X-ray Absorption Spectroscopy

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Modern Methods in
Heterogeneous Catalysis Research

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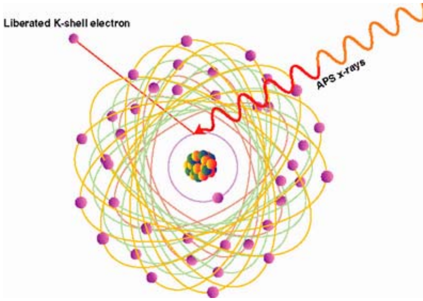


Outline

- X-ray absorption process
- Introduction to information content of x-ray absorption spectroscopy
- Elements of an x-ray absorption spectroscopy experiment
- Data analysis & development of EXAFS equation
- Examples of application to catalyst characterization: XANES
- Examples of application to catalyst characterization: EXAFS

Acronyms

EXAFS – Extended X-ray Absorption Fine Structure

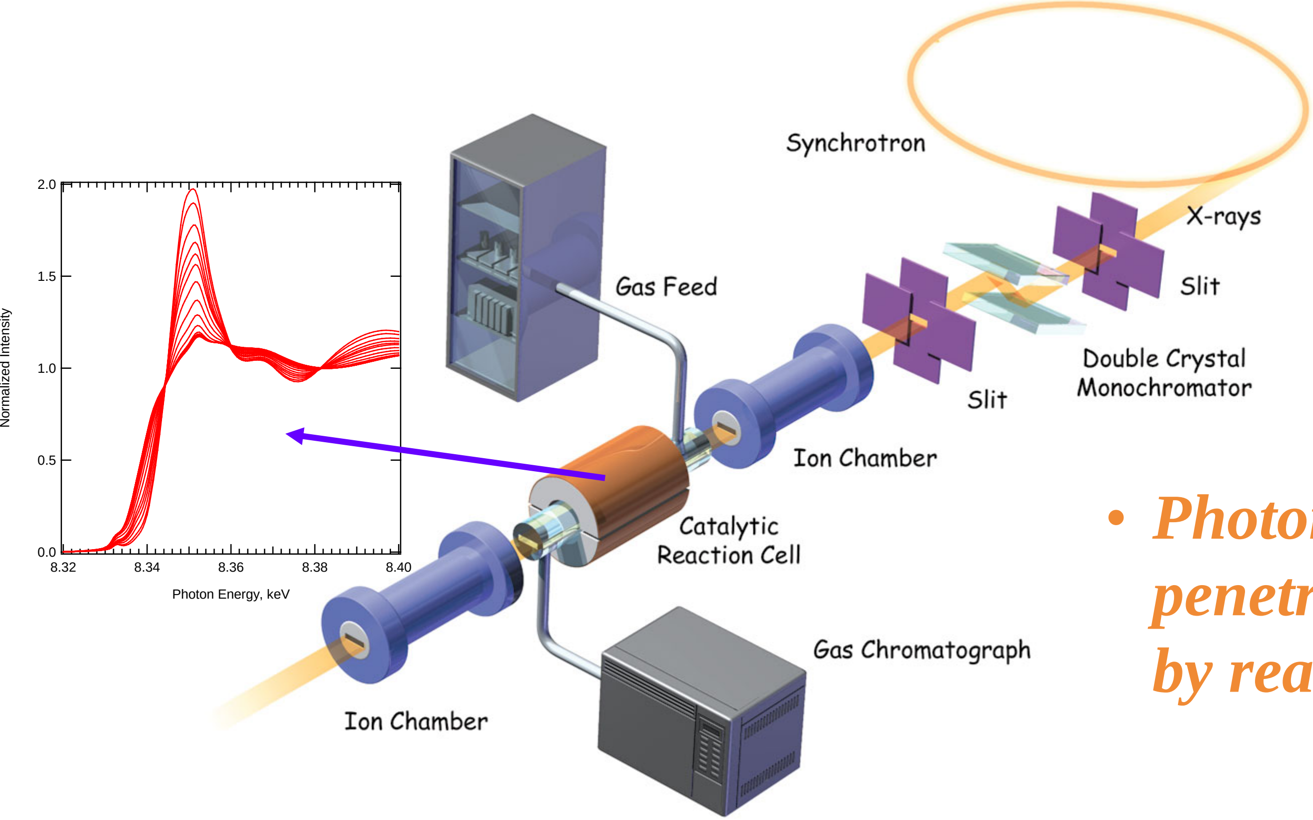
XAS – X-ray Absorption Spectroscopy

XAFS – X-ray Absorption Fine Structure

XANES - X-ray Absorption Near Edge Structure

NEXAFS- Near-Edge X-ray Absorption Fine Structure

Why X-ray Absorption Spectroscopy for Catalyst Characterization?



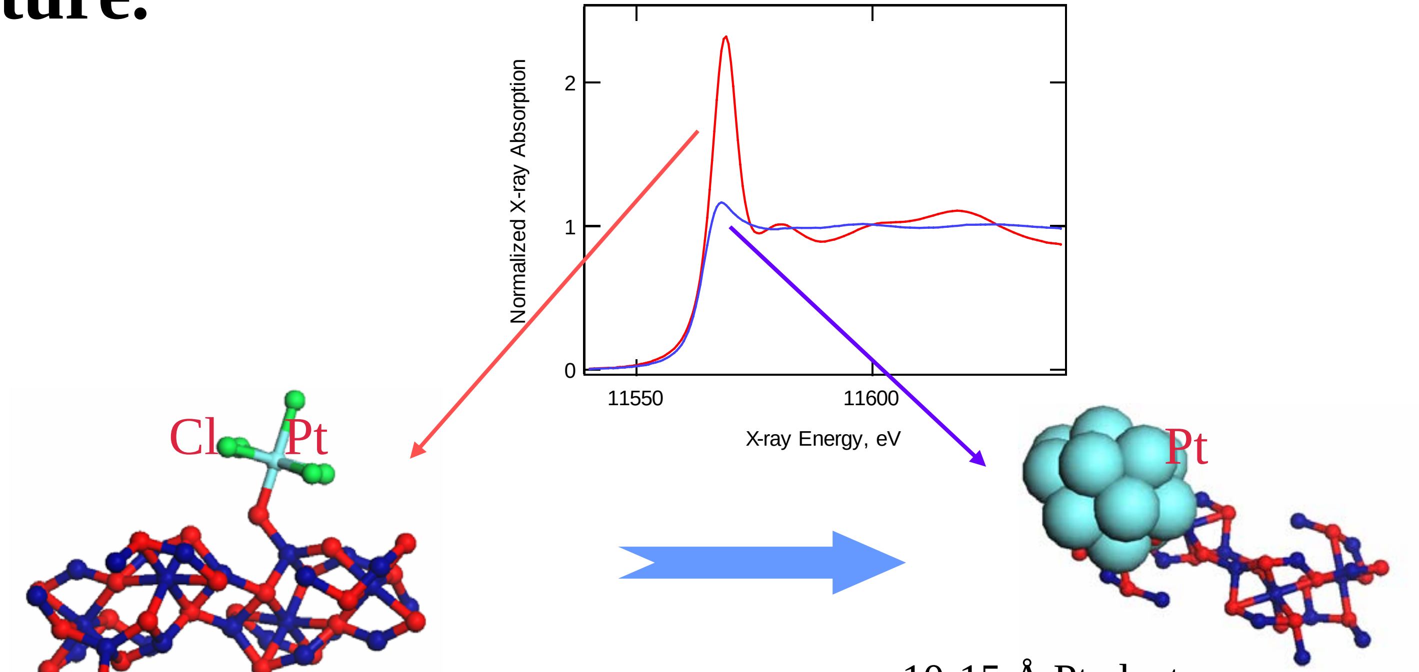
In situ!

- ***Photons sufficiently penetrating that absorption by reaction gas is minimal.***

Can probe the catalyst structure under reaction conditions!

Why are we Interested in XAFS?

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

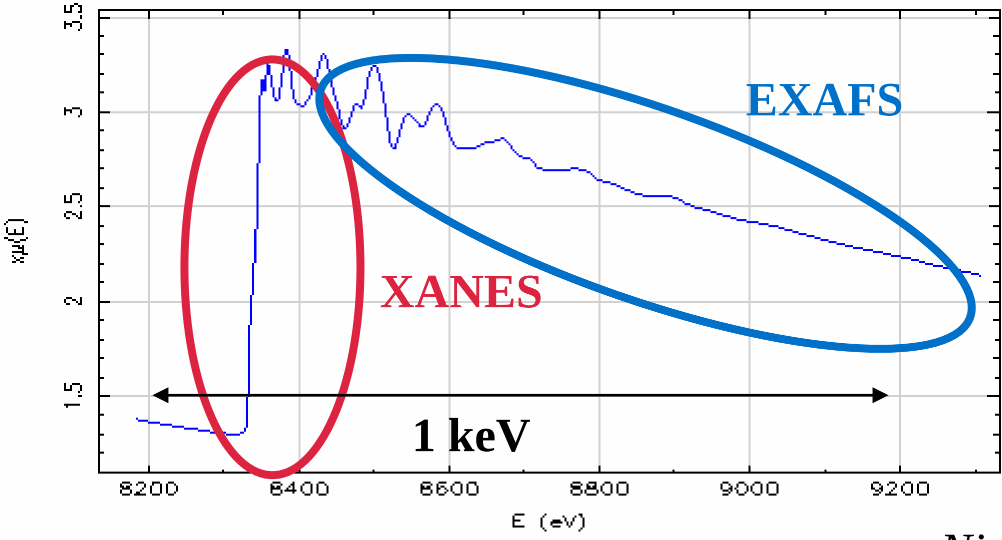


Chloroplatinic acid complex on Al_2O_3

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!

Extended X-ray Absorption Fine Structure (EXAFS)

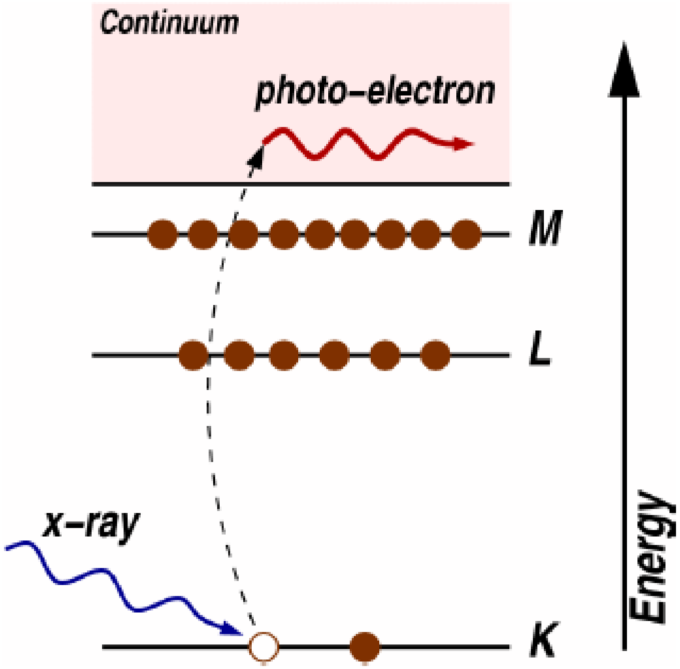
- **Provides quantitative information on:**
  - **Distance to neighboring atoms (average bond length, R_j)**
  - **Coordination number and type of the neighboring atoms (N_j)**
  - **Mean-square disorder of neighboring atoms (σ_j^2)**

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

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.**

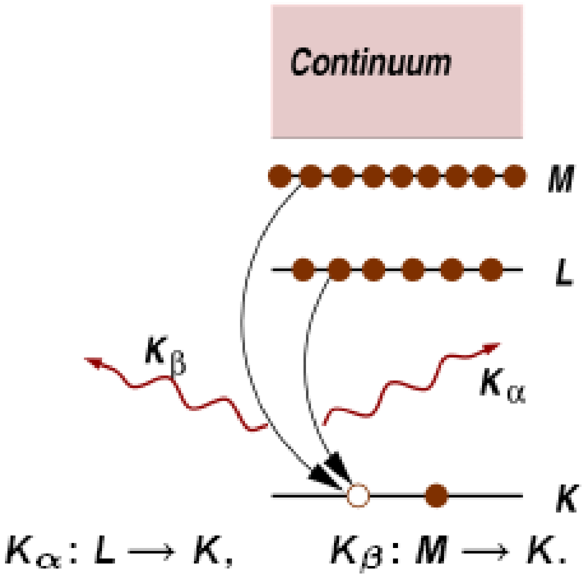


Absorption Edges: Nomenclature

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.**



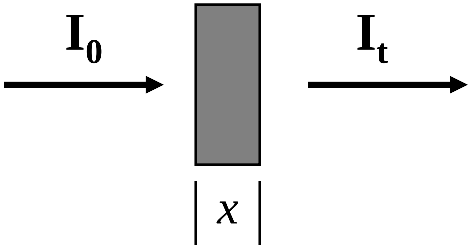
X-ray Fluorescence: An x-ray with energy equal to the difference in core-levels is emitted.

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:**

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



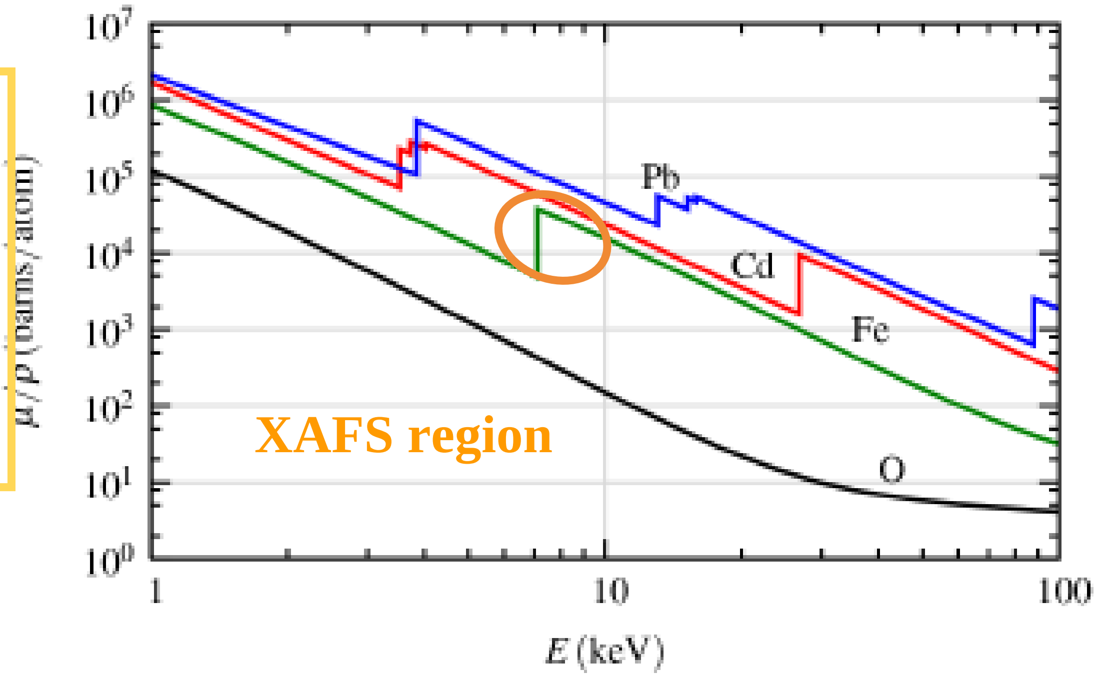
Where I_0 is the x-ray intensity impinging on the material and I_t is the intensity transmitted through the material.

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:

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



X-ray Absorption Spectroscopy

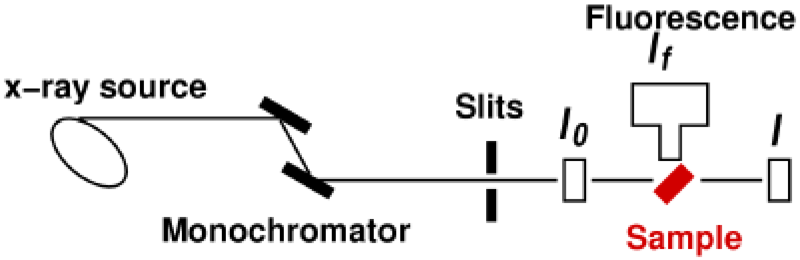
- **XAS measures the energy dependence of the x-ray absorption coefficient $\mu(E)$ above the absorption edge of a particular element.**
- **$\mu(E)$ is measured in one of two ways:**
  - **Transmission: the absorption is measured by detecting the transmitted x-ray flux through the sample:**

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

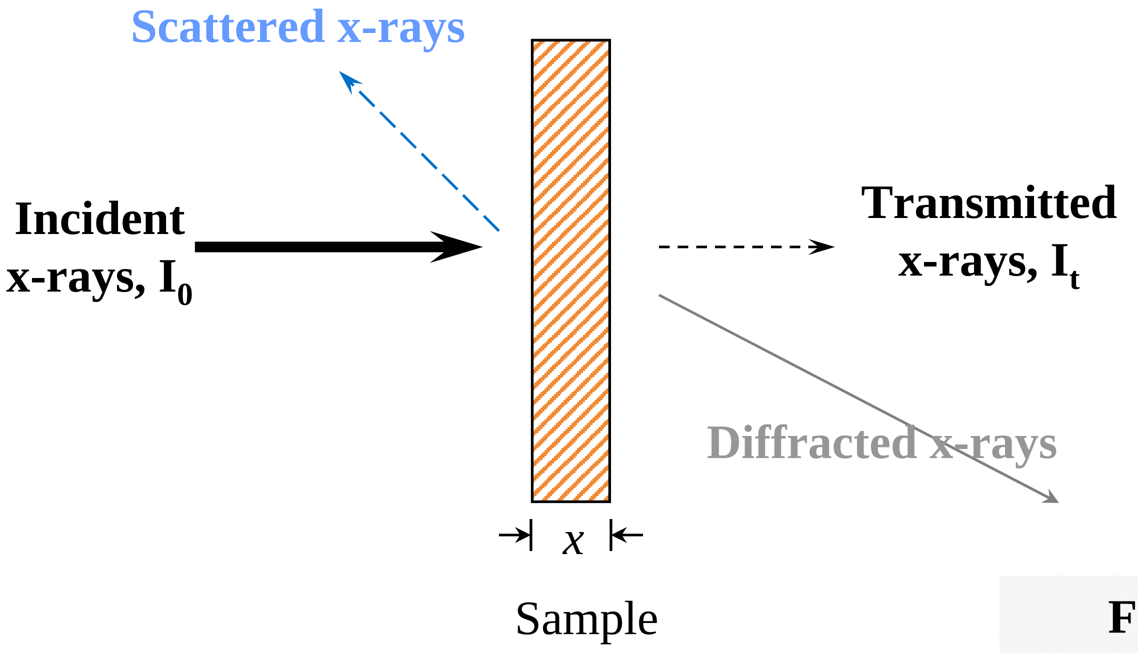
$$\mu(E)x = \ln(I/I_0)$$

  - **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



Scattered x-rays

Incident x-rays, I_0

Transmitted x-rays, I_t

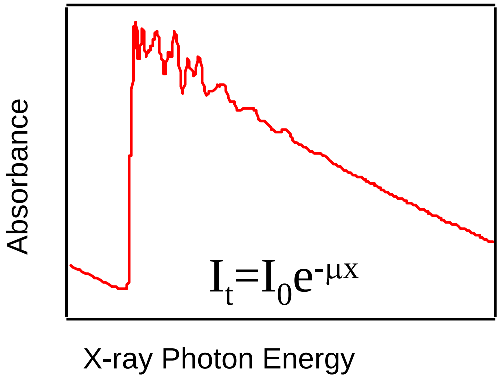
Diffracted x-rays

Sample

X-ray Absorption

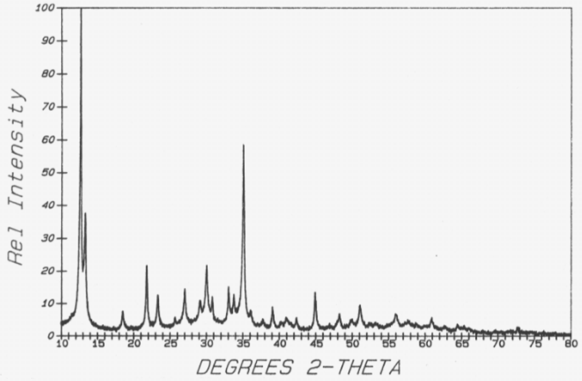
Incident Energy Varied

Short range order



X-ray Diffraction

Fixed Incident Energy

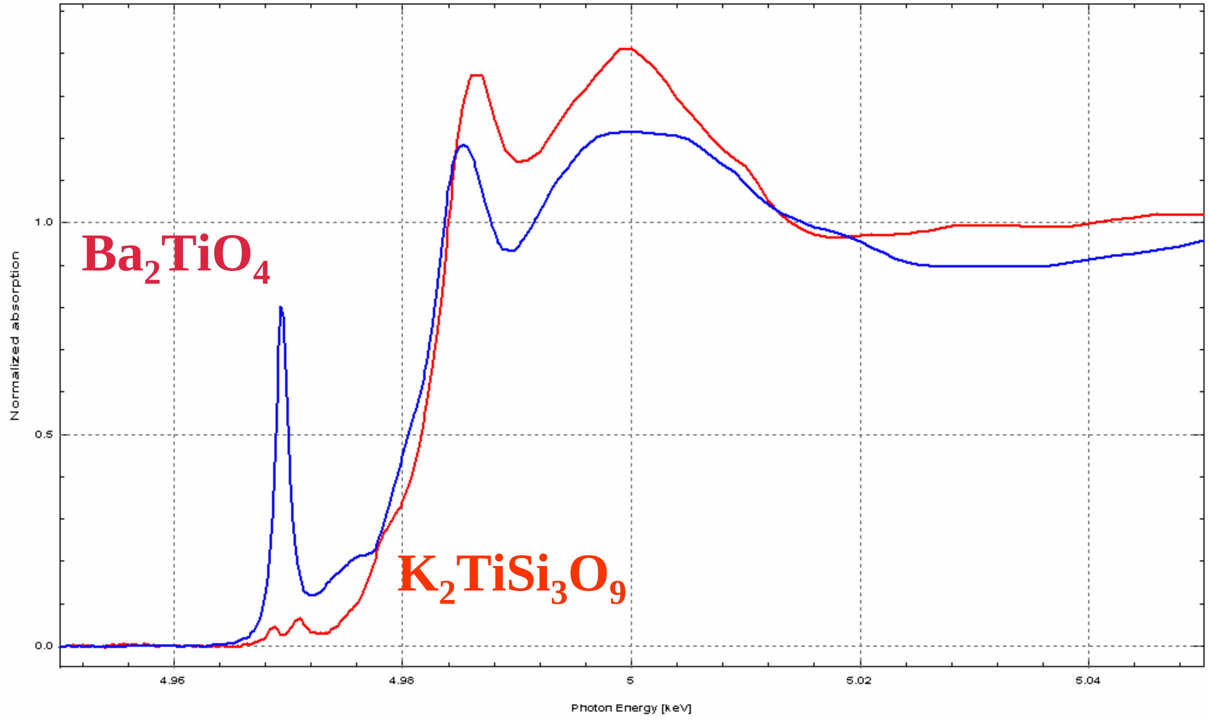


Long range order

XAFS

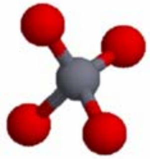
- **Can be used for *in situ* structure determination: photon-in / photon-out.**
- ***Elementally specific*: information around each element in multi-element catalyst can be determined separately.**
- **X-ray absorption is a *bulk technique* - but if the element of interest if highly dispersed then majority 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.**
- ***Spatial information* - with specialized experiments.**

