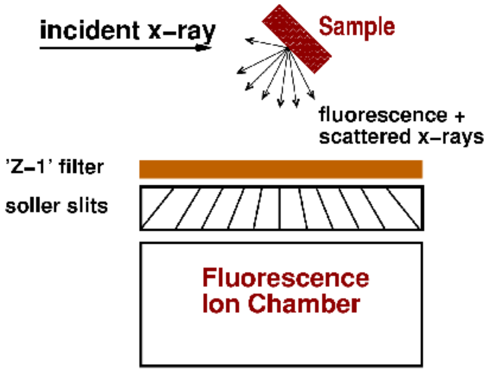
- Simple method of energy discrimination uses a filter of "Z-1" (for K-edges up to Z=42) from the element of interest.
- For Fe, a Mn filter absorbs the scatter, while passing the Fe K_α line.
- Choice of filter more complex for L-edges



Fluorescence XAFS Experiment

- Typical fluorescence setup with filter using an ion chamber with no energy resolution – but high count rate and linearity, and reasonable solid angle.

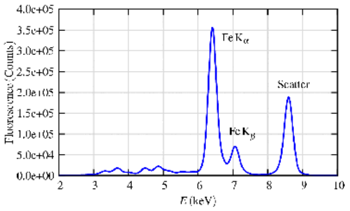

Five grid fluorescent x-ray ion chamber detector

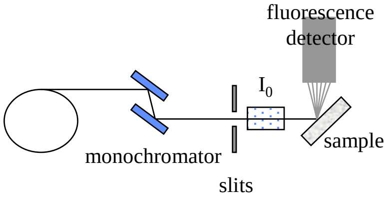


- Sample at 45° to the beam to minimize scatter.
- Because the filter absorbs the scattered beam, it can itself re-radiate X-rays.
- Set of Soller slits used to "see" the sample, but absorb most of the re-radiate scatter from the filter.
- Very effective arrangement for FY XAFS.

Fluorescence XAFS Experiment: Solid State Detectors

- Alternative is to use a solid state detector with active element of Ge or Si as the x-ray absorber. This uses electronic energy discrimination.
- Typical energy resolution 200-300 eV.
- Has advantage of measuring the full x-ray fluorescence spectrum, so useful for identifying other elements in sample.
- Can be used for XAFS measurements with concentration to 10's of ppm.





Fluorescence XAFS Experiment: Self Absorption

UOP
A Honeywell Company

- The fluorescent x-ray has to get out of the sample to be detected and can be attenuated by the sample itself. The self-absorption can severely damp the XAFS – both XANES and XAFS
- Do not record XAFS of bulk reference compounds (foils) in fluorescence if you want to use these data to calibrate intensity of the XAFS signal (S_0^2), or to conduct linear combination fitting of XANES spectra.

Specialized XAFS Experiments

UOP
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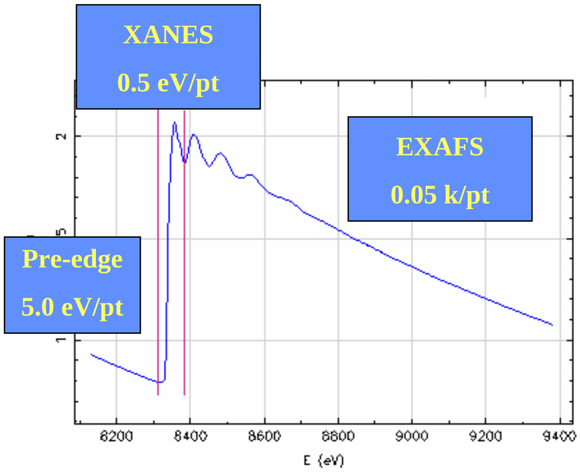
- XAFS spectra can also be measured using other modes of detection:
    - Total electron yield
    - Partial electron yield
- XAFS can also be detected using glancing incident angle to limit penetration into sample (ReflEXAFS).
- XAFS can also be measured making use of the polarization dependence of the x-rays.