XANES: Local Coordination Environment



Both Ti^{4+}

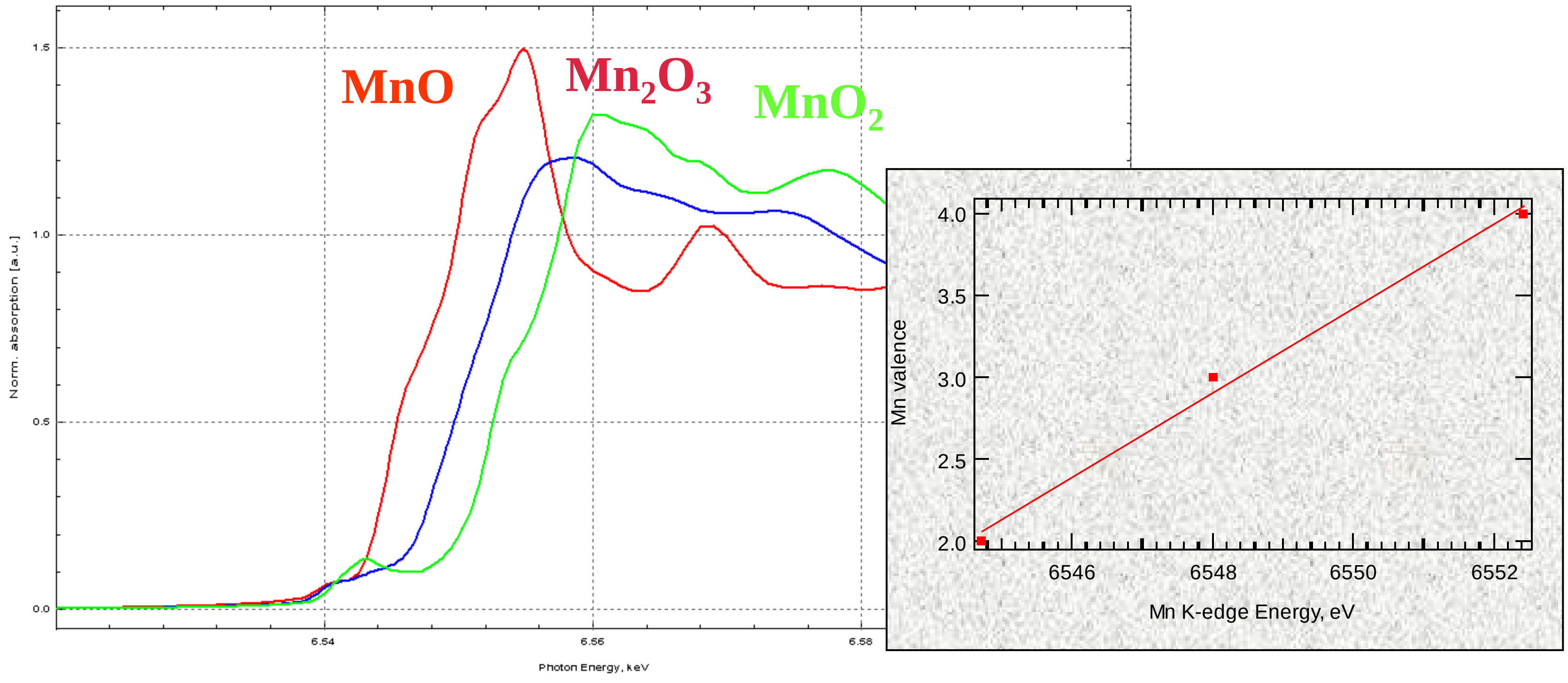
Ba$_2$TiO$_4$



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

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

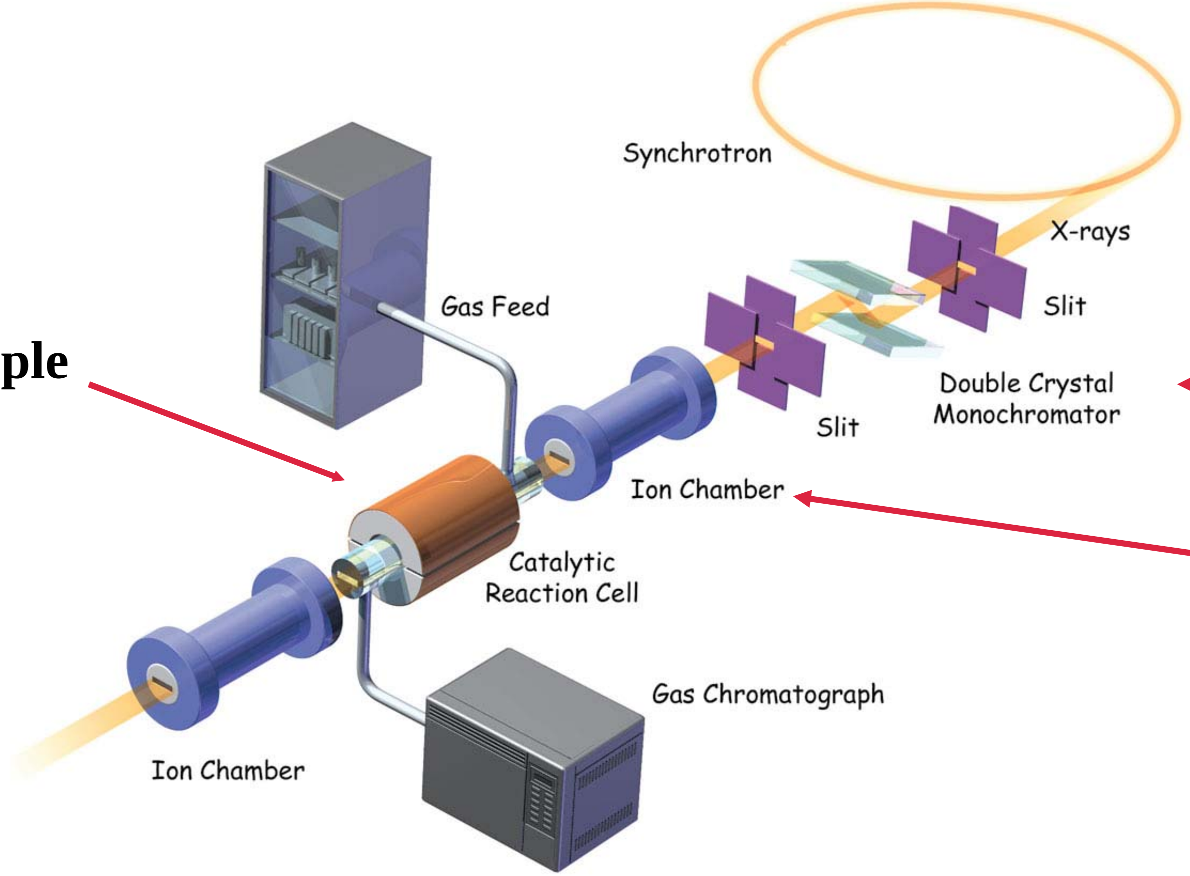
XANES: Oxidation State



- 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)

Elements of an XAFS Experiment



X-ray source

Beam line

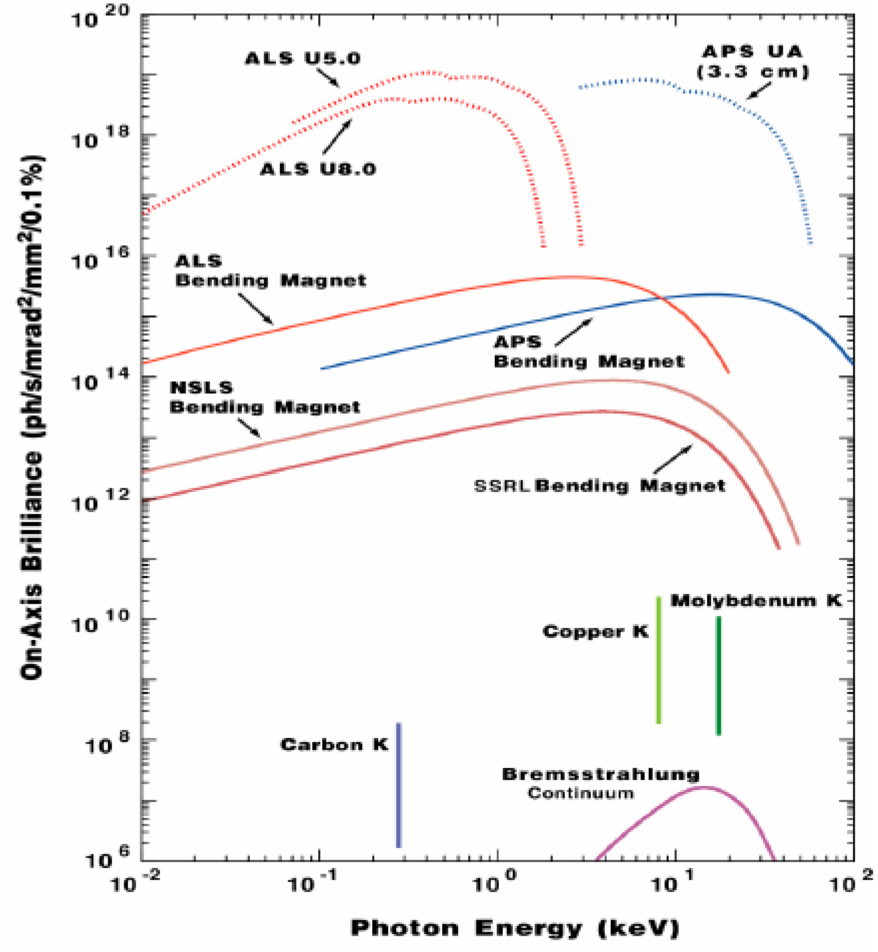
Sample

X-ray detectors

X-ray Source: Synchrotron

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

Synchrotron Radiation



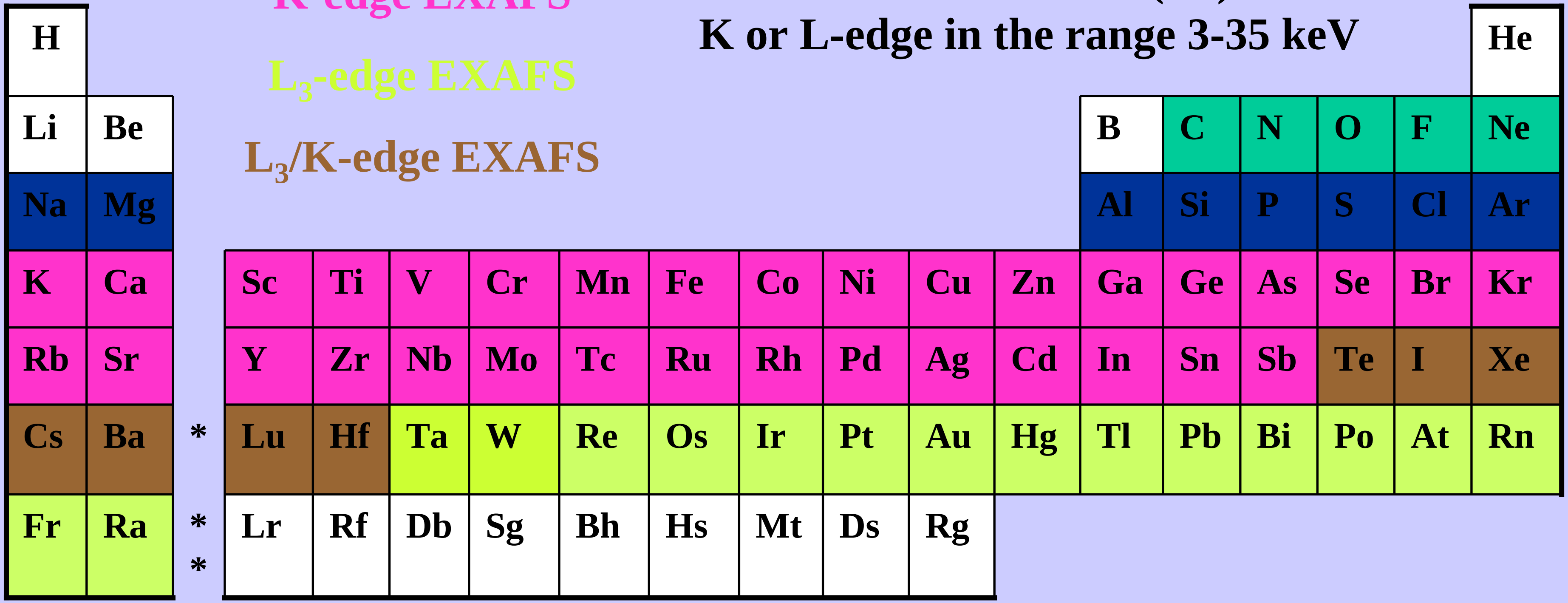
XAS Accessible Elements

K-edge EXAFS

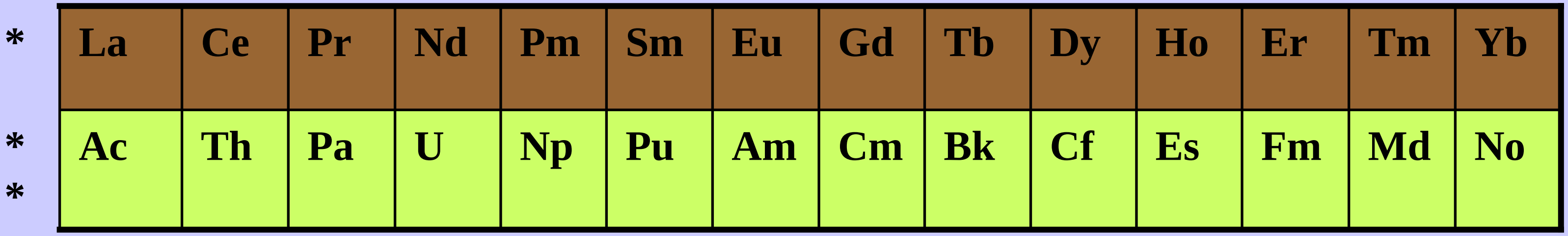
L_3-edge EXAFS

L_3/K-edge EXAFS

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



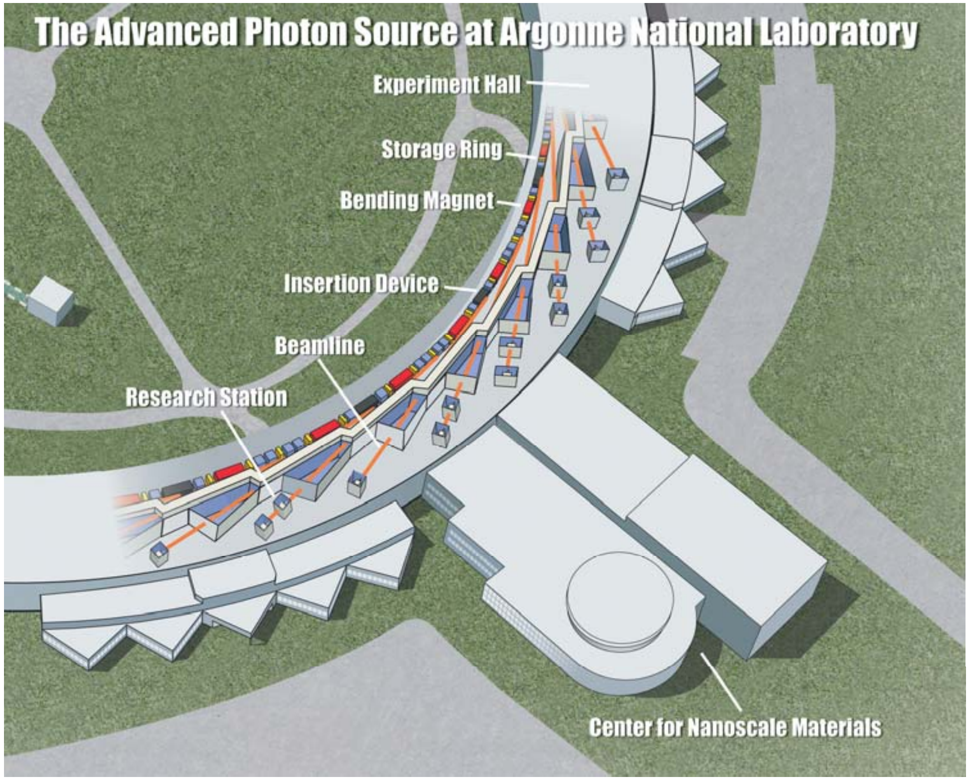
H																		He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

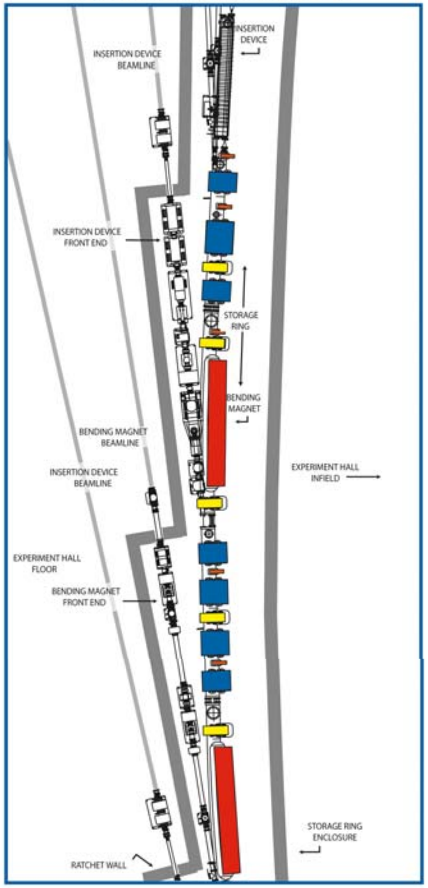


*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

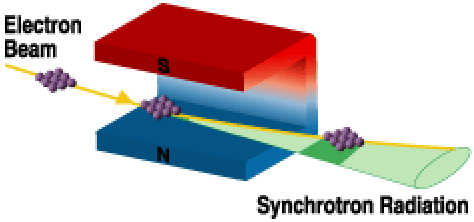
X-ray Source: Synchrotron

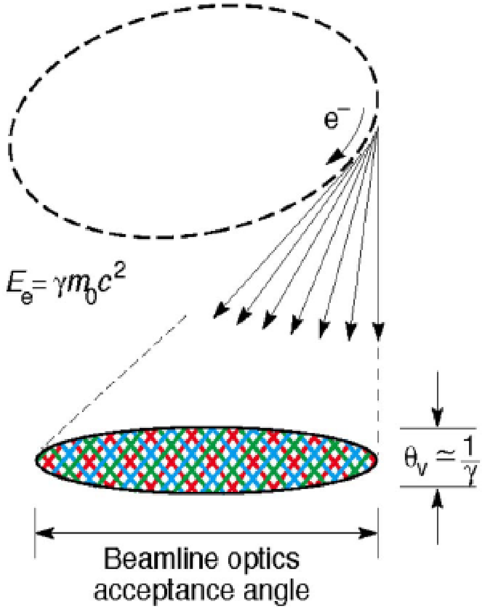
- **Typical layout of sector of a synchrotron source (Advanced Photon Source, Argonne National Laboratory)**

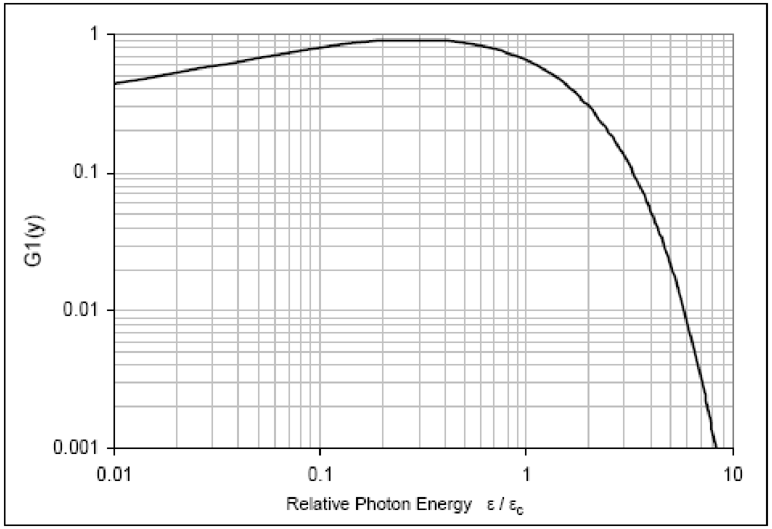



Typical APS Storage Ring Sector, Beamline, and Front End Configuration

Bending Magnets







Emitted Radiation has Characteristic Photon Energy

$$\varepsilon_c = 0.665\, B_\circ\, E^2$$

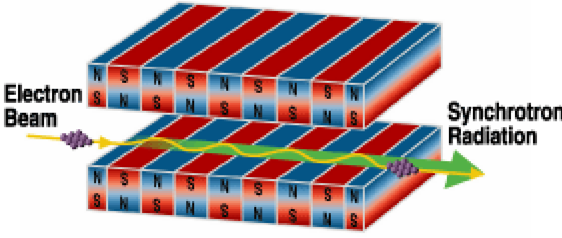
ε_c – Critical Photon Energy [keV]

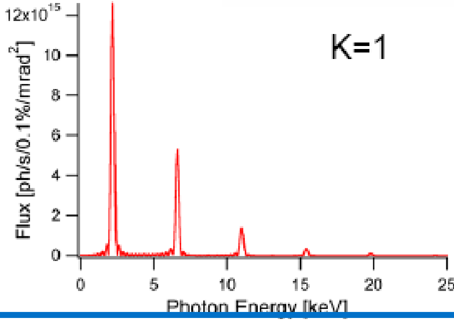
E – Electron Energy in [GeV]

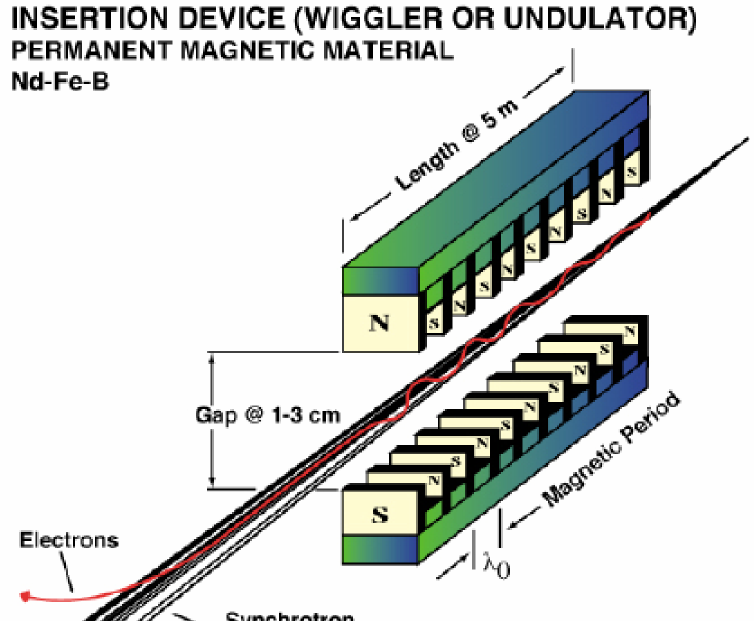
B_o – Magnetic Field in [Tesla]

- **Continuous source of radiation**
- **Spatially broad**

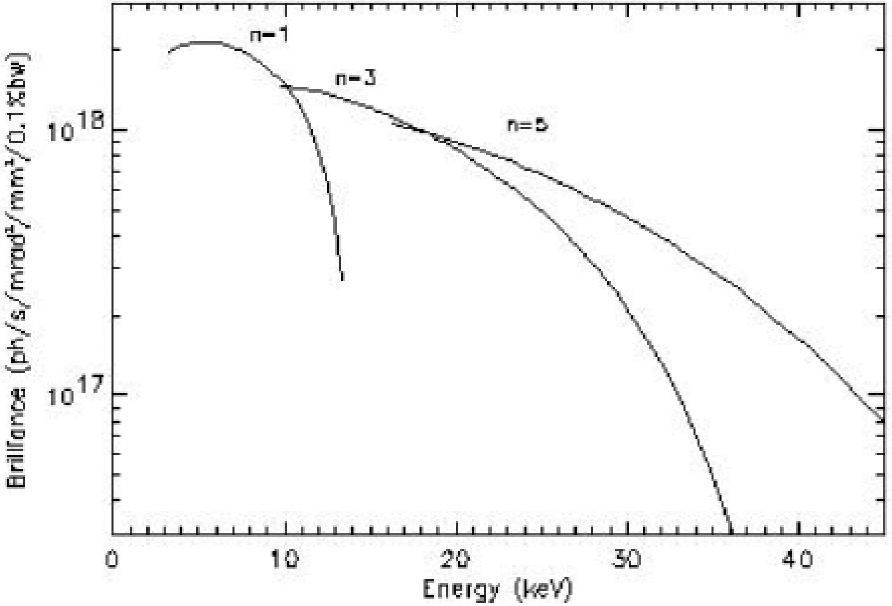
Undulator







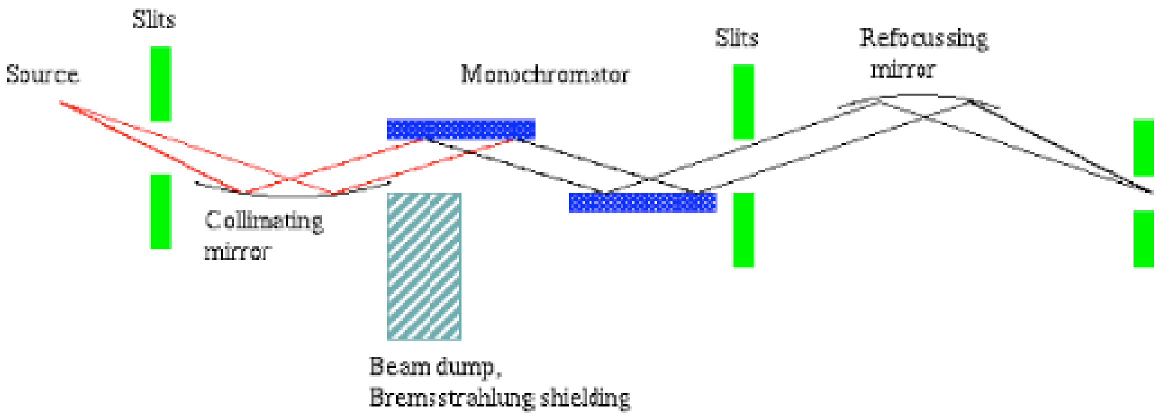
Undulator tuned by varying the magnetic gap



“Laser-like” radiation

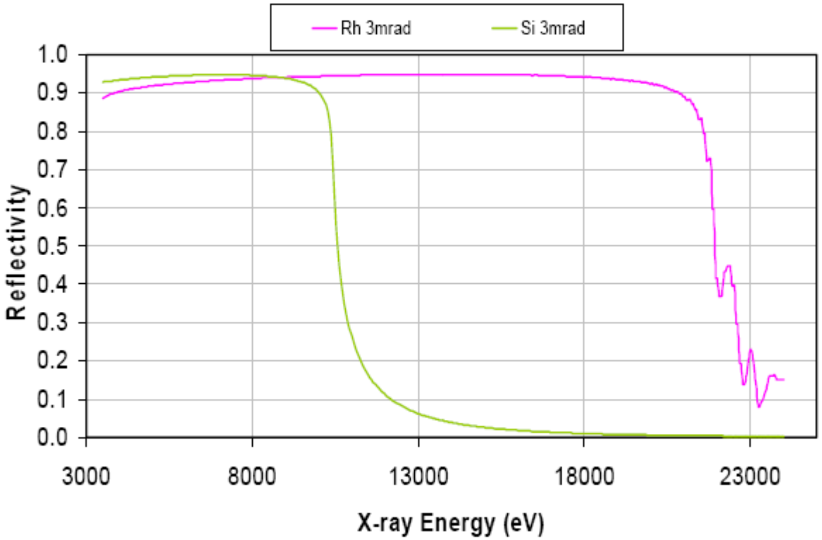
Beamline

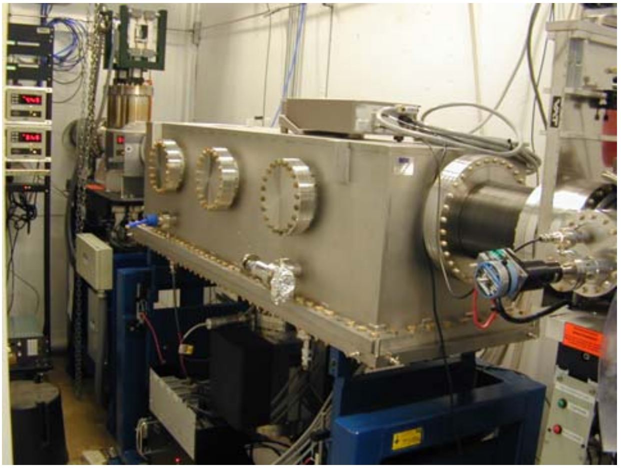
- **Used to "transport" and condition the synchrotron radiation for the XAFS experiment.**
- **Slits, mirrors, monochromator, shutter – similar to any other electromagnetic radiation source e.g. FTIR – only on a larger scale.**
- **Slits used to define beam size.**