The EXAFS Scan

- Setting up the scan parameters:



XANES

0.5 eV/pt

EXAFS

0.05 k/pt

Pre-edge

5.0 eV/pt

The EXAFS Scan

- Need to scan the monochromator using appropriate settings for an EXAFS experiment.

Region	Starting Energy (eV)	Ending Energy (eV)	Step Size (eV)
Pre-edge	-200	-20	5.0
XANES	-20	+30	0.5
EXAFS	+30	~900	0.05 Å^{-1}

All values relative to a nominal x-ray absorption edge energy, E_0

- In EXAFS range common to step in units of k rather than energy.
- Typical counts times are 1-15 s per point, so EXAFS measurements take few minutes to many hours.
- Some beamline software allows you to weight the time with increasing k.

K-range

- k has been defined as:

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

- But in a more useful form:
  - $k = (0.2625 \times E)^{1/2}$

E (eV)	k (Å-1)
10	1.6
20	2.3
30	2.8
40	3.2
50	3.6
75	4.4
100	5.1
150	6.3
200	7.2
250	8.1
500	11.5
750	14.0
1000	16.2

XAFS Data Reduction

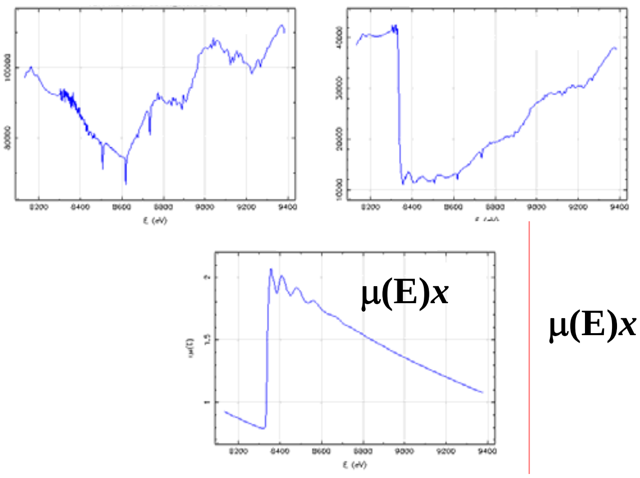
Data Reduction: Strategy

- **Steps for reducing measured data to $\chi(k)$:**

1. **Convert measured intensities to $\mu(E)$**
2. **Subtract a smooth pre-edge function, to get rid of instrumental background, and absorption from other edges.**
3. **Normalize $\mu(E)$ to from 0 to 1, so that it represents absorption on a per atom basis.**
4. **Remove a smooth, post-edge background function to approximate m0(E) to isolate the XAFS, χ.**
5. **Identify the threshold energy, E_0, and convert from E to *k* space.**
6. **Weight the XAFS $\chi(k)$ and Fourier transform from k to R space.**

Data Reduction: Converting Raw Data to $\mu(E)$

- **Starting with measured intensities before (I_0) and after the sample (I_t), we construct $\mu(E)$ for transmission XAFS:**

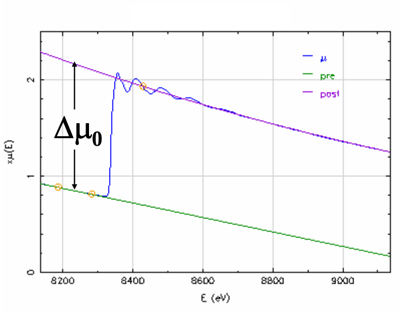


$$\mu(E)x = -ln(I/I_0)$$

Data Reduction: Pre-edge Subtraction, Normalization

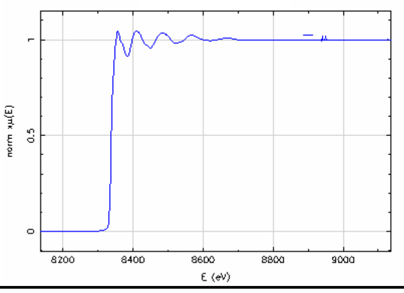
Pre-edge Subtraction

- Subtract away the background that fits the pre-edge region. This removes the absorption due to other edges in the sample.