X-ray Mirrors

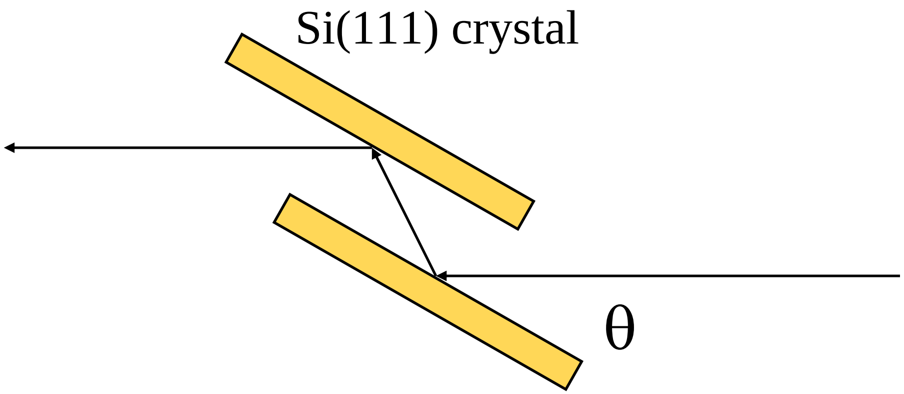
- **Glancing incidence needed for reflectivity in x-ray energy range.**
- **Ultra-smooth surfaces needed (<1nm rms roughness).**
- **Small angles mean mirrors need to be long.**
- **Mirrors used to collimate and focus the beam by bending.**
- **Also used for harmonic rejection.**





Monochromator

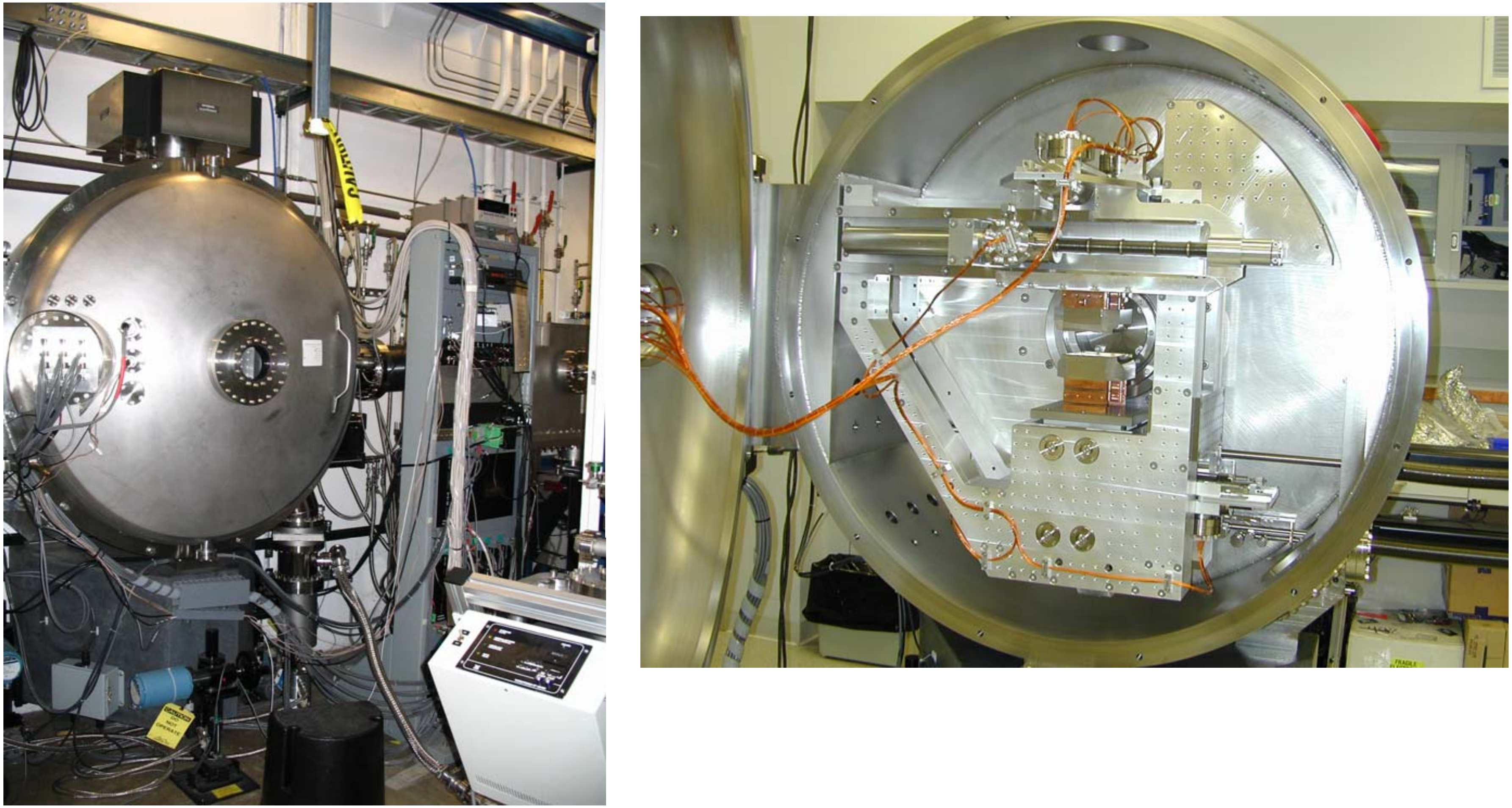
- Used to select energy (wavelength) of interest.
- Must be able to scan the energy for XAFS.
- Must be very stable.



Si double crystal monochromator – energy scanned by rotating θ

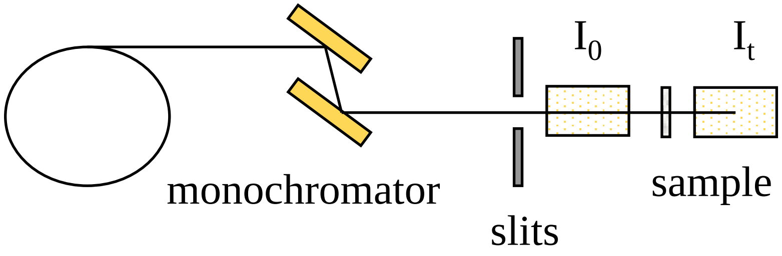
- White beam impinges on perfect single crystal of Si of specific orientation.
- Photons that meet the Bragg diffraction condition $n\lambda = 2d_{hkl}\sin(\theta)$ are diffracted.
- Second crystal simply redirects the beam parallel to incident beam.

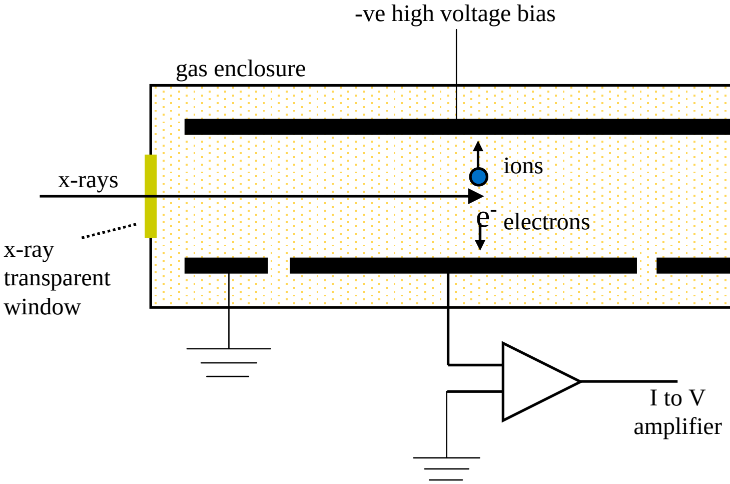
Monochromator



Detectors: Ionization chamber

- **Used for transmission experiments**





Typical values: at 10 keV, G_{amp} = 1x10^8 V/A, measuring 1V means 2 x 10^8 photons/s

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

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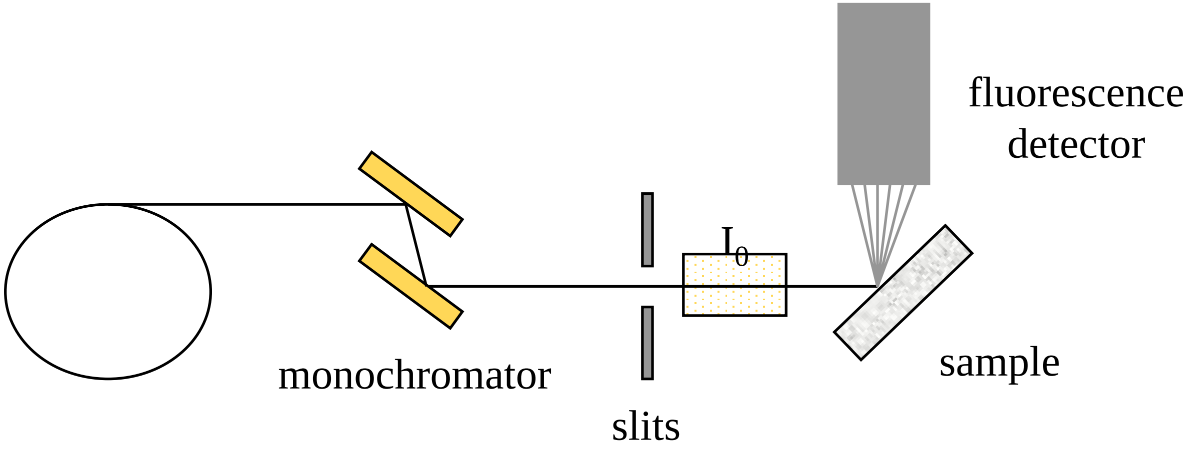
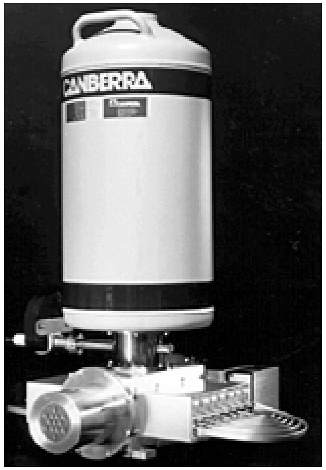
Detectors: Fluorescence





Multi-element solid state (Si or Ge) detector

Measures charge from individual photon rather than average

Small solid angle

Energy resolution 200-300 eV

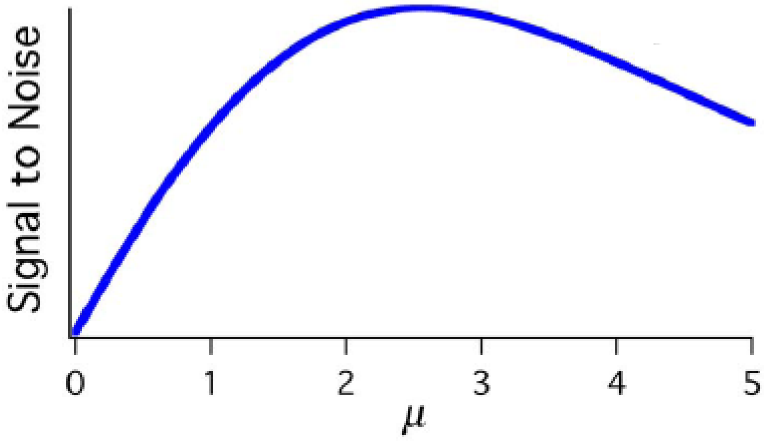
Individual element limited to 10^5 counts/s

Dead-time correction important

Used for low concentration of element (<0.5 wt%)

The Sample

- **“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”**



If sample too thick most photons do not get through

If sample too thin most photons do not interact

Ideal: μ ~ 2-3

The Sample: 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*

The Sample: 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

$$\mu = 5.2\ \text{g/cm}^3 \times [(0.724 \times 393.5\ \text{cm}^2/\text{g}) + (0.276 \times 15.0\ \text{cm}^2/\text{g})]$$
$$= 1503\ \text{cm}^{-1}$$
$$= 0.15\ \mu\text{m}$$

Absorption length = 1/0.15 µm = 6.7 µm

The Sample

- **Use as homogeneous (uniform) sample as possible: logarithms do not add!**

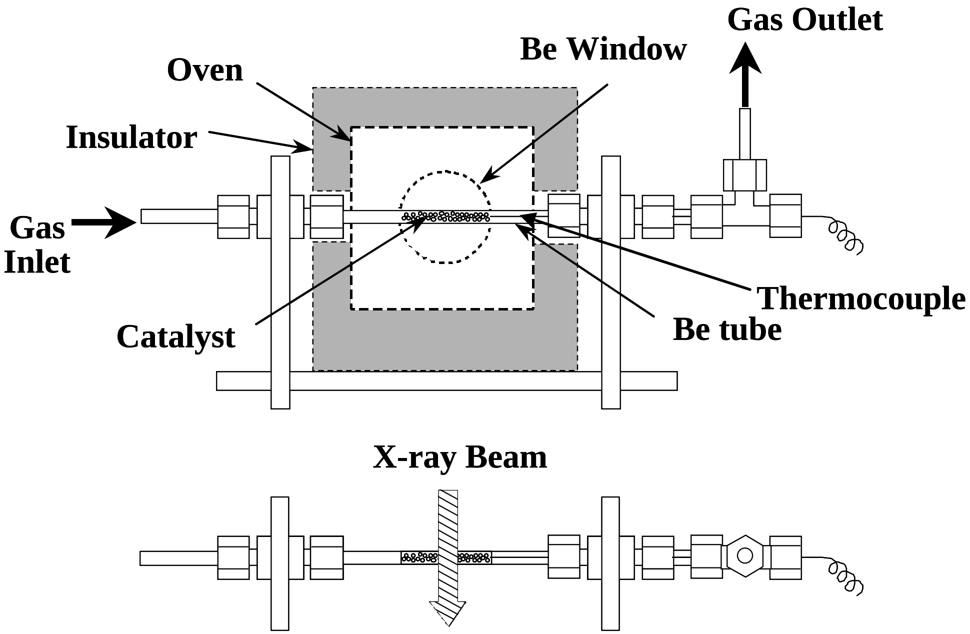
$$\ln\left(\frac{I_{01}}{I_{t1}}+\frac{I_{02}}{I_{t2}}\right)\neq\ln\left(\frac{I_{01}}{I_{t1}}\right)+\ln\left(\frac{I_{02}}{I_{t2}}\right)\Rightarrow\mu_{combined}\neq\mu_1+\mu_2$$

- **Fluorescence detection measurements have fewer requirement on the sample. Usually used for dilute samples.**

In situ XAFS Measurements

- **Key strength of the technique.**
- **Ability to probe the local atomic and geometric structure of the catalyst under reaction conditions.**
- **Need some type of reaction vessel that holds the sample that is compatible both with the spectroscopy and with the catalysis.**
- **Many, many different designs in the literature.**
- **Many factors to consider: temperature, pressure, transmission, fluorescence, x-ray energy, form of catalyst, etc.**

In situ cell



Gas Outlet

Be Window

Oven

Insulator

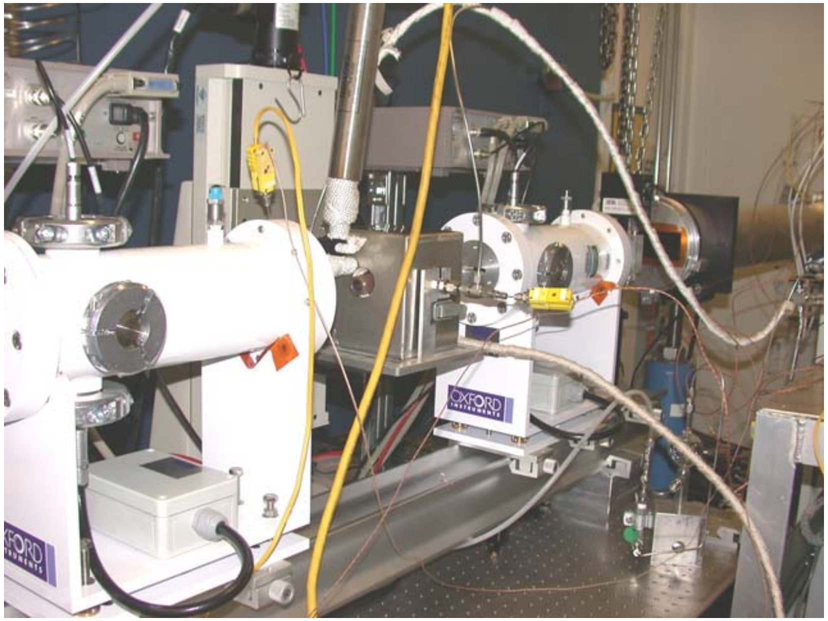
Gas Inlet

Thermocouple

Be tube

Catalyst

X-ray Beam



Important Considerations

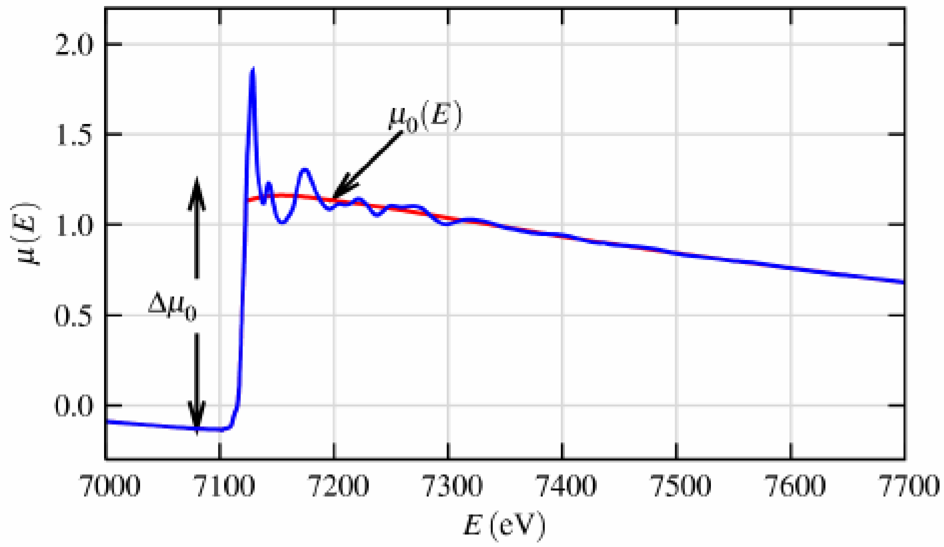
- **Monochromatic x-rays: need x-rays with small energy spread ΔE ~1 eV at 10 keV**
- **Linear Detectors: the XAFS signal is small, so lots of photons needed and detectors that are linear in x-ray intensity**
- **Well-aligned Beam: the x-ray beam hitting the detectors should be the same as that hitting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

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:

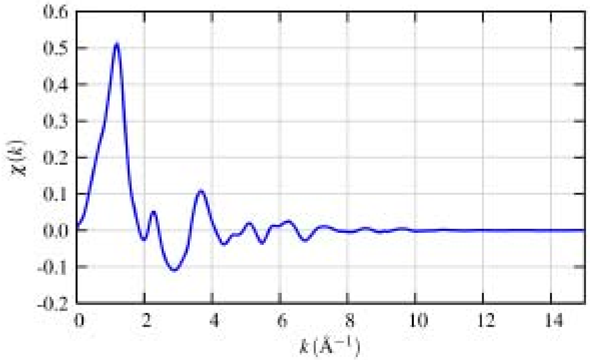


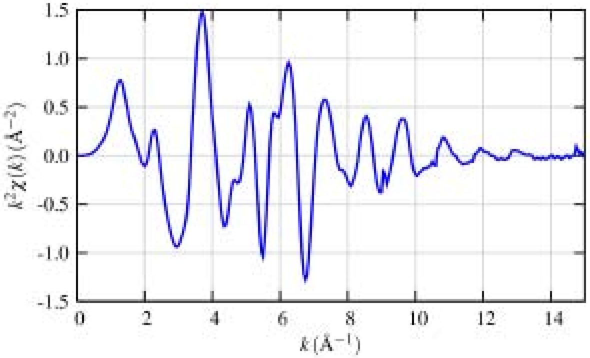
EXAFS: $\chi(k)$

- **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:**

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

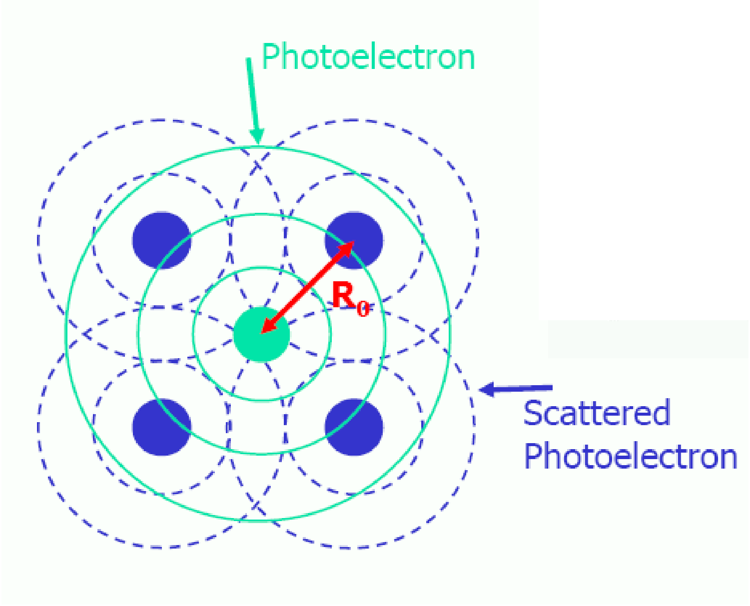
- **$\chi(k)$ is often weighted (multiplied) by k^2 or k^3 to amplify the oscillations at high-k**

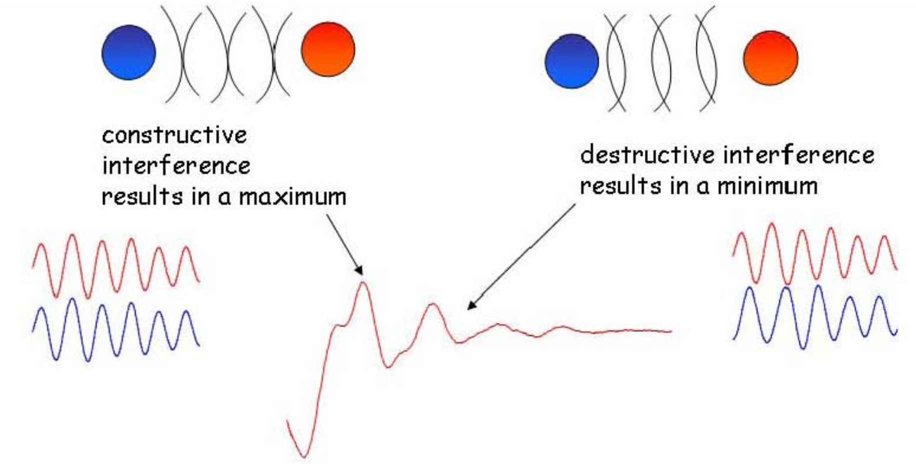




EXAFS: An interference effect

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

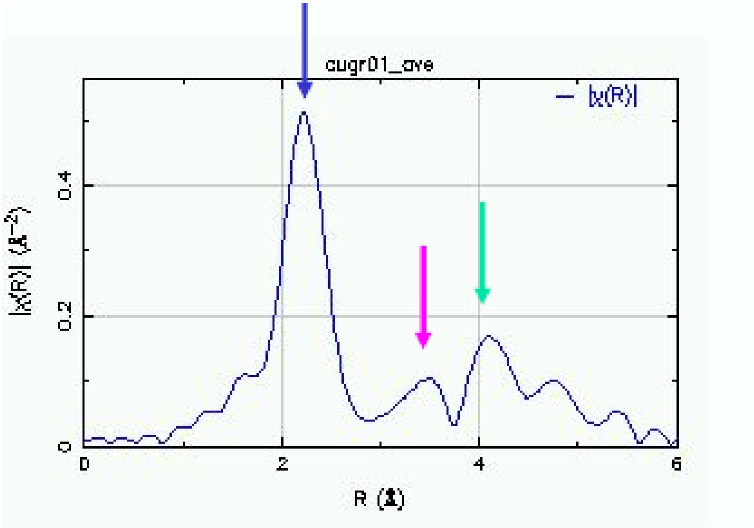


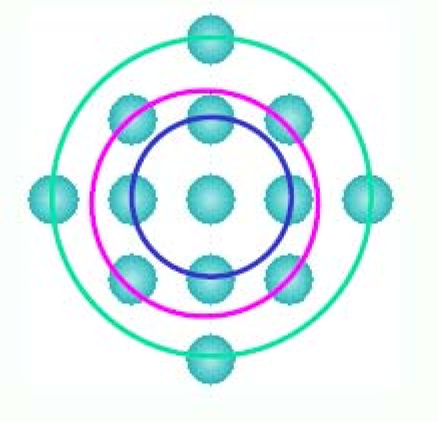


- **EXAFS spectrum comprised of a series of sine waves of different amplitude representative of the different scattering paths undertaken by the photoelectron wave.**

Fourier Transform

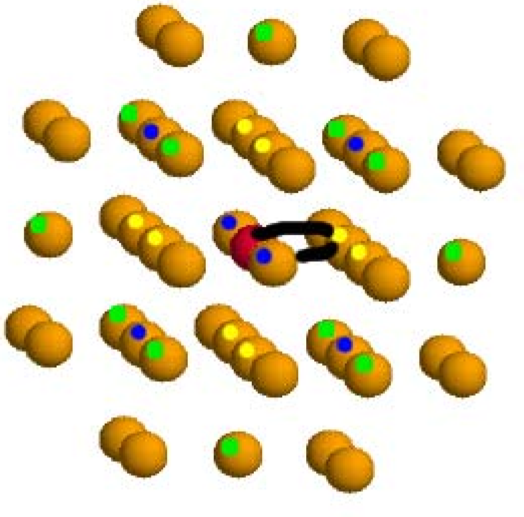
- **One way to separate the sine waves from one another is to perform a Fourier transform.**
- **The resulting magnitude of the transform now has peaks representative of the different scattering paths of the photoelectron.**