Normalization

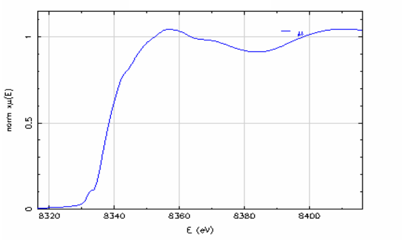
- Edge step $\Delta\mu_0(E_0)$ is estimated by extrapolating a simple fit to $\mu(E)$ above the edge. Normalize by dividing by this value to get unity absorption.



Data Reduction: Normalized XANES and E_0

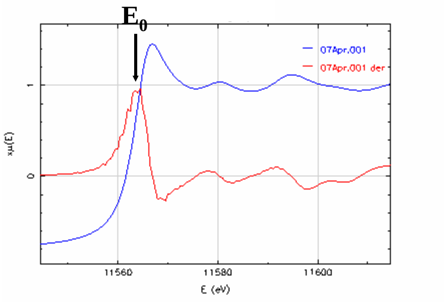
XANES

- XANES portion of spectrum often shows rich spectral detail. Can be used to supply significant information about the sample.



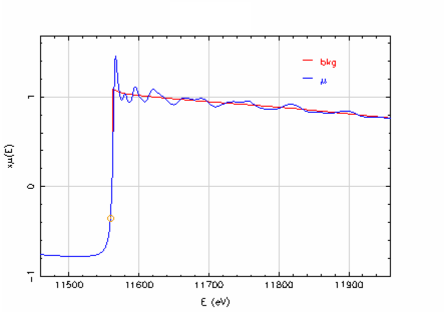
Derivative

- E_0 selected roughly as the energy with the maximum derivative. This is somewhat arbitrary – this may need to be refined during an EXAFS fit.



Data Reduction: Post-edge Background Subtraction

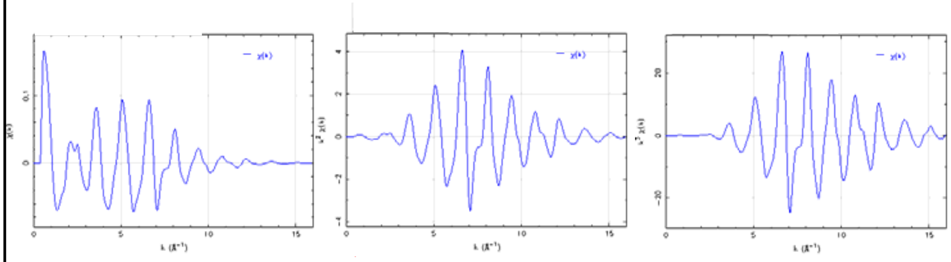
- **Post-edge Background**
- **It is not possible to independently measure $\mu_0(E)$ (the absorption coefficient without neighboring atoms). It is approximated by and adjustable, smooth function – a *spline*.**
- **This must be done with some care. A flexible enough spline could match the frequency of $\mu(E)$ and remove all the EXAFS.**



Data Reduction: $\chi(k)$, k-weighting

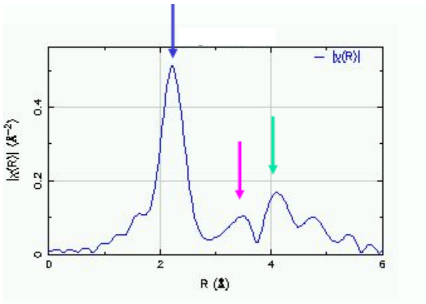
$\chi(k)$

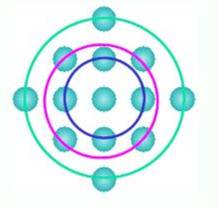
- **The raw EXAFS $\chi(k)$ usually decays quickly with k, and difficult to assess quality and interpret by itself.**
- **It is customary to weight the higher-k portion of the spectra by multiplying by k^2 or k^3.**



Data reduction: Fourier Transform

- One way to separate the sine waves from one another is to perform a Fourier transform.
- The resulting magnitude of the transform now has peaks representative of the different scattering paths of the photoelectron.





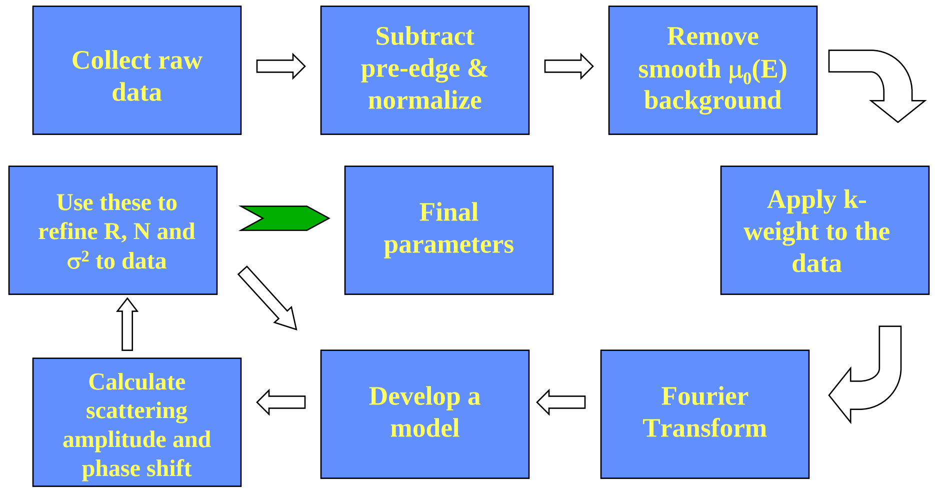
EXAFS Analysis: Modeling the Data

- The experimental EXAFS data are now ready for fitting to a structure:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

- This is what this course is all about – and you will hear much more about this in the coming week.
- Important point – EXAFS is not a real-space structural technique: a model of the presumed structure is needed to fit the data.

EXAFS Analysis



Collect raw data

Subtract pre-edge & normalize

Remove smooth $\mu_0(E)$ background

Apply k-weight to the data

Fourier Transform

Develop a model

Calculate scattering amplitude and phase shift

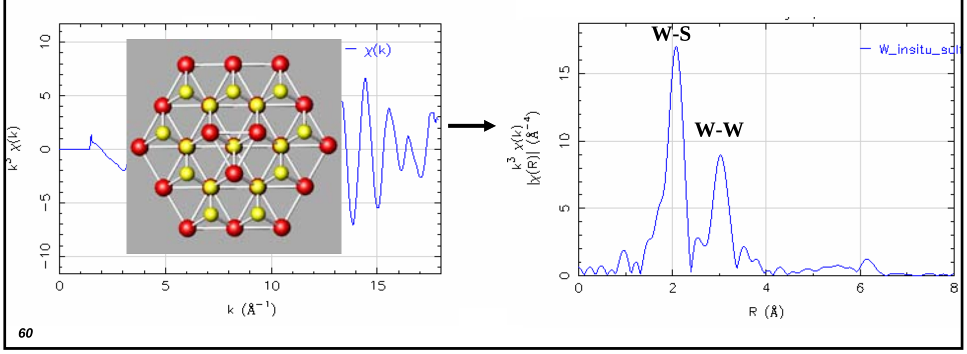
Use these to refine R, N and σ^2 to data

Final parameters

EXAFS

- EXAFS provides quantitative information on:
  - Distance to neighboring atoms (average bond length, R)
  - Coordination number and type of the neighboring atoms (N_j)
  - Mean-square disorder of neighboring atoms (σ_j^2)

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$



XANES

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!