Scattering Paths: Fe metal

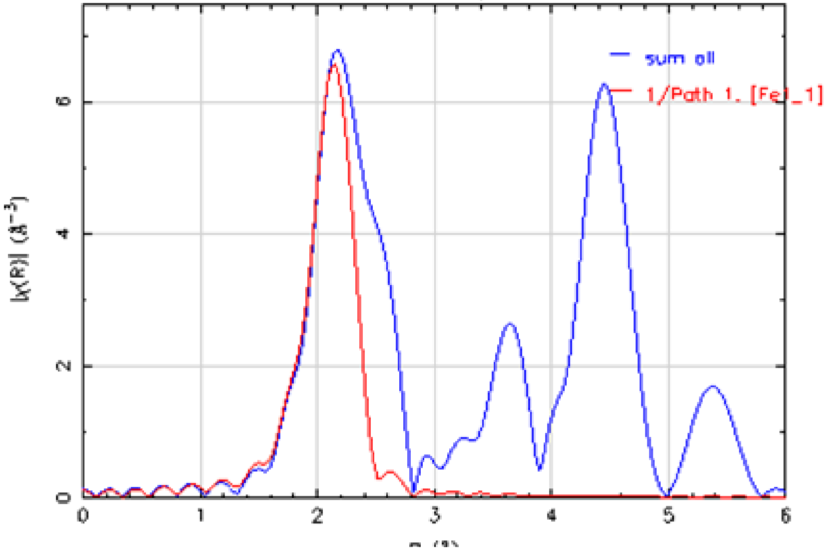
1st scattering path in Fe metal

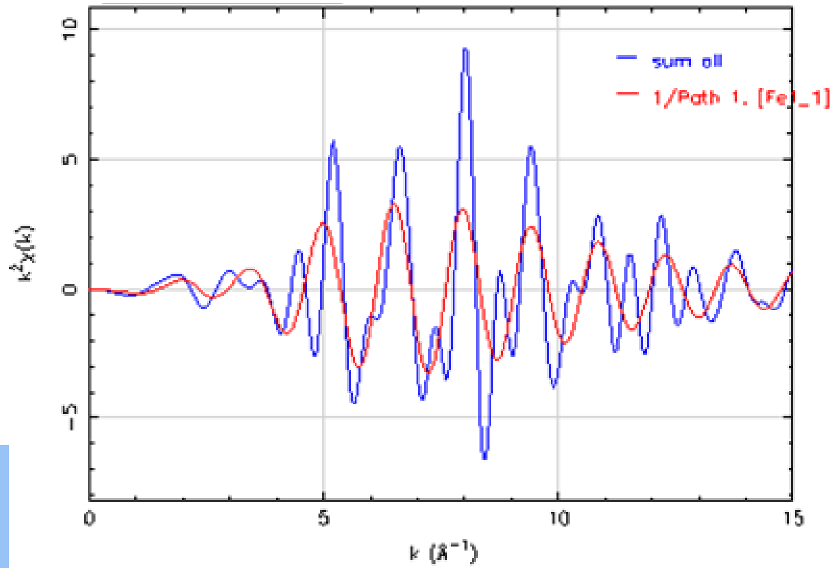


8 nearest neighboring Fe atoms at 2.49 Å

Single scattering path

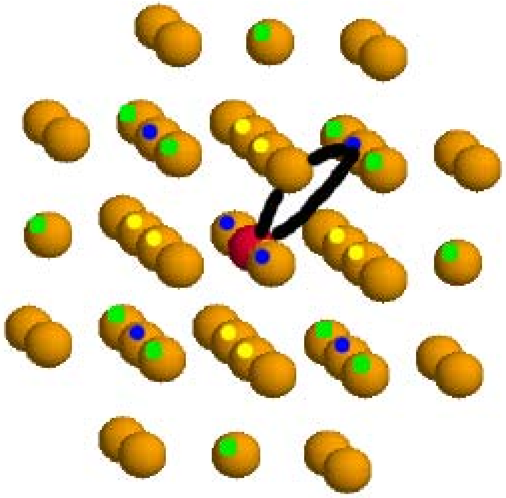
“1st shell”





Scattering Paths: Fe metal

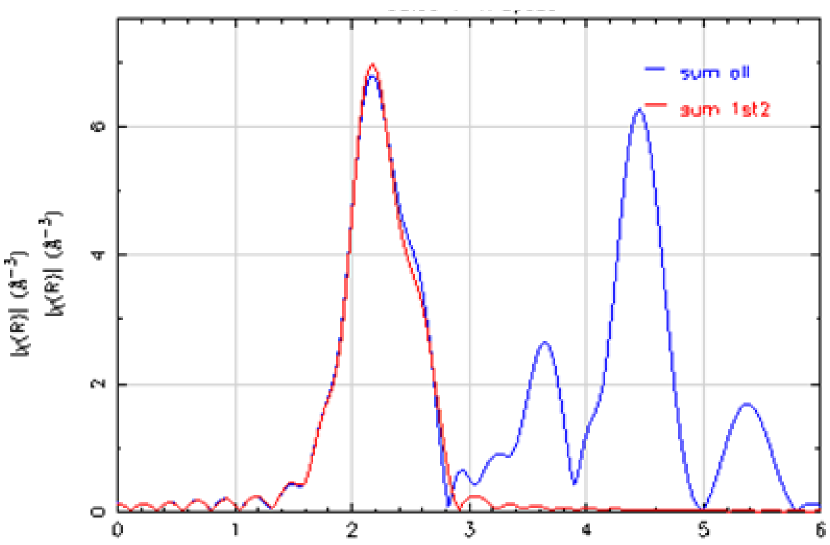
2nd scattering path in Fe metal

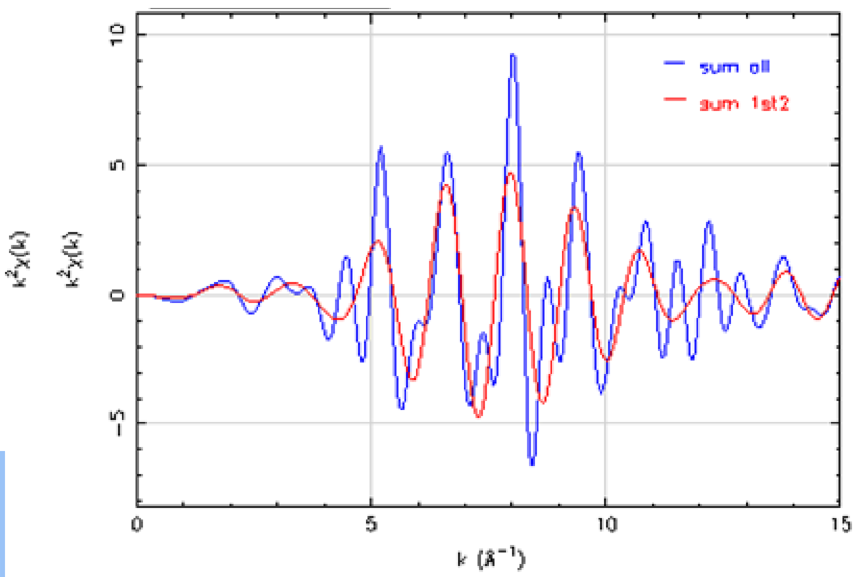


6 nearest neighboring Fe atoms at 2.87 Å

Single scattering path

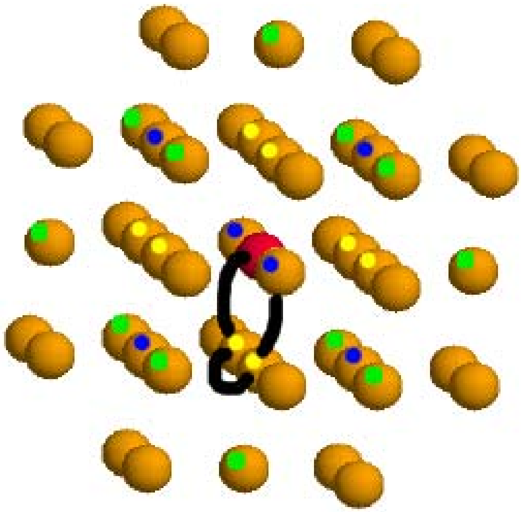
“2nd shell”

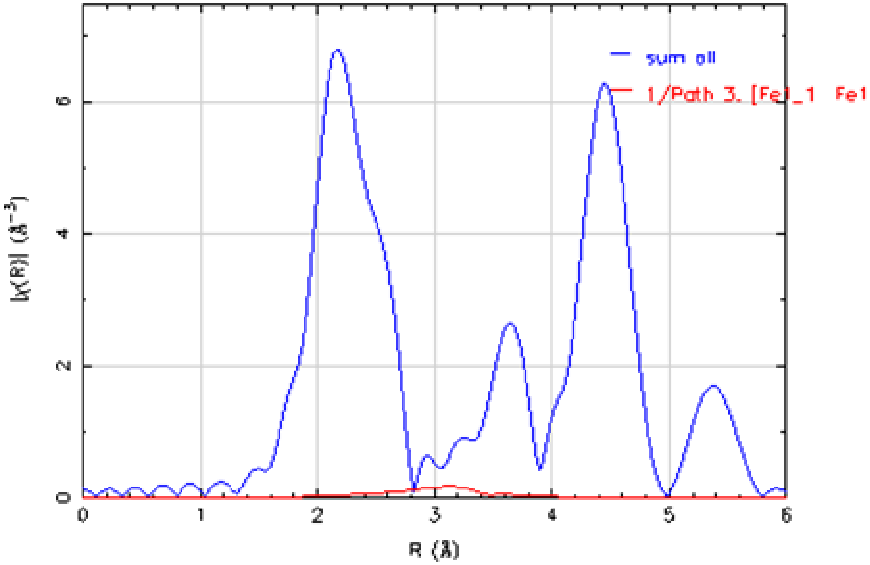




Scattering Paths: Fe metal

3rd scattering path in Fe metal

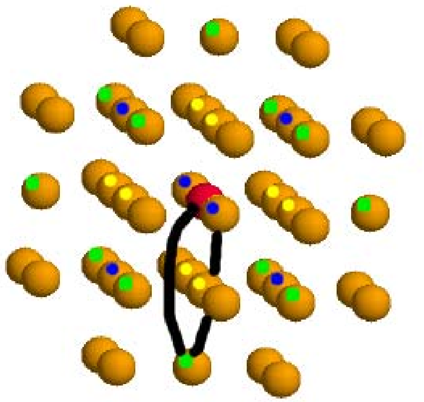


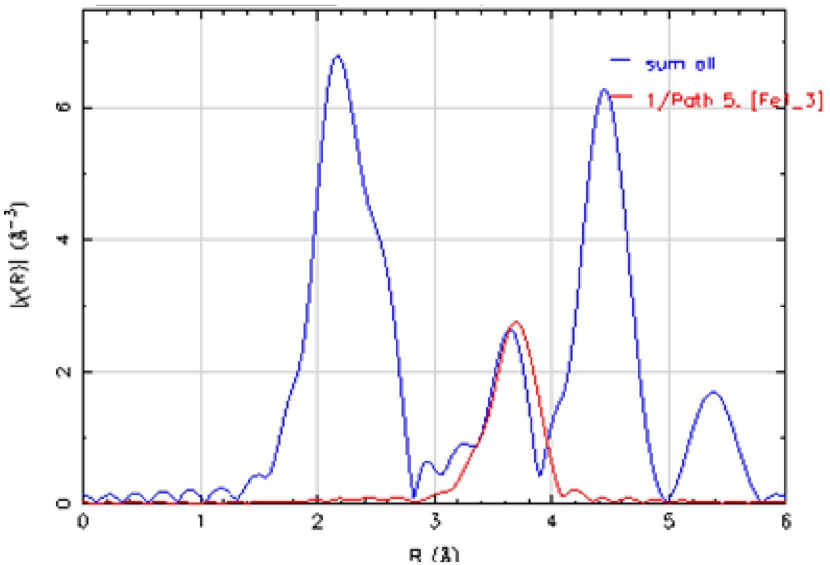


3-legged scattering path: 24 similar paths at this distance but small amplitude. Most multiple-scattering paths are weak – except co-linear paths!

Scattering Paths: Fe metal

5th scattering path in Fe metal

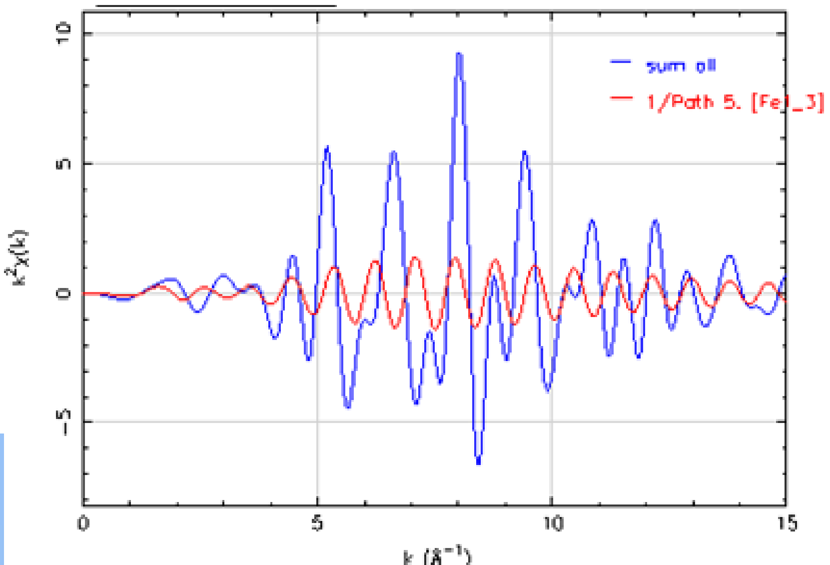




12 nearest neighboring Fe atoms at 4.06 Å

Single scattering path

“3rd shell”



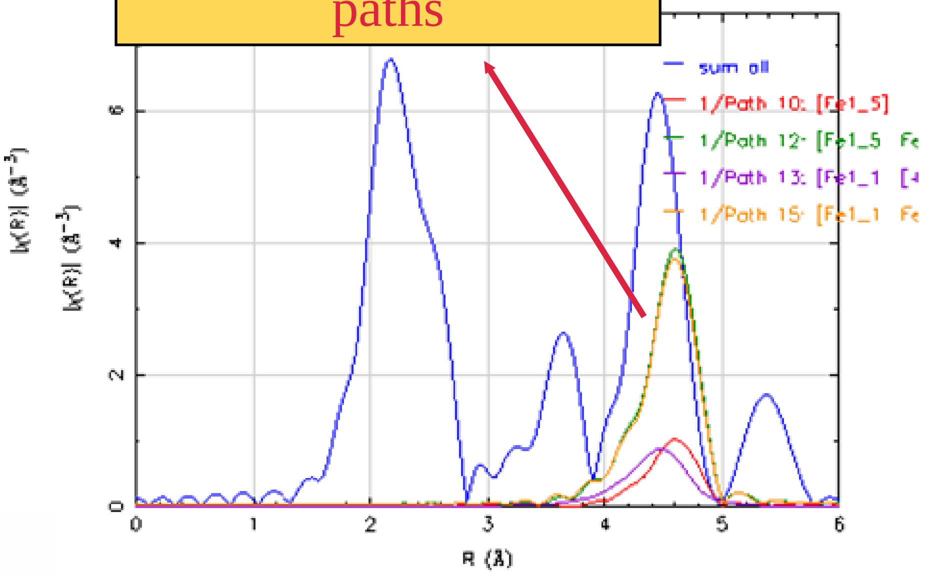
Scattering Paths: Fe metal

8 Fe atoms at 4.97 Å

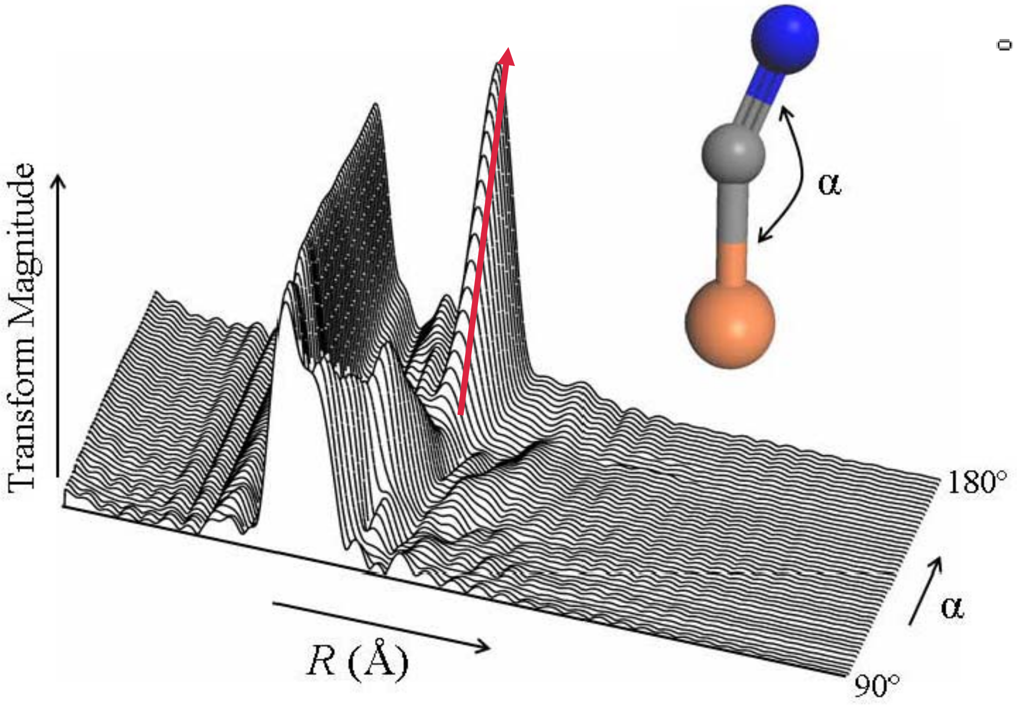
Single scattering path

“5th shell”

Co-linear multiple scattering paths are larger than the single scattering path!



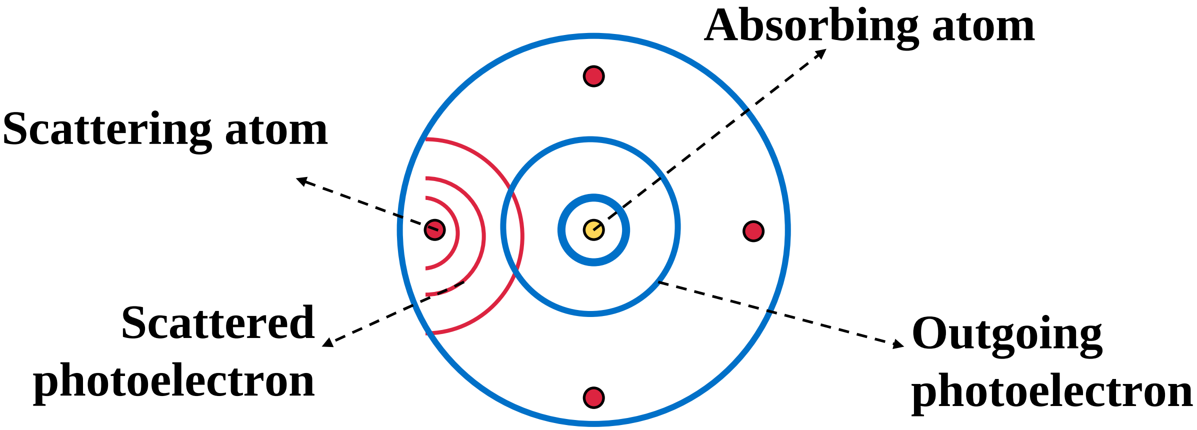
Multiple scattering paths



In reality…..

- In previous example we knew the structure and were able to determine the individual scattering paths.
- In a “real” situation we have the EXAFS data and wish to determine the scattering paths in order to determine the local structure around the element of interest in the catalyst.
- Therefore we have to fit the experimental spectrum with scattering paths from a model.

The EXAFS Equation: simple description



With a spherical wave e^{ikR}/kR for the propagating photoelectron, and a scattering atom at a distance R, we get:

$$\chi(k) = \frac{e^{ikR}}{kR}\left[2kf(k)e^{i\delta(k)}\right]\frac{e^{ikR}}{kR} + C.C.$$

Where the neighboring atom gives the amplitude ***f(k)*** and phase shift ***δ(k)*** to the scattered photoelectron

The EXAFS Equation: simple description

Combining the terms (including the complex conjugate) we get:

$$\chi(k) = \frac{f(k)}{kR^2}\sin\left[2kR + \delta(k)\right]$$

for one scattering atom.

For **N** scattering atoms, and the thermal and static disorder of **σ^2**, resulting in the mean-square disorder in **R**, we get:

$$\chi(k) = \frac{Nf(k)e^{-2k^2\sigma^2}}{kR^2}\sin\left[2kR + \delta(k)\right]$$

A real system will have neighboring atoms at different distances and of different types. If these are added we get:

$$\chi(k) = \sum_i \frac{N_i f_i(k)e^{-2k^2\sigma_i^2}}{kR_i^2}\sin\left[2kR_i + \delta_i(k)\right]$$

The EXAFS Equation

$$\chi(k) = S_0^2 \sum_i N_i \frac{|f_i(k)|}{kR_i^2} e^{(-2\sigma_i^2 k^2)} e^{(-2R_i/\lambda(k))} \sin(2kR_i + 2\delta_i + \varphi_i)$$

$\mathbf{N_i}$	is the number of scattering atoms of type *i*
$\mathbf{R_i}$	is the distance from the central atom to the scattering atom
S_0^2	is the amplitude reduction factor (due to multielectron processes).
$e^{(-2\sigma_i^2 k^2)}$	is a term to account for the disorder in the position of the atoms.
$e^{(-2R_i/\lambda(k))}$	is a damping factor to account for the fact that the photoelectron wave is only scattered elastically over a short distance.
$\boldsymbol{f_i(k)}$	is the scattering amplitude at atom *i*
$\boldsymbol{\delta_i}$	is the phase shift undergone by the photoelectron at the central atom
$\boldsymbol{\varphi_i}$	is the phase shift undergone by the photoelectron when it bounces off the scattering atom

The EXAFS Equation

$$\chi(k) = S_0^2 \sum_i N_i \frac{|f_i(k)|}{kR_i^2} e^{(-2\sigma_i^2 k^2)} e^{(-2R_i/\lambda(k))} \sin(2kR_i + 2\delta_i + \varphi_i)$$

- **The scattering amplitude**
- **The phase shift**

these depend on the atomic number of the scattering atom so we can determine the species of the neighboring atom

- **The mean free path, λ, depends on *k*, but in EXAFS *k*-range, λ<25Å**
- **1/R^2 term**

these terms make EXAFS a local probe (short range order)

The EXAFS Equation

$$\chi(k) = \sum_i \chi_i(k)$$

The measured EXAFS is a sum of all of the individual scattering paths

$$\chi_i(k) = \mathrm{Im}\left(\frac{\left(N_i S_0^2\right) F_i(k)}{kR_i^2} \exp(i(2kR_i + \varphi_i(k)) \exp(-2\sigma_i^2 k^2) \exp\left(\frac{-2R_i}{\lambda(k)}\right) \right)$$

$$R_i = R_0 + \Delta R \qquad k^2 = 2m_e(E - E_0)/\hbar$$

Theoretically calculated values:

$F_i(k)$ effective scattering amplitude

$\varphi_i(k)$ effective scattering phase shift

$\lambda(k)$ mean free path

Starting Values:

R_0

Parameters determined in fit:

N_i degeneracy of path

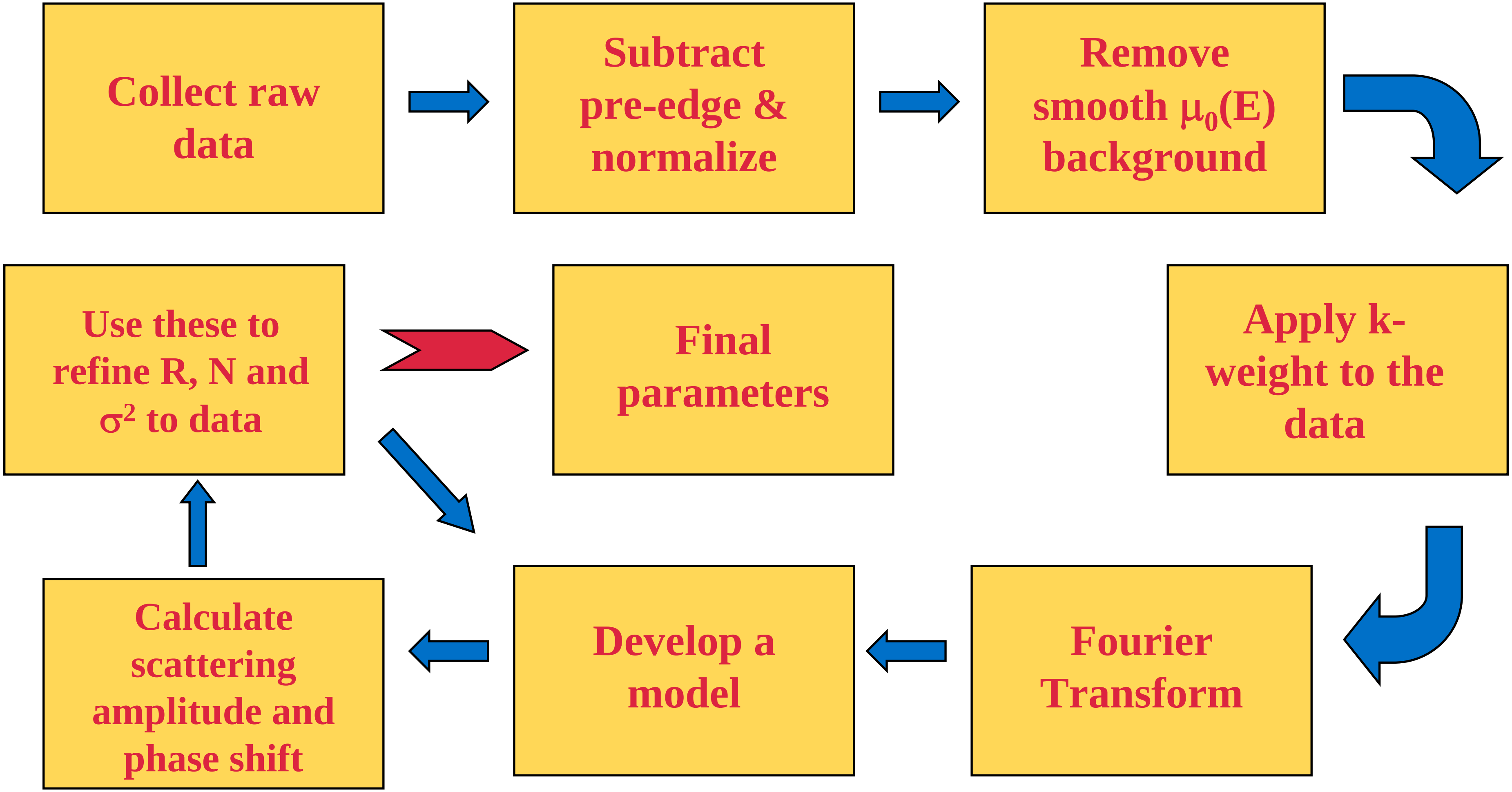
S_0^2 passive electron reduction factor

σ_i^2 mean square displacement

E_0 energy shift

ΔR change in path length

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

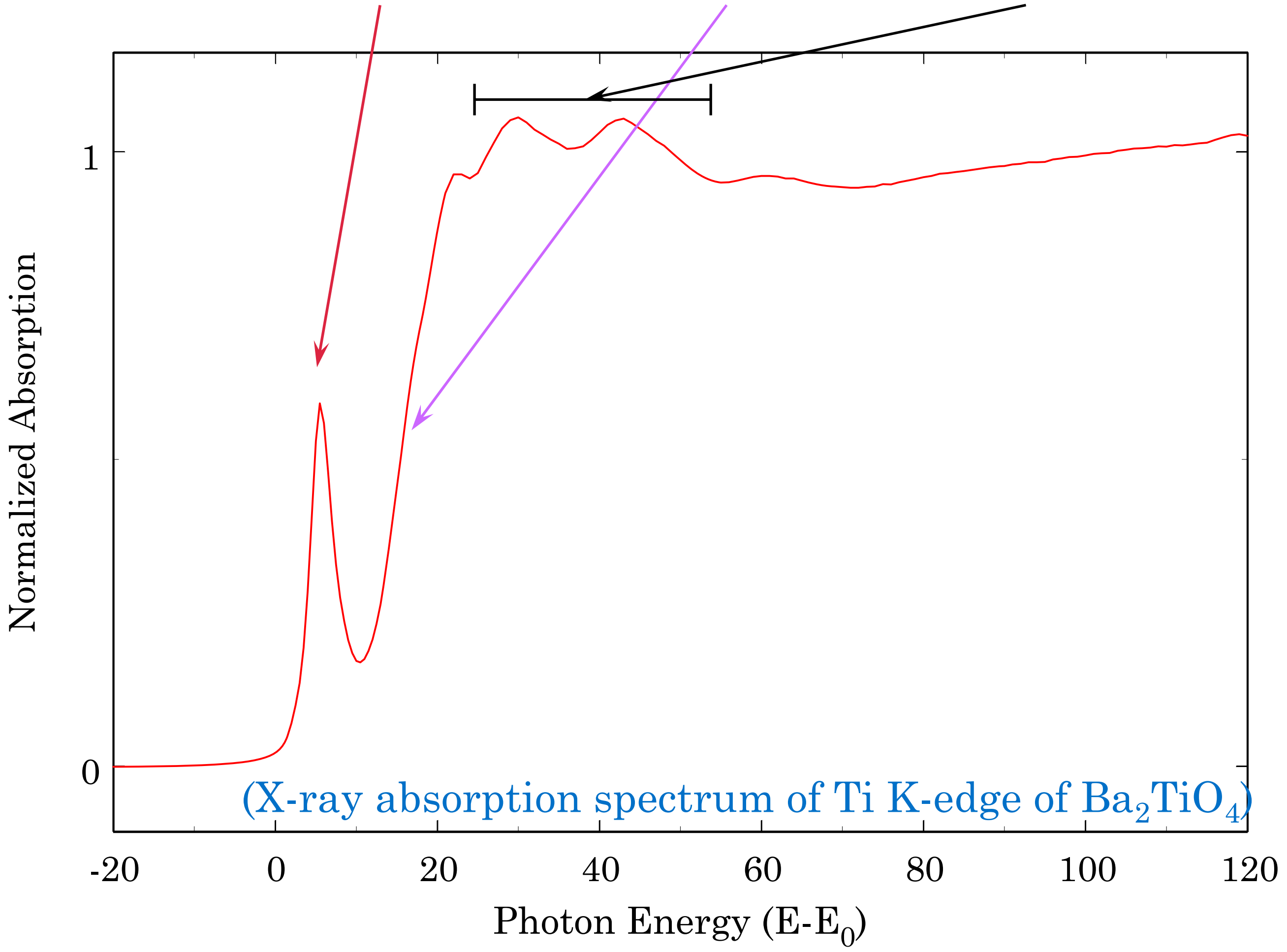
Final parameters

Examples of Application of XAFS to Catalyst Characterization

- **XANES**

What Is ***XANES***?

XANES= Pre-edge + Edge + XANES



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

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?

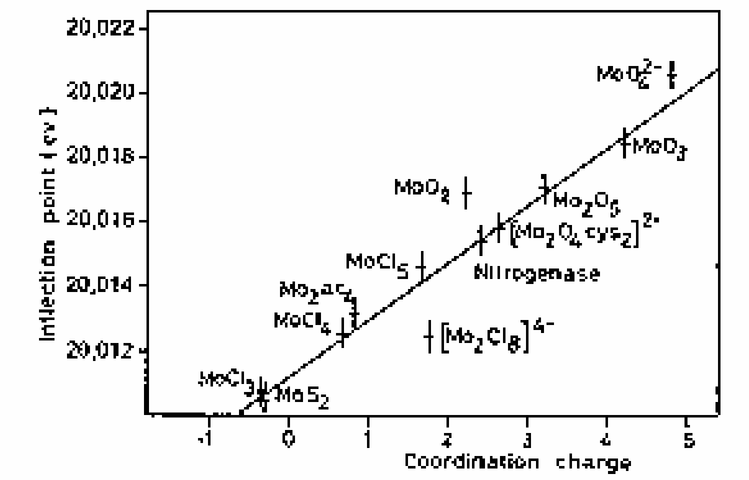
Advantages of XANES vs. EXAFS

- Spectra simpler to measure than EXAFS: features intense, concentrated in small energy region.
- Weak temperature dependence (Debye-Waller), so spectra can be recorded at reaction temperature (*in situ*):
  - $\mathrm{Exp}(-2k^2\sigma^2) = \exp(-2(0.5)^2 \times 0.005) \sim 1$
- Faster to measure than full spectrum: <msec demonstrated.
- Sensitive to chemical information: valence, charge transfer.
- Probes unoccupied electronic states: important in chemistry.
- Often used as simple “fingerprint” to identify presence of a particular chemical species.
- Beamlines with micro-probe capabilities can also scan energy and obtain XANES spectra with elemental distribution.

XANES Analysis: Oxidation State

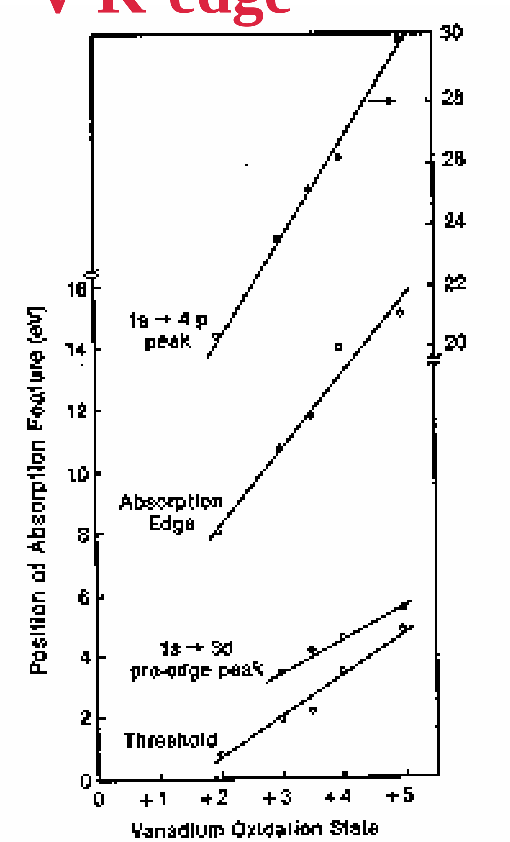
Many, many examples in the literature…...

Mo K-edge



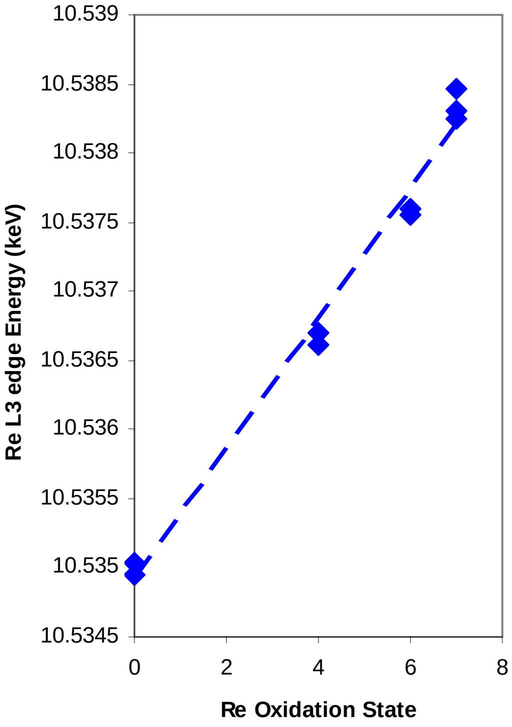
Ref: Cramer et al., JACS, 98 (1976) 1287

V K-edge



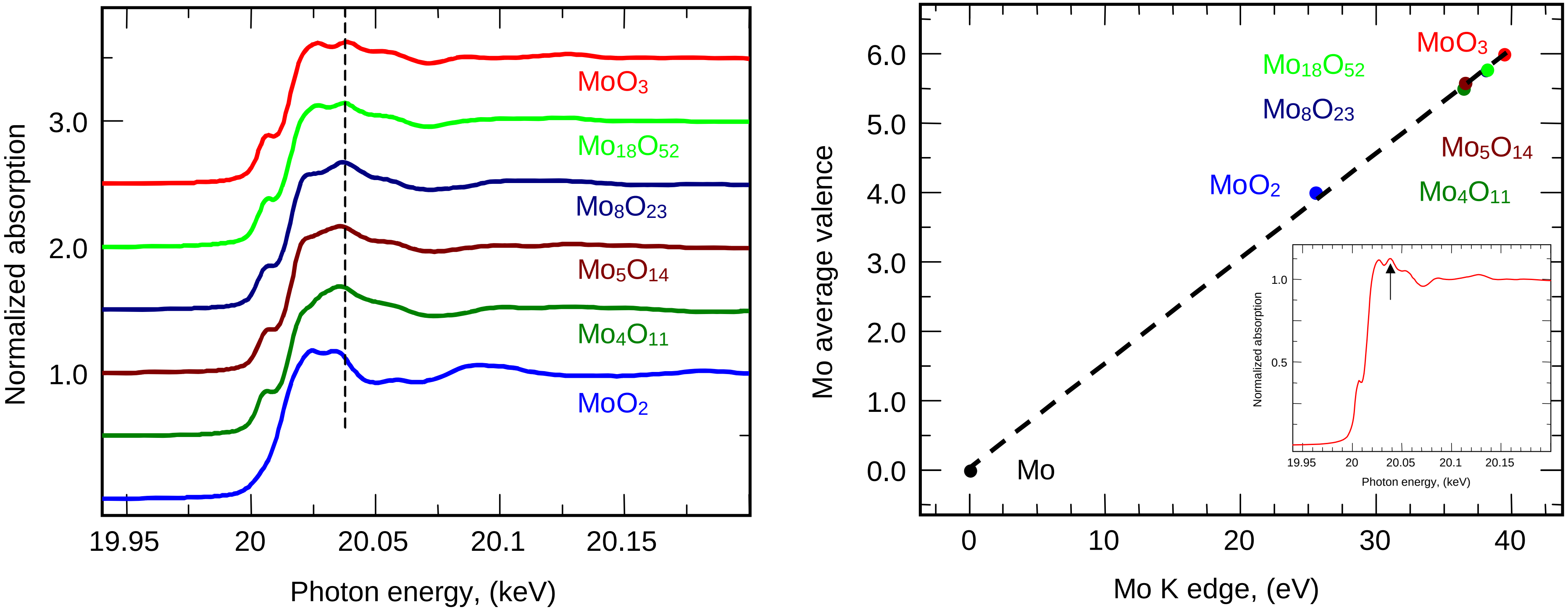
Ref: Wong et al., Phys Rev. B 30 (1984) 5596

Re L_3-edge



XANES Analysis: Oxidation State

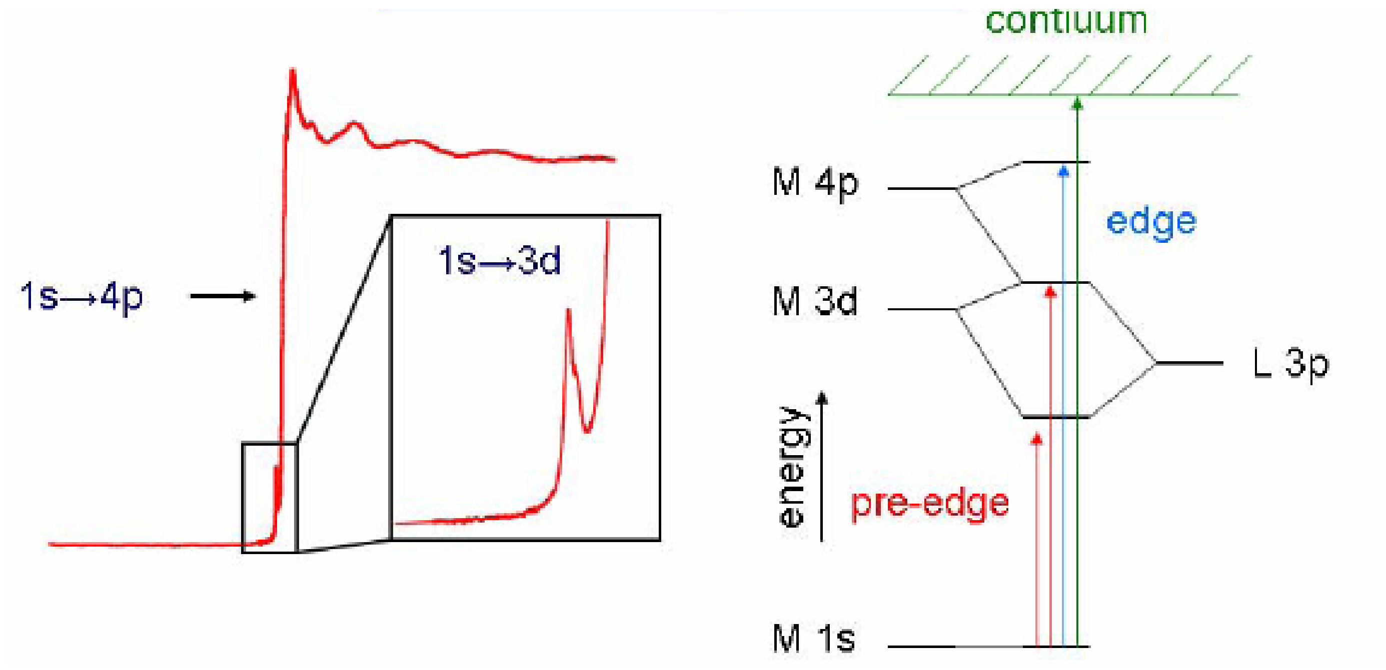
Mo K-edge XANES of Mo oxides



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

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

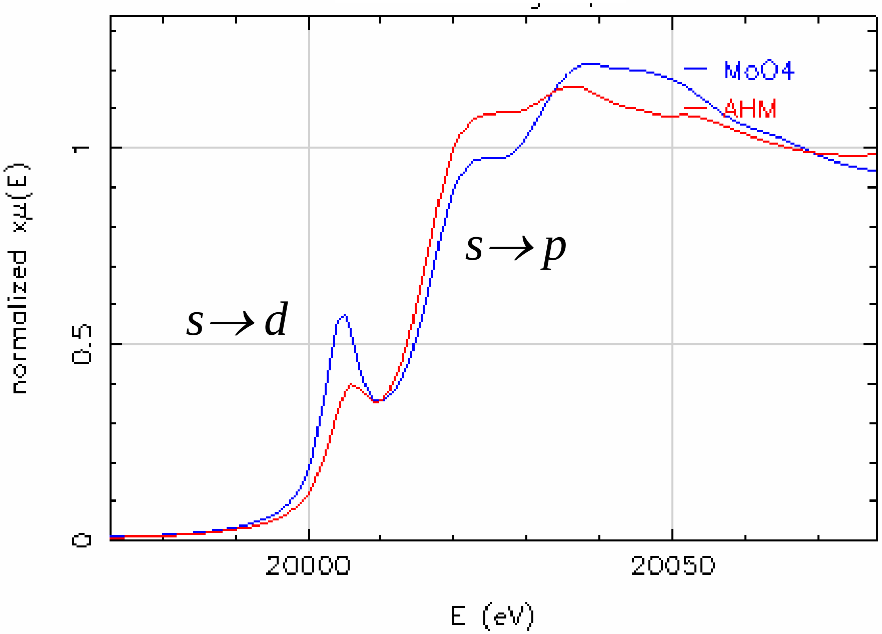
Metal K-edge XANES

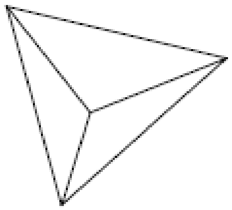


- Intense edge absorption due to dipole allowed s → p transition (Δl = ±1).
- Weaker pre-edge feature results from mixing of 3d-4p orbitals of suitable symmetry (or from quadrupolar allowed transition ~2 orders magnitude weaker).

Molybdenum Oxides

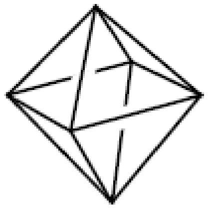
Mo K-edge XANES





Na_2MoO_4

Tetrahedral coordination

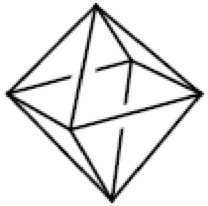


$(NH_4)_6Mo_7O_{24}$

Distorted octahedral coordination

- Both nominally +6 oxidation state, but distinctly different XANES spectra.
- Slight edge shift – different degree of covalency of the Mo.
- Pre-edge peak more intense for tetrahedral coordination compared to distorted octahedral.

Transition Metal K-edge Pre-edge Peaks

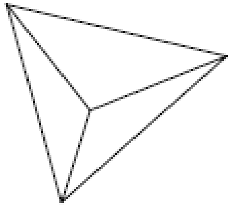


Pure octahedral case

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

Distortion from octahedral

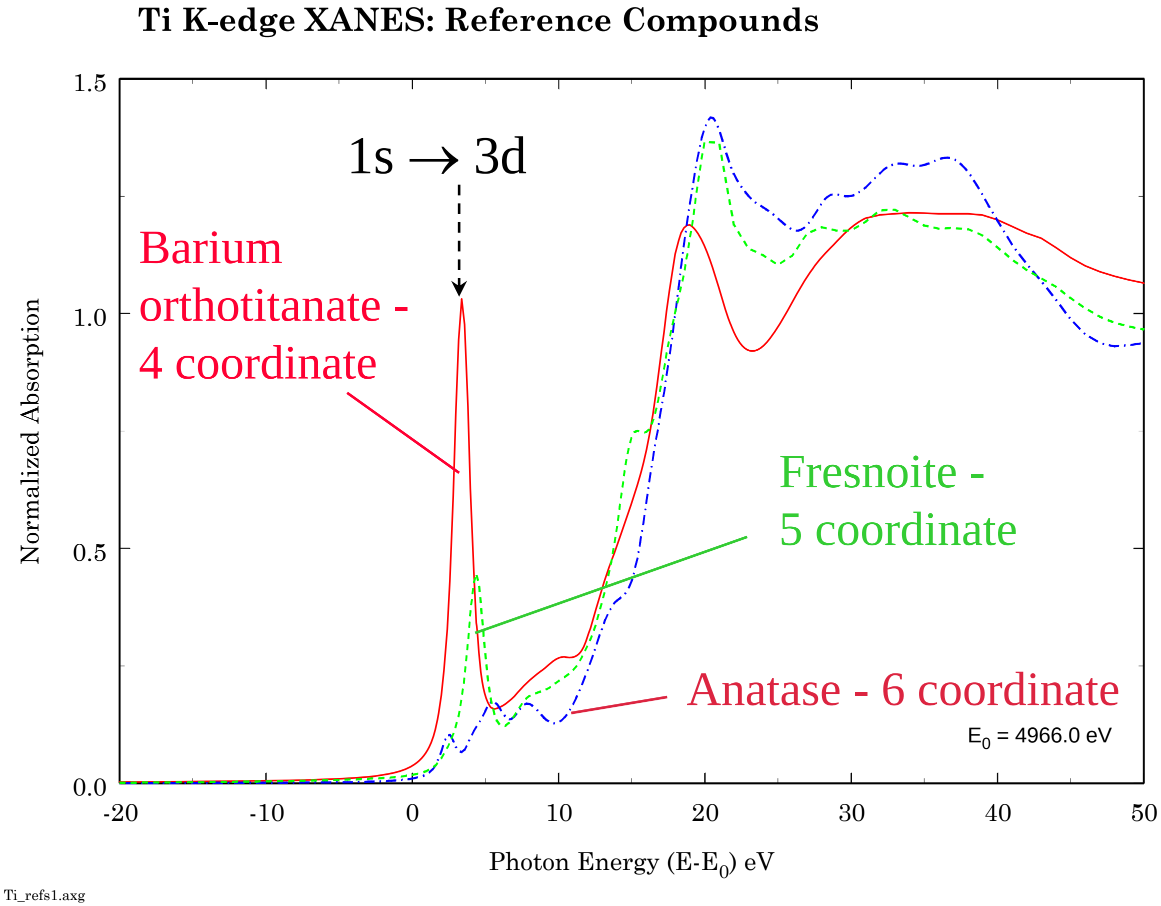
p-d mixing allowed: dipole transition in pre-edge – increasingly larger intensity.



Pure tetrahedral

Largest pre-edge intensity.

Local Site Symmetry in Ti-containing Compounds



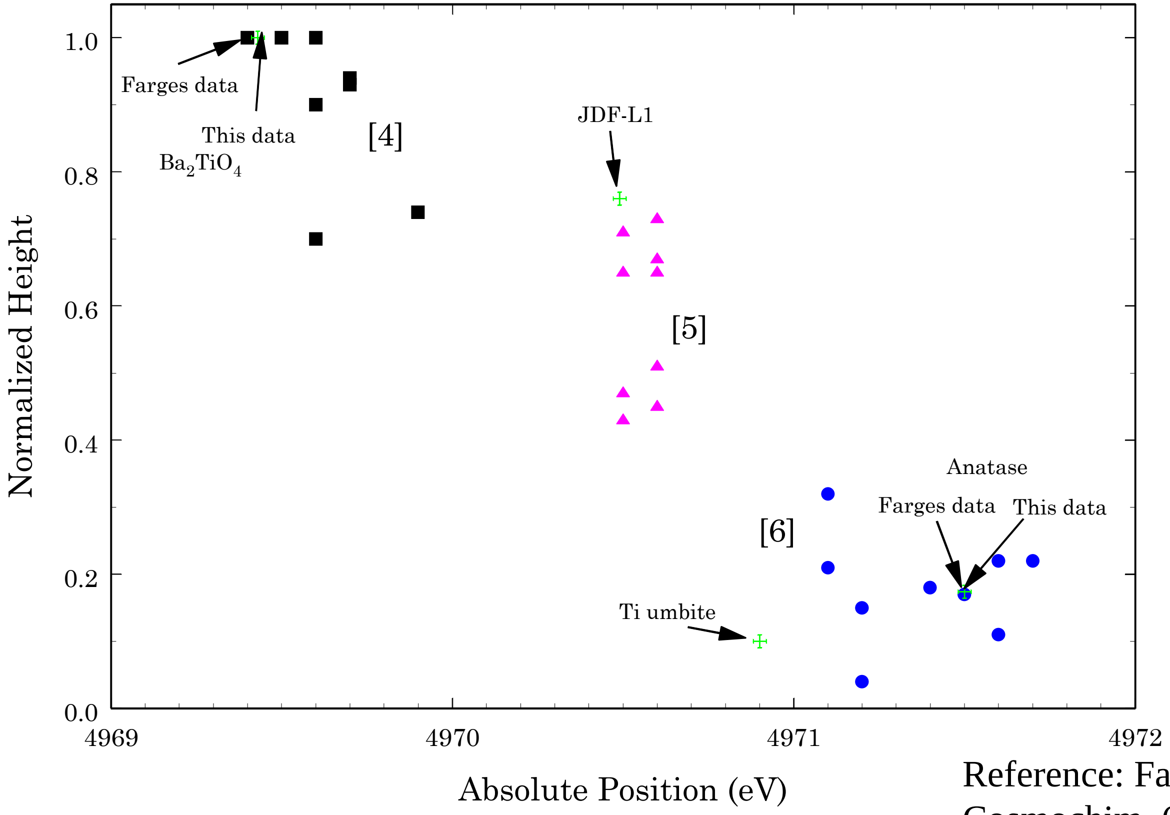
Anatase

- 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

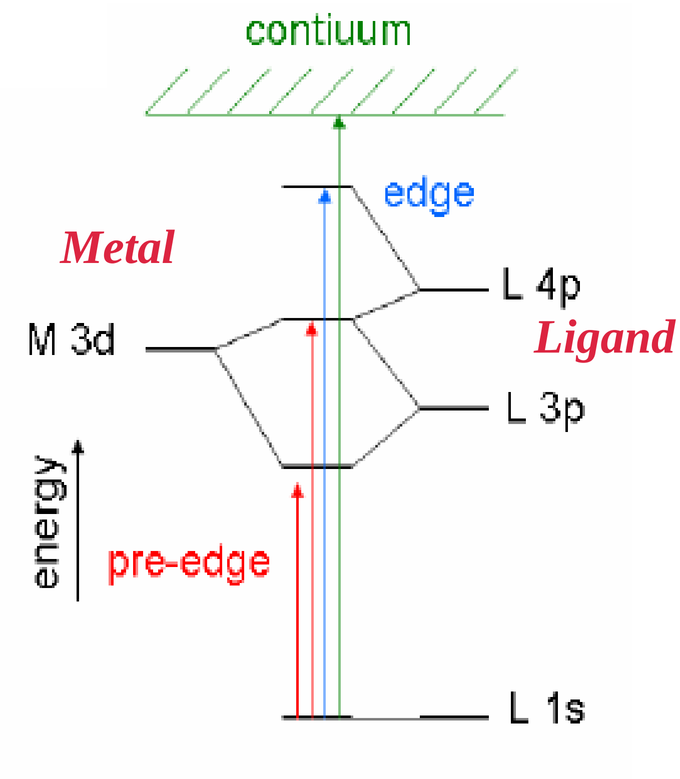
- Correlation between **absolute position and peak height** of pre-edge peak: all 4-fold, 5-fold and 6-fold coordinated Ti compounds fall into separate domains.
- Ability to distinguish Ti coordination from pre-edge peak information.