* Some transitions are true quadrupolar transitions. These are usually very weak.

l=0 is s-orbital; l=1 is p-orbital; l=2 is d-orbital

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

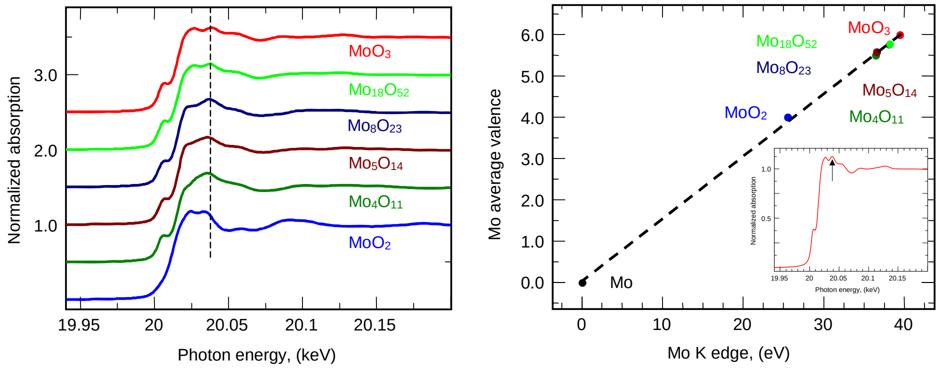
- These chemical and physical interpretations are all related:
  - What electronic states can the photoelectron fill?

XANES: Advantages

- 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

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!

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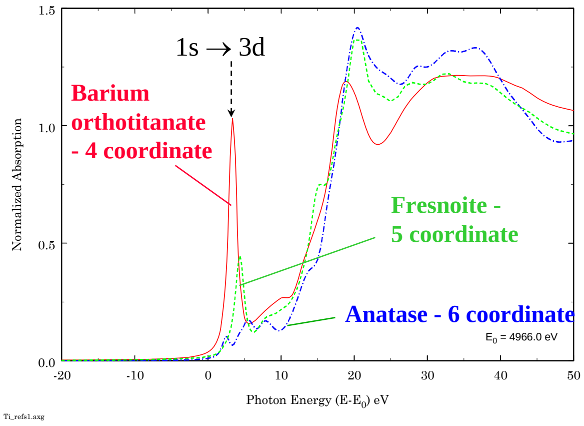
XANES: Geometry

Ti K-edge XANES: Reference Compounds



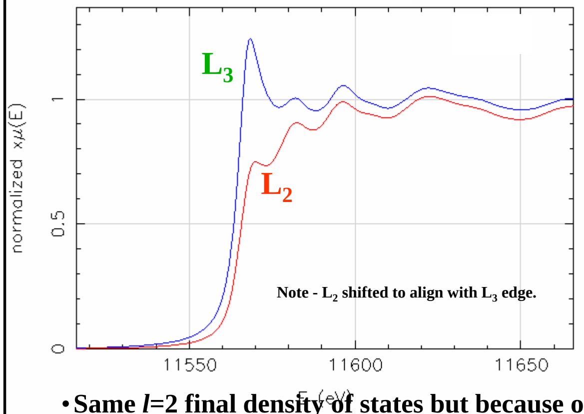
Anatase

- 3d split by mixing with O2p into t_{2g} and e_g like orbitals.
- 3rd peak is quadrupolar in nature

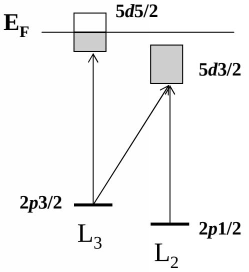
- **Symmetry around absorbing atom strongly affects pre-edge transition: ability to differentiate 4, 5, 6-fold coordination.**

XANES: Pt L_3 and L_2 Edge

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



Note - 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, Δ*j* = ±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.**

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- **Many websites: e.g. http://www.xafs.org and http://www.i-x-s.org/**