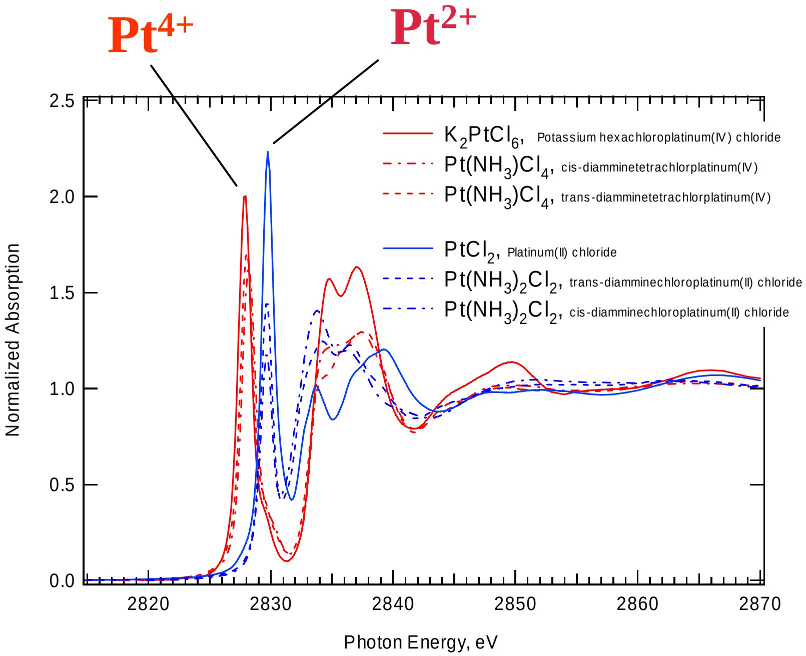
Reference: Farges et al., Geochim. Cosmochim. 60 (1996) 3023

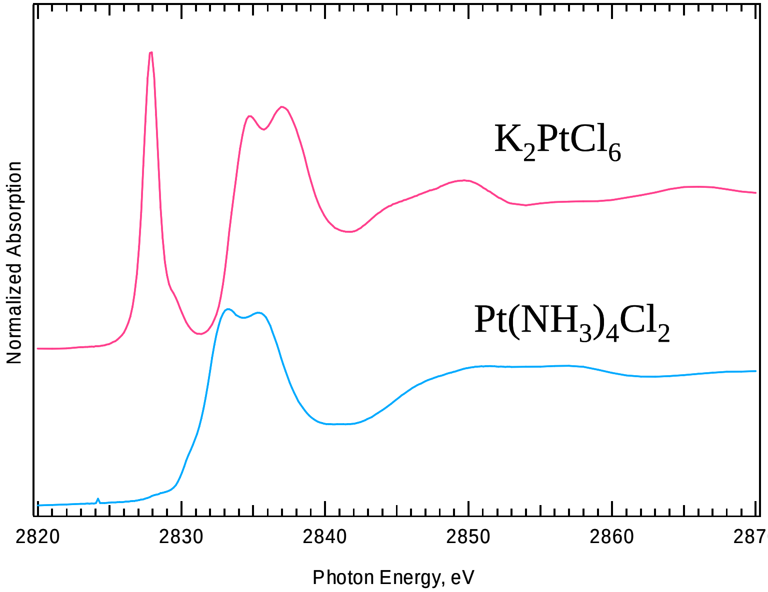
Ligand-Metal Binding from Ligand K-edge XANES

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



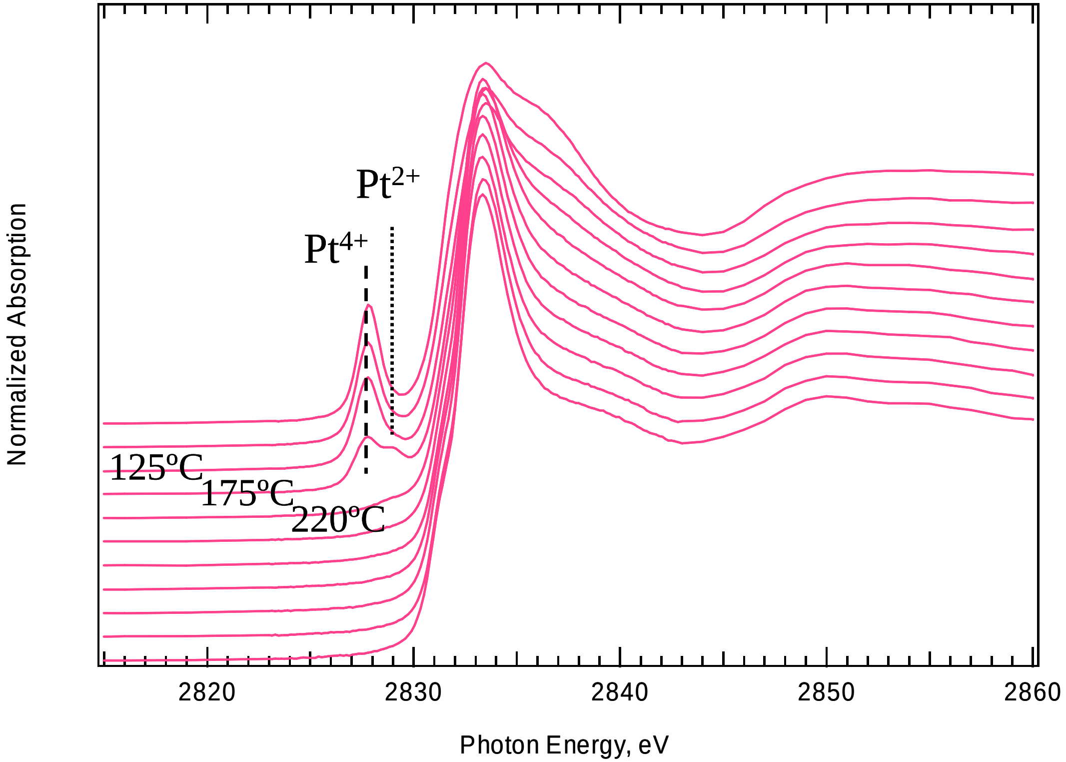
Ligand-Metal Binding: Cl K-edge XANES





- Position of the ligand pre-edge peak depends primarily on the d manifold energy (metal oxidation state). 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.

Chlorine K-edge XANES of Pt/γ-Al_2O_3

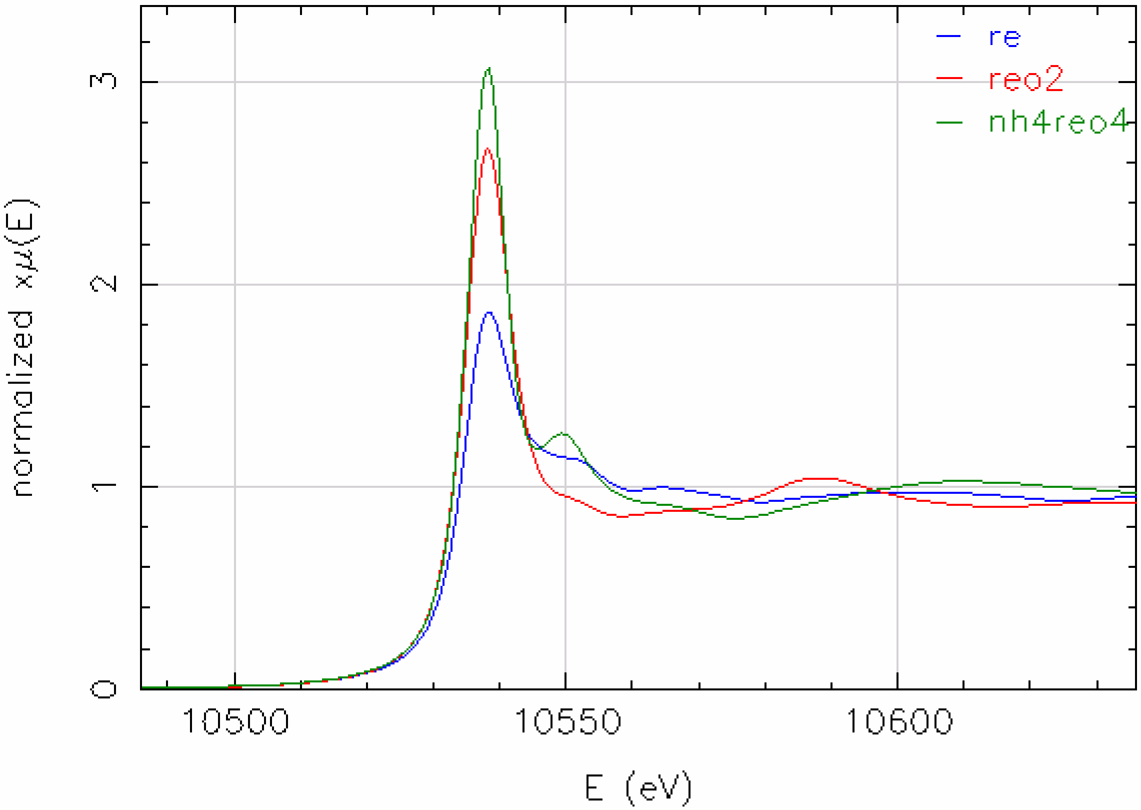


- **Use Cl K-edge XANES as in situ diagnostic tool for presence of Pt-Cl bonding.**

- Reduction of Pt from Pt^{4+} → Pt^{2+} → Pt^0 with loss of Pt-Cl bonds.
- Total loss of Pt-Cl bonding by 250ºC.

“White Line” Intensity: Oxides

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



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

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

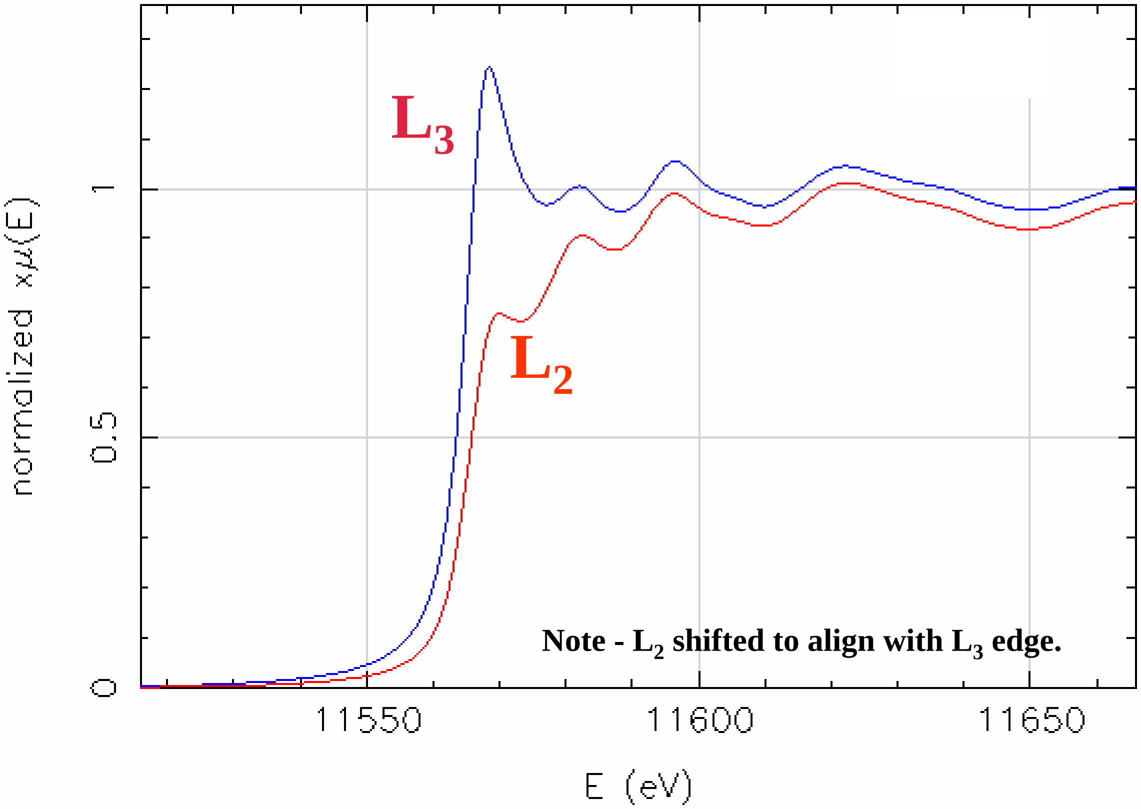
NH_4ReO_4 (Re^{7+}) - 5d^0

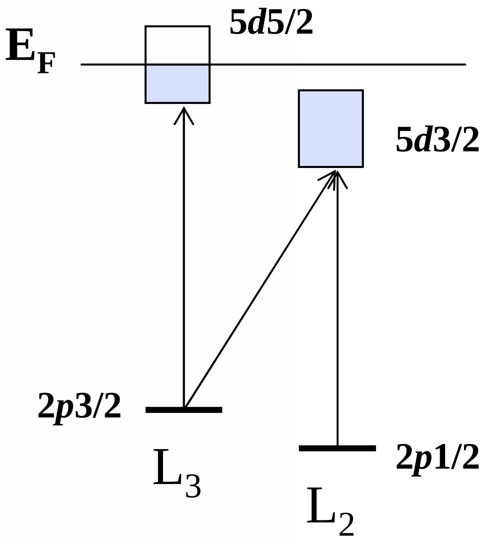
- Intensity of Re L_3 white line probes Re LDOS

***Note - Spectra aligned in energy**

Pt L_3 and L_2 Edge XANES

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



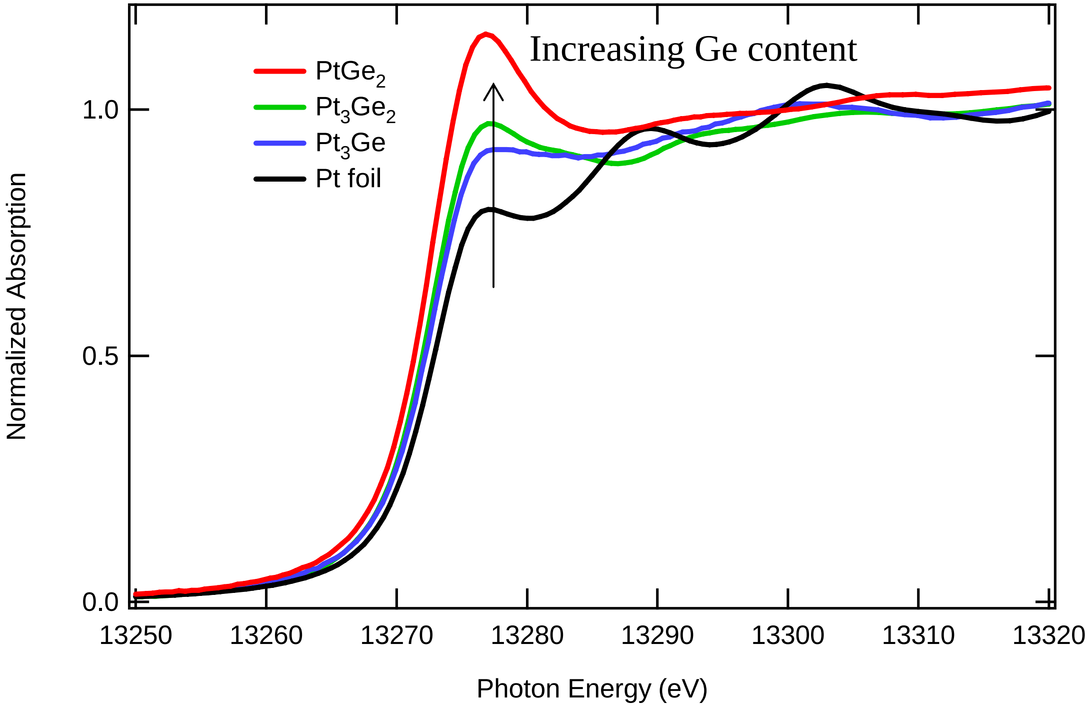


- Pt 5*d*3/2 filled, so no white line.

- Same *l*=2 final density of states but because of selection rule, $\Delta j = \pm1$, 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.

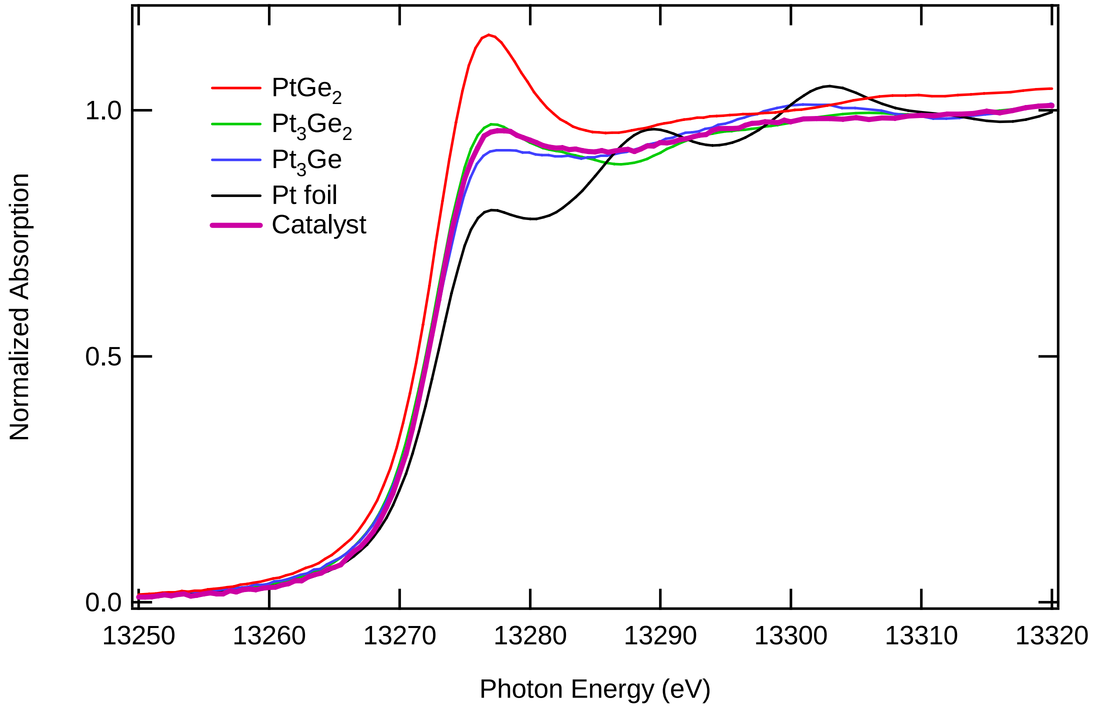
XANES to Probe Charge Transfer in Alloys: PtGe



Pt L_2-edge
XANES

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

XANES to Probe Charge Transfer in Alloys: PtGe/γ-Al_2O_3 catalysts

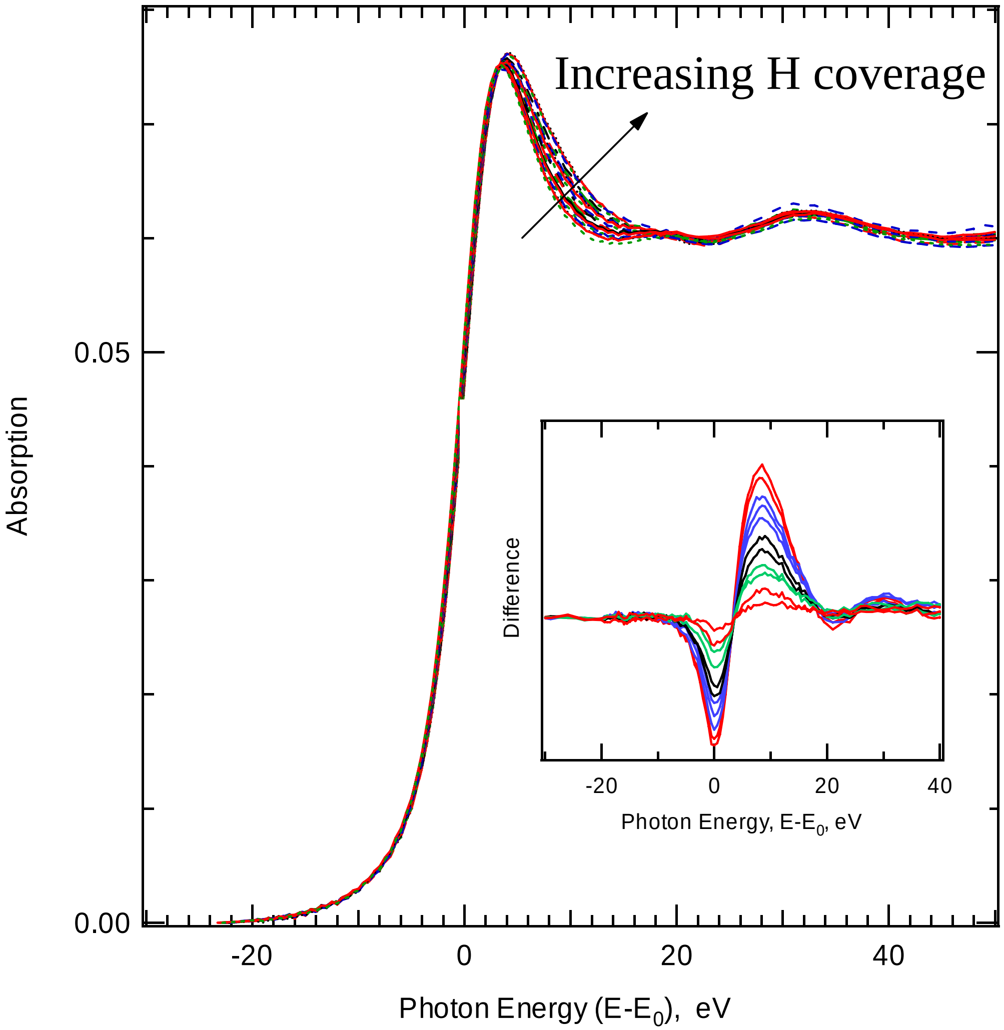


- Pt in the reduced catalyst is primarily present as a Pt_3Ge_2 alloy cluster

Effect of Adsorbed Molecules on XANES of Dispersed Metal Clusters

- **Have to be careful and consistent as to how your data are collected.**
- **Is there hydrogen (or any other molecule) adsorbed on the metal cluster?**
- **If there is then the “chemistry” of the metal-adsorbed molecule could affect the XANES.**
- **Combination of *ab initio* theory and (high resolution) XANES potential powerful tool for determining adsorption site.**

Effect of Adsorbed Hydrogen on Pt L_3 XANES



10-15Å Pt clusters supported on Al_2O_3

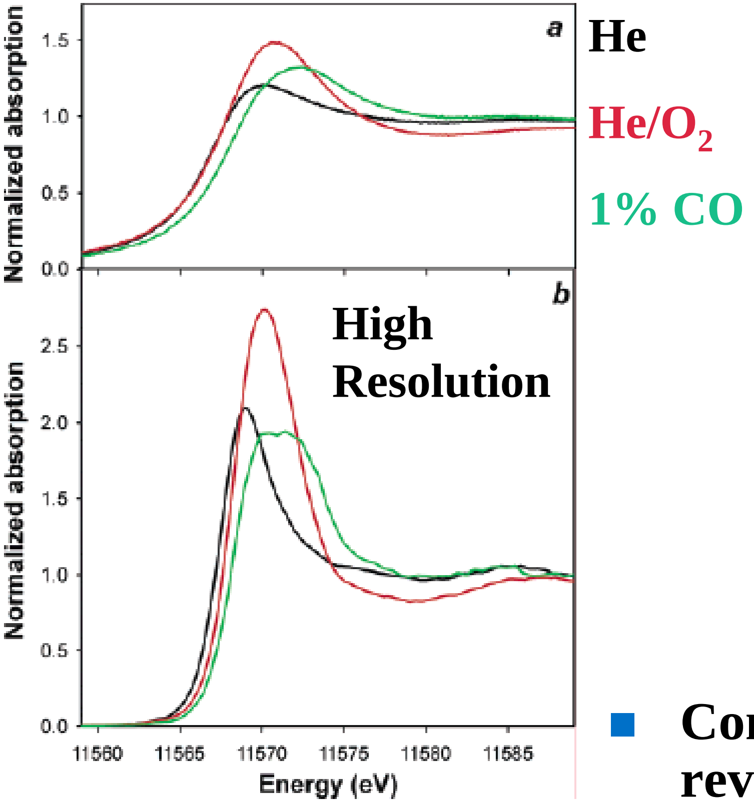
- White-line intensity decreases and spectra broaden to higher energies as H is added.
- Difference signal typically leads to broad structure ~8 eV above absorption edge.
- Several different interpretations in the literature.

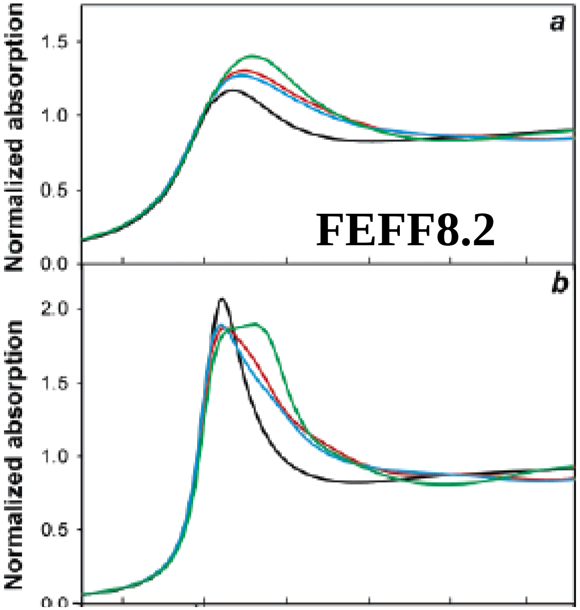
Adsorption Sites by XANES

Identification of CO Adsorption Sites in Supported Pt Catalysts Using High-Energy-Resolution Fluorescence Detection X-ray Spectroscopy

5wt% Pt/γ-Al_2O_3

Olga V. Safonova,[†] Moniek Tromp,[*,‡] Jeroen A. van Bokhoven,[*,§] Frank M. F. de Groot,[‖]
John Evans,[‡,⊥] and Pieter Glatzel[†]





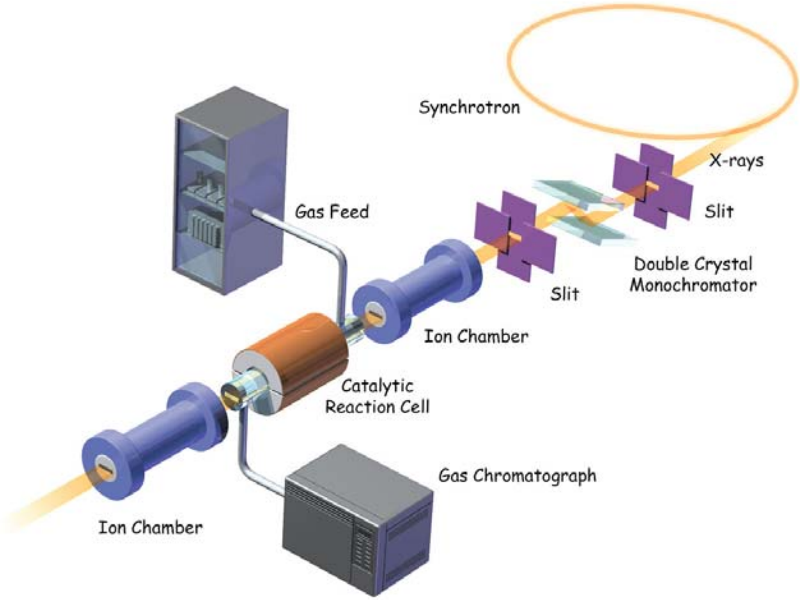
- **Best agreement with data: CO on atop site on a Pt_6 cluster**
- **Other configurations tried: bridge and face bridging**

- **Combination of high resolution XAFS and FEFF8.2 reveals adsorption site for CO in Pt catalysts**

J. Phys. Chem. B110 (2006) 16162

Time-Resolved XANES

- Can obtain kinetic information on the catalyst structure by recording the XANES in situ as a function of some parameter (temperature, pressure, flow rate, etc.).
- Observe structural changes with e.g. time.



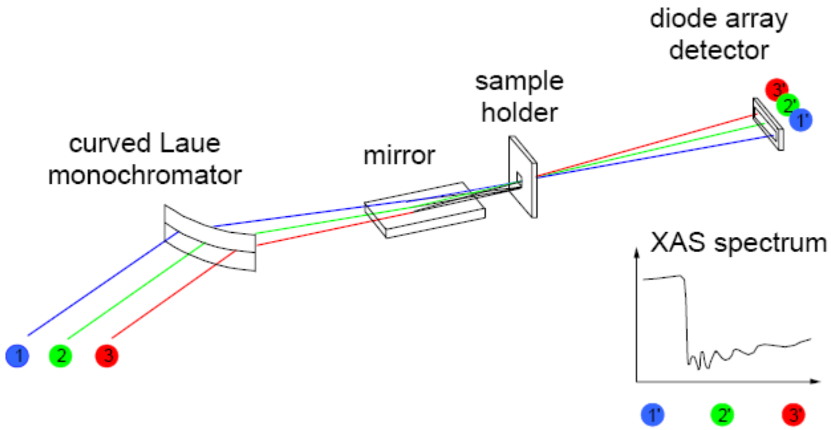
Q-XANES & D-XANES

Quick XANES

- Slew monochromator continuously to obtain a XANES spectrum in few seconds (X18B).
- All modes of detection.

Dispersive XANES

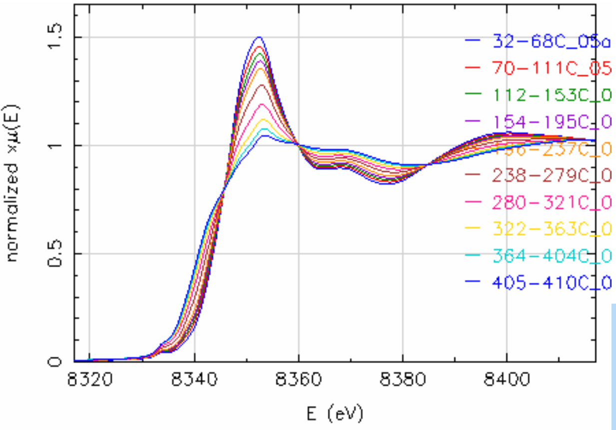
- Polychromatic beam dispersed onto linear detector.
- XANES spectrum in msec.
- Transmission only.
- Need extremely uniform samples.

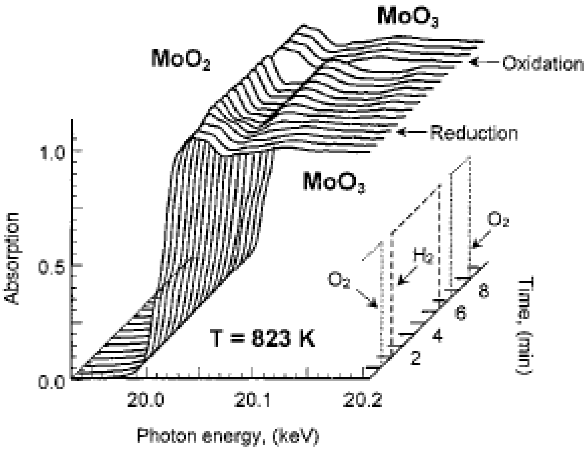


ESRF ID-24

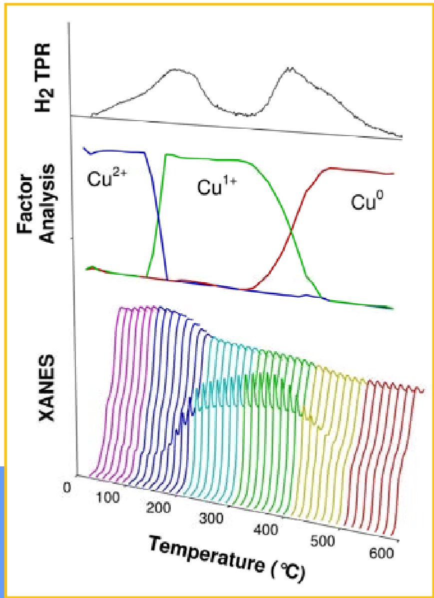
TPR-XANES: In situ Kinetics of Transformations

- **Many, many examples in the literature of using in situ XANES to monitor the transformation of the catalyst from one species/oxidation state to another.**
- **This is the most frequent current use of in situ XANES and catalysis.**
- **No "knowledge" of EXAFS fitting required.**
- **Use linear combination or PCA to determine the absolute amount of each species during the transformation.**





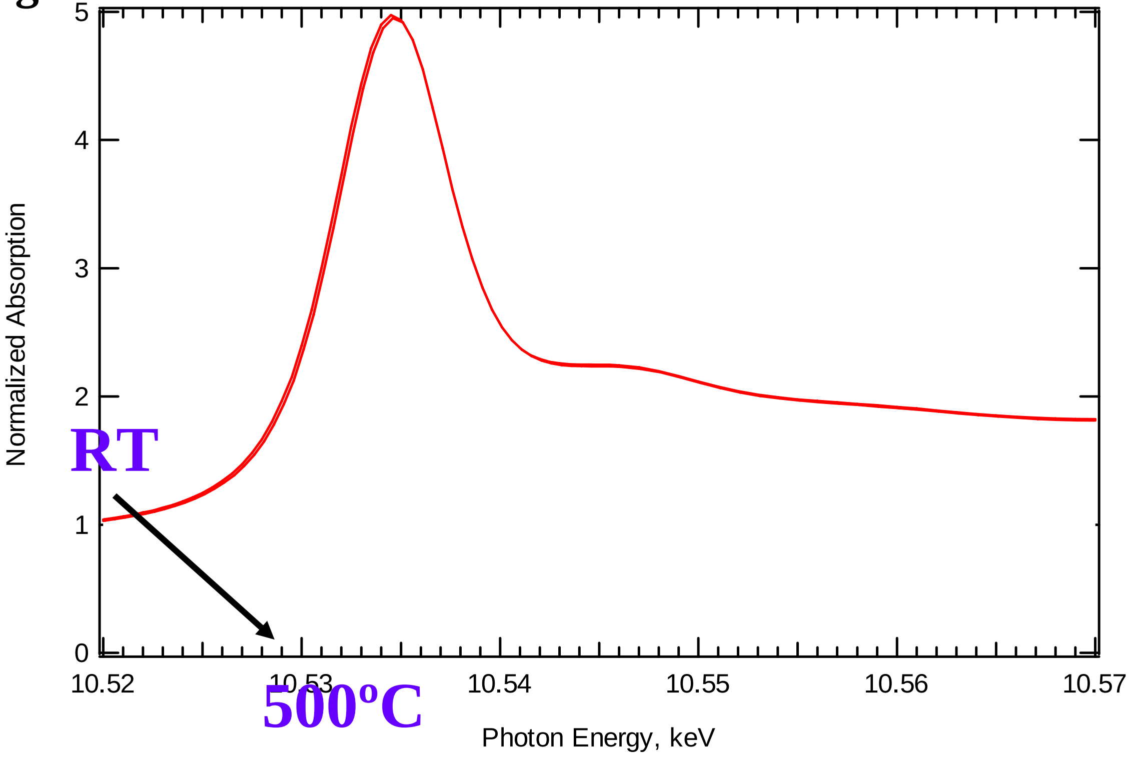
Cu-ZSM-5



In situ TPR-XANES Studies

In situ reduction of 0.7wt% Re/Al_2O_3

100% H_2; 1 deg/min

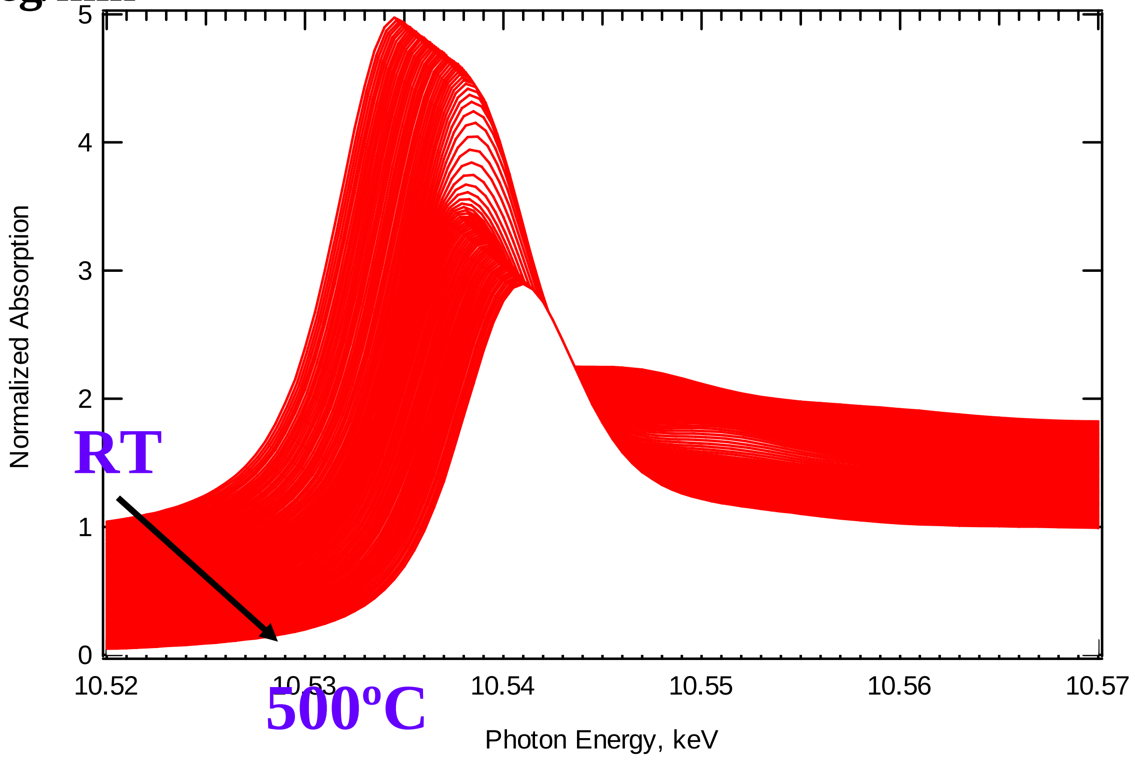


- **Collect Re L_3-edge XANES while heating catalyst in flow of H_2**

In situ TPR-XANES Studies

In situ reduction of 0.7wt% Re/Al_2O_3

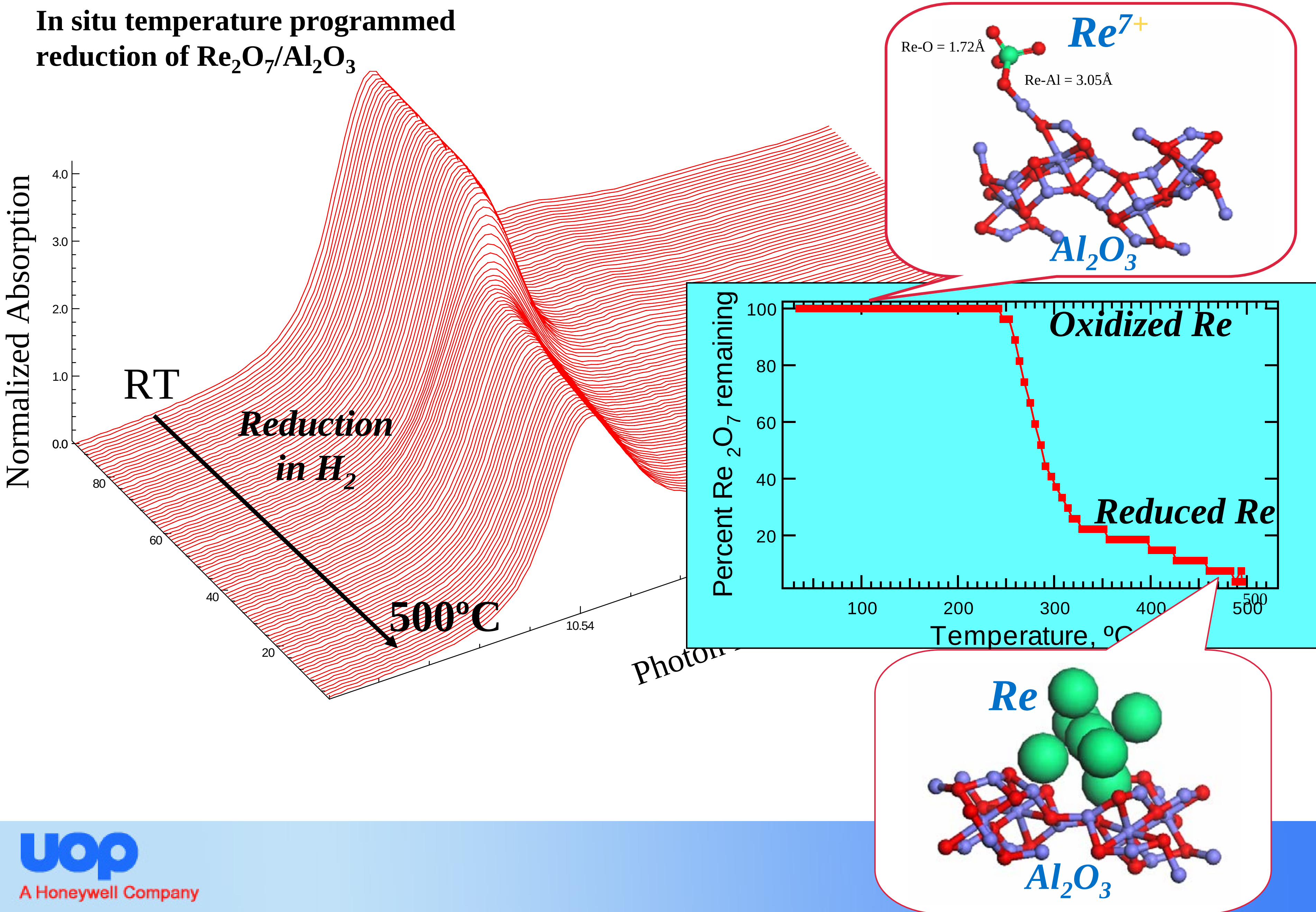
100% H_2; 1 deg/min



- **Collect Re L_3-edge XANES while heating catalyst in flow of H_2**

Time Evolution of XANES: Kinetics

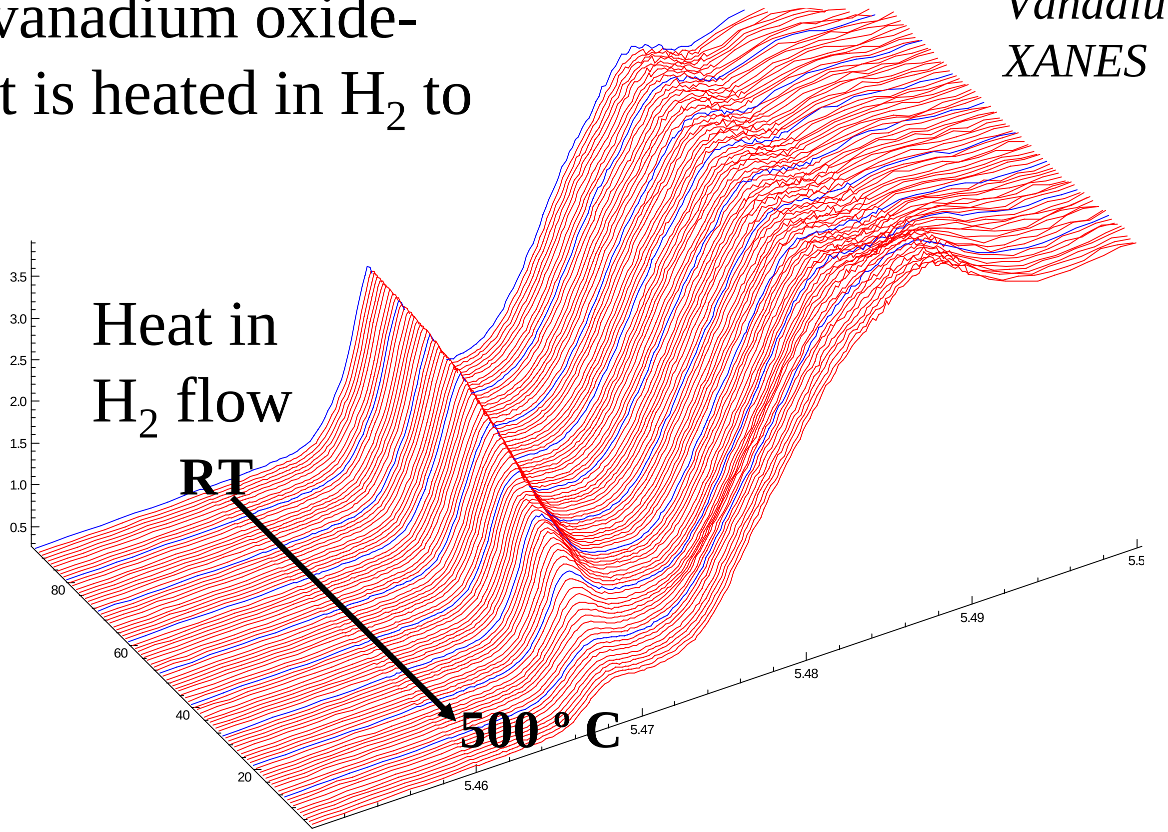
In situ temperature programmed reduction of Re_2O_7/Al_2O_3



Time Evolution of XANES: Kinetics

TPR-XANES showing reduction of vanadium oxide-based catalyst is heated in H_2 to 500°C

Vanadium K-edge XANES



Heat in H_2 flow

RT

500 °C

80 sec/scan at X19A

Analysis of Mixtures

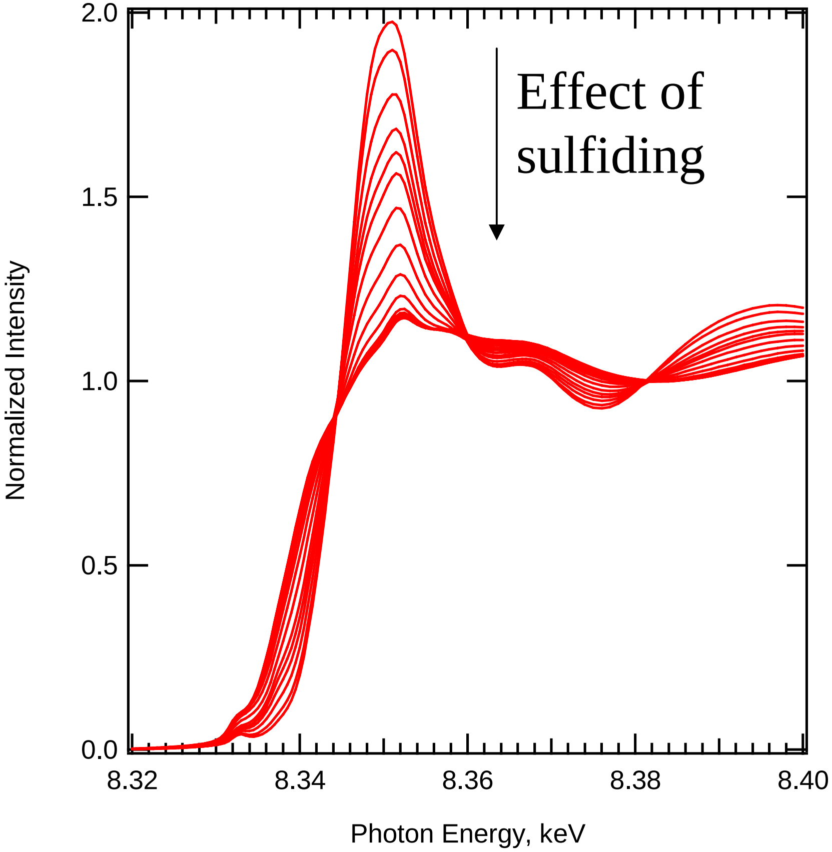
- XANES useful technique to quantitatively determine composition of a mixture of species.
- Useful for following time evolution of species during a chemical reaction.
- Two most common methods:
  - Least squares linear combination fitting
  - Principal component analysis

Least Squares Linear Combination Fitting

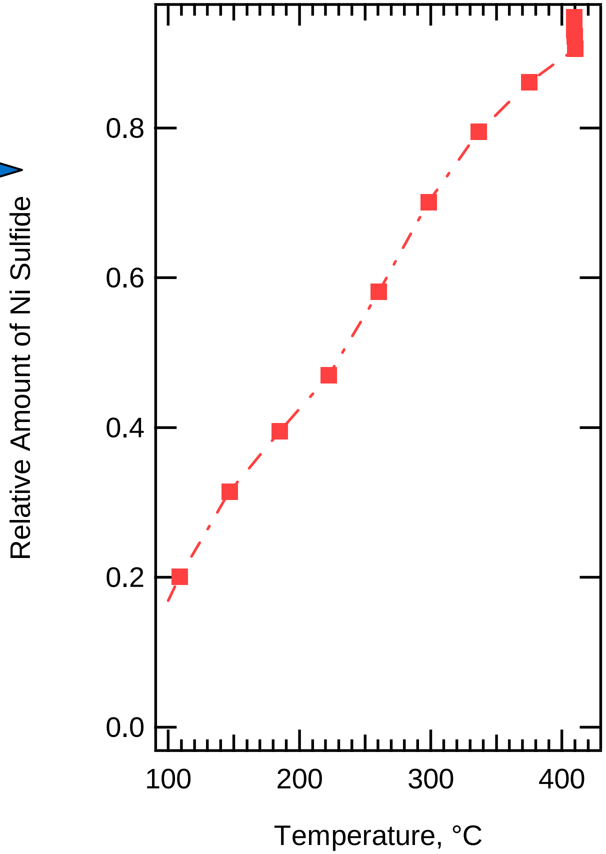
- Use a linear combination of spectra of various reference samples.
- Allows quantification of species in multiple-component mixture from their fingerprint in the XANES region.
- Use a least-squares algorithm to refine the sum of a given number of reference spectra to an experimental spectrum.
- Simple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

Linear Combination Fitting

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



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



Future Prospects

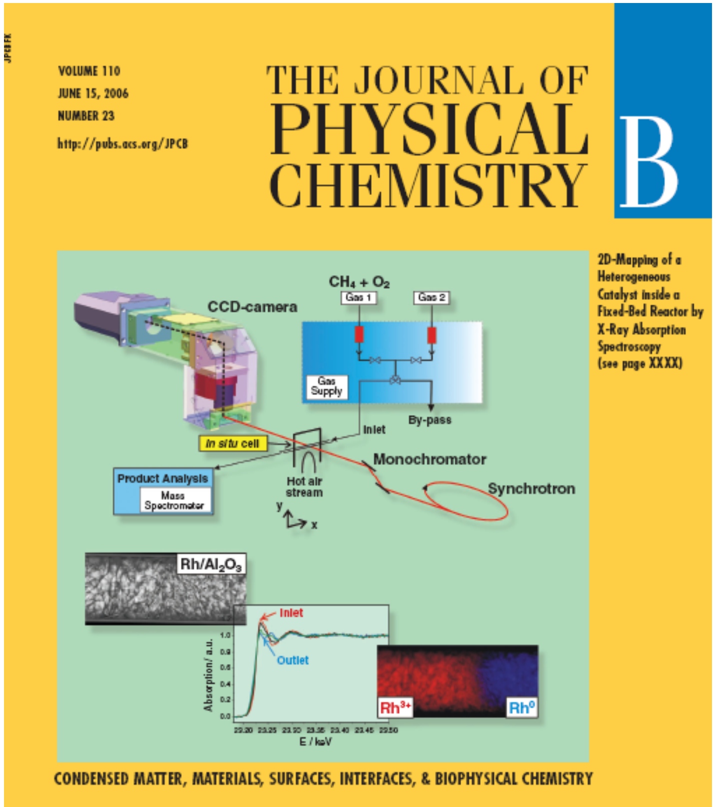
- **Imaging XANES**
- **High resolution XANES**
- **Selective XANES**

2D Imaging of Catalyst Structure

2D-Mapping of the Catalyst Structure Inside a Catalytic Microreactor at Work: Partial Oxidation of Methane over Rh/Al_2O_3

Jan-Dierk Grunwaldt,[*,†] Stefan Hannemann,[†] Christian G. Schroer,[‡] and Alfons Baiker[†]

Department of Chemistry and Applied Biosciences, ETH Zurich, CH-8093 Zurich, Switzerland and HASYLAB at DESY, Notkestrasse 85, D-22607 Hamburg, Germany



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http://pubs.acs.org/JPCB

THE JOURNAL OF
PHYSICAL
CHEMISTRY
B

2D-Mapping of a Heterogeneous Catalyst inside a Fixed-Bed Reactor by X-Ray Absorption Spectroscopy (see page XXXX)

CONDENSED MATTER, MATERIALS, SURFACES, INTERFACES, & BIOPHYSICAL CHEMISTRY

2D Imaging of Catalyst Structure

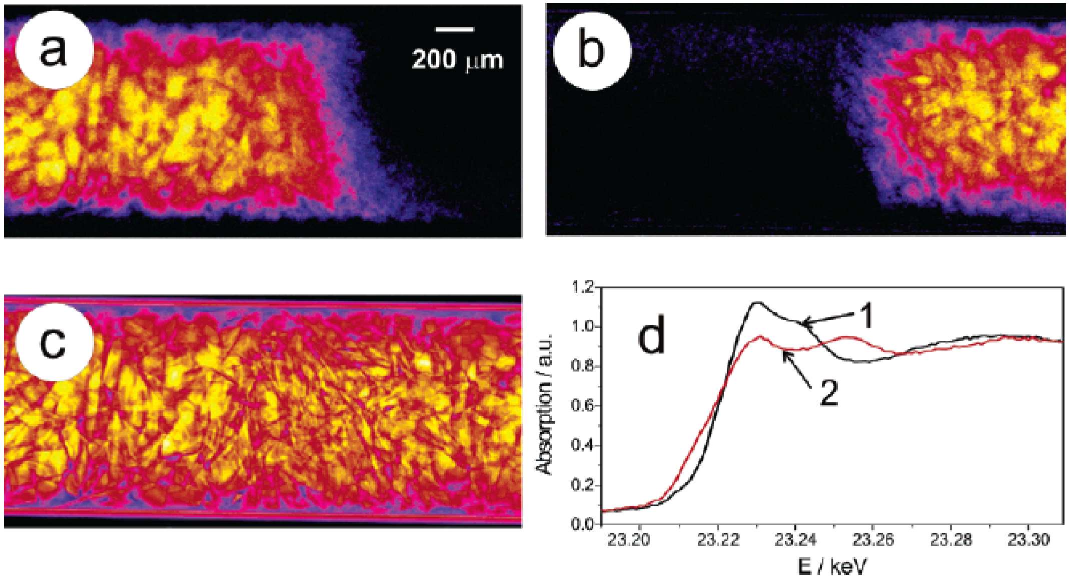


Figure 5. Amount of oxidized Rh-species (depicted in (a), oxidized species 1 in (d)), reduced Rh-species (depicted in (b), reduced species 2 in (d)) and the distribution of other elements that show a featureless absorption spectrum in the given energy range (c) along the capillary (original image taken by CCD-camera was 3.0 mm × 1.5 mm; the reaction gas mixture 6%CH_4/3%O_2/He enters from the left).

X-Selective XANES

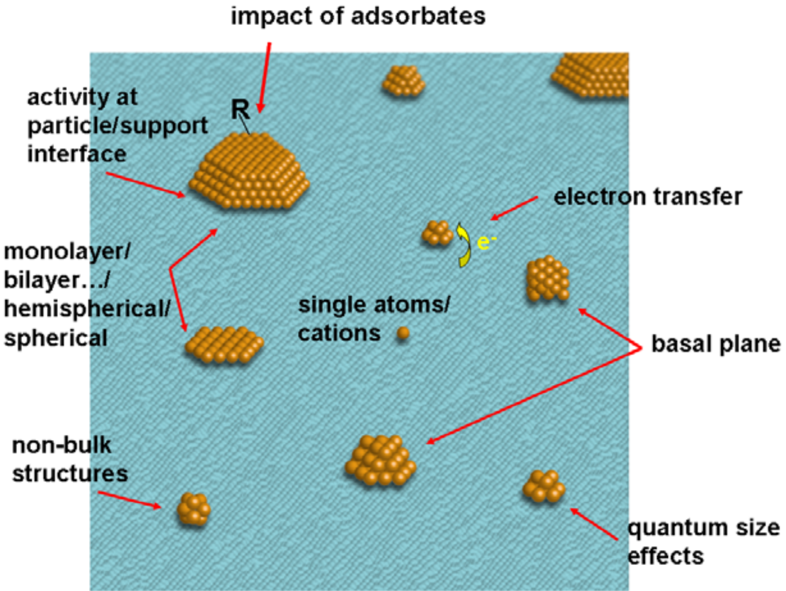
- **In concept by selecting a single fluorescence decay channel there are many different types of XANES either already demonstrated or feasible:**
  - **Spin-selective**
  - **Edge-selective**
  - **Valence-selective**
  - **Neighbor-selective**

Examples of Application of XAFS to Catalyst Characterization

- **EXAFS**

Supported Metal Clusters: Information from in situ XAFS

- **Average metal cluster size (and shape)**
- **Average composition of bimetallic alloy clusters – is an alloy formed?**
- **d-density of states of metal clusters**
- **Effect of adsorbates on cluster structure and electronic properties.**

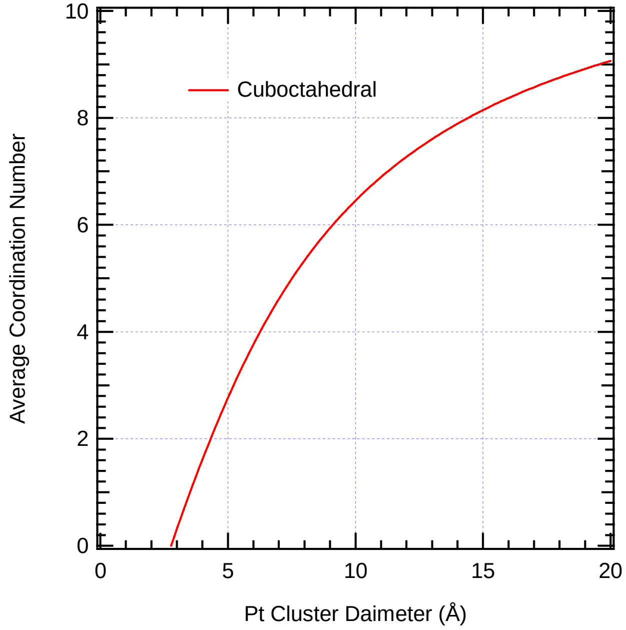


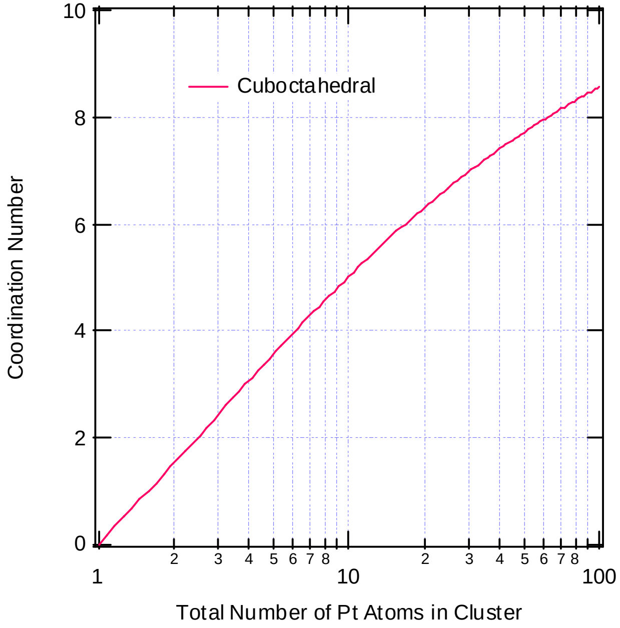
In situ XAFS and Cluster Size

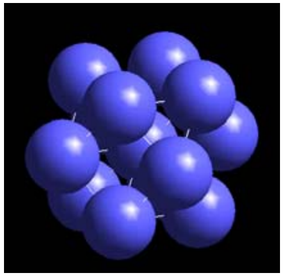
- **The average coordination number is a strong function of cluster size for clusters <15Å diameter.**

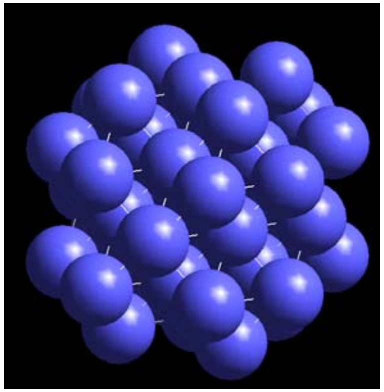
$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$

- **Use this to estimate average cluster size.**



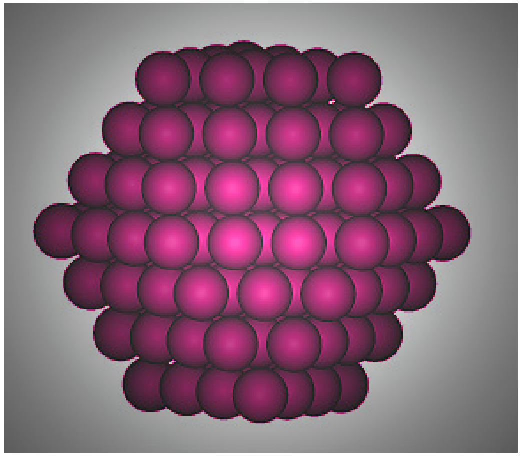






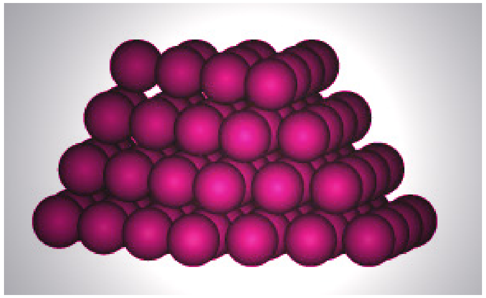
Supported Metal Cluster Size & Morphology

Shape
and
texture



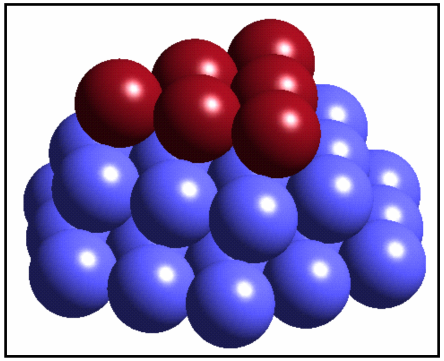
Cuboctahedron

or



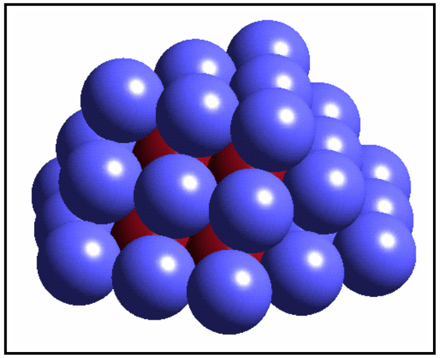
Hemispherical
Cuboctahedron (111)

Bimetallic
alloy
clusters



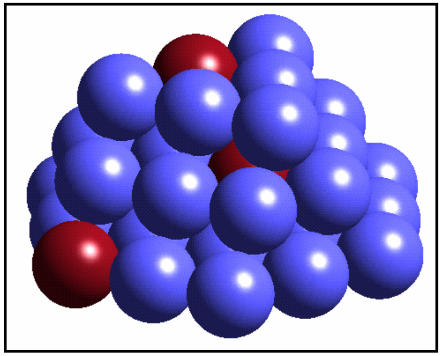
Surface segregation

or



Core segregation

or



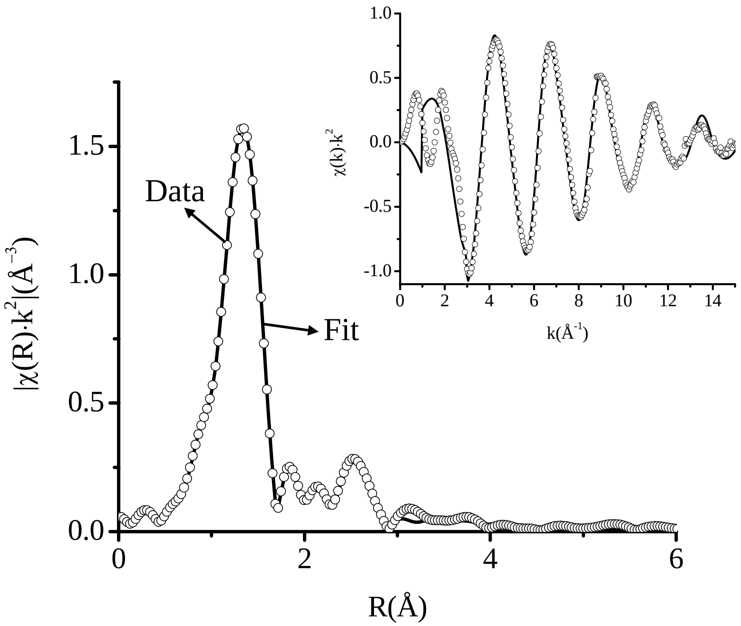
Random

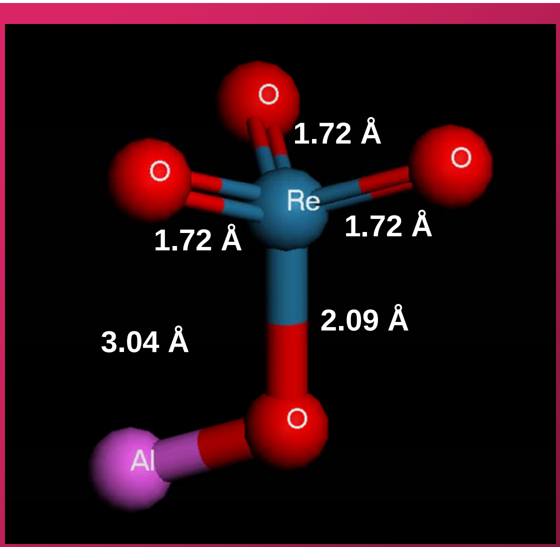
EXAFS Analysis to Determine Size & Shape of Re clusters on γ-Al_2O_3

- **Re supported on γ-Al_2O_3 is catalyst is has been shown to have high activity and high selectivity in olefin metathesis in oxidic form; when Re forms a bimetallic cluster with Pt then the subsequent Pt-Re clusters are used in petroleum reforming catalysts.**

- **What is the structure of Re species on the γ-Al_2O_3 surface after the alumina is impregnated with perrhenic acid, calcined, dried and reduced?**

Re L_3-edge EXAFS of in situ Dried Oxidized Catalyst





Implied structure of *in situ* dried calcined catalyst

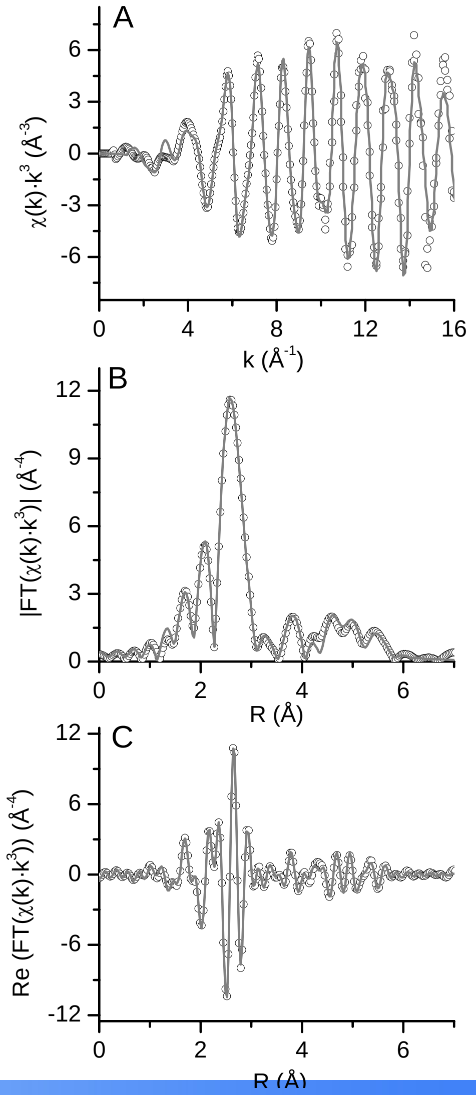
- **Four O atoms in distorted tetrahedral arrangement (3 short, 1 long)**
- **[ReO_4] is anchored to the alumina surface through Re-O-Al linkage.**
- **Similar structure for 0.5-10 wt% Re.**
- **Structure consistent with indirect characterization data in the literature (laser Raman & FTIR).**

J. Phys. Chem. B (2006) submitted.

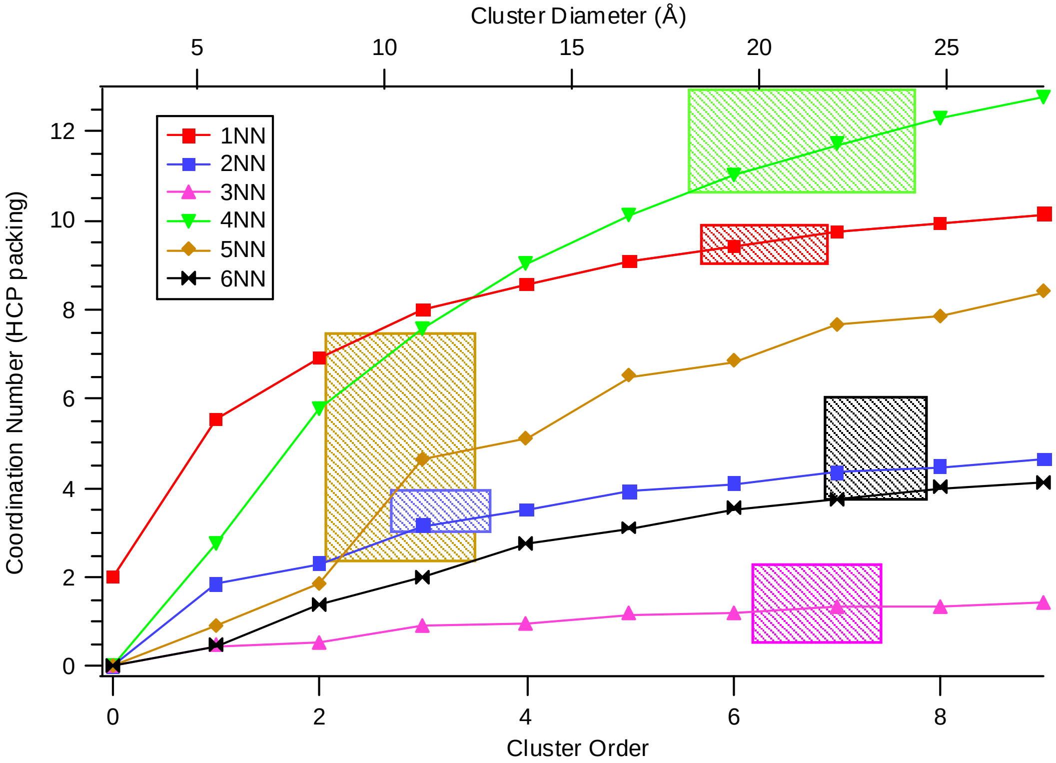
Wet Reduced Re clusters on Al_2O_3

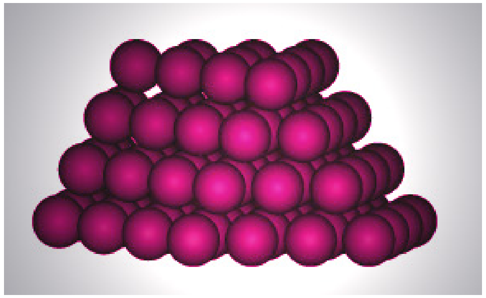
- **Reduction of oxidized Re in wet hydrogen leads to agglomeration of the Re clusters.**
- **EXAFS used to estimate both the average size and shape of the resulting Re clusters.**

Bulk Structure					
12	6	2	18	12	6
EXAFS fit to Wet Reduced					
9.6 ± 0.4	3.3 ± 0.5	1.3 ± 0.9	11.7 ± 1.4	4.4 ± 2.6	5.2 ± 0.6



Wet Reduced Re Clusters on Al_2O_3



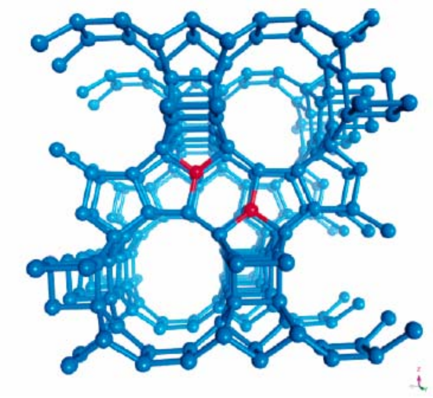


- Average cluster size not consistent with spherical or cuboctahedron or hemispherical models.
- Best fit to EXAFS data consistent with a 5 layer sheet-like Re cluster, with average diameter of ~30Å.

J. Phys. Chem. B, 2006, submitted.

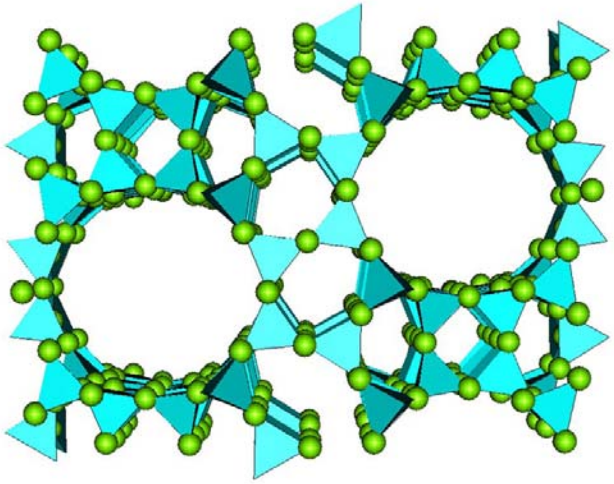
Definitive Structure of "Active Site"

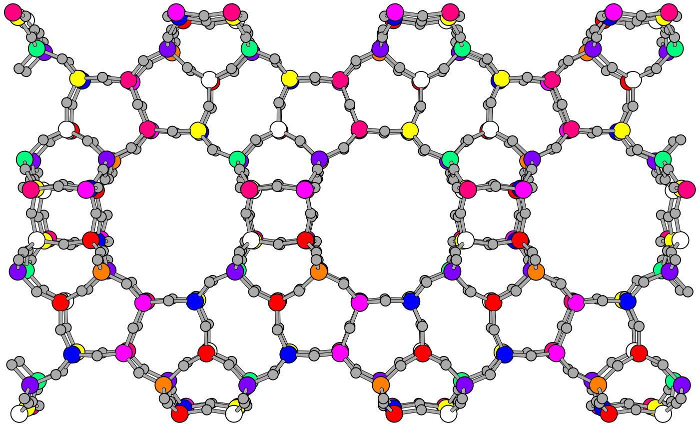
- EXAFS can be used to obtain detailed structural information of the "active site" – the species present on the catalyst surface after some pre-treatment but prior to reaction, or even during the reaction.
- Ideally suited when there is a well-defined bonding arrangement between surface species of interest and the support *and* all the species are the same, or when heteroatom substituted into a zeolite.
- No other way to obtain this information.



EXAFS analysis of Sn-beta Zeolite: location of Sn atoms

- **Sn-beta is an excellent catalyst for some oxidation reactions.**
- **Wanted to determine if the Sn is substituted into the zeolite framework, and if so, where in the framework.**

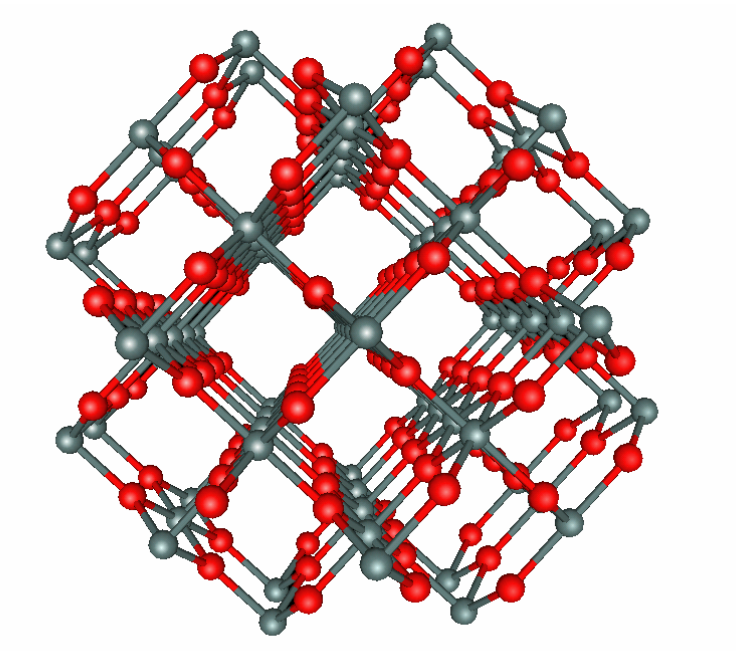




Key: T5 T6 T3 T4 T1 T2 T9 T7 T8 O

J. Am. Chem. Soc. **127** (2005) 12924-12932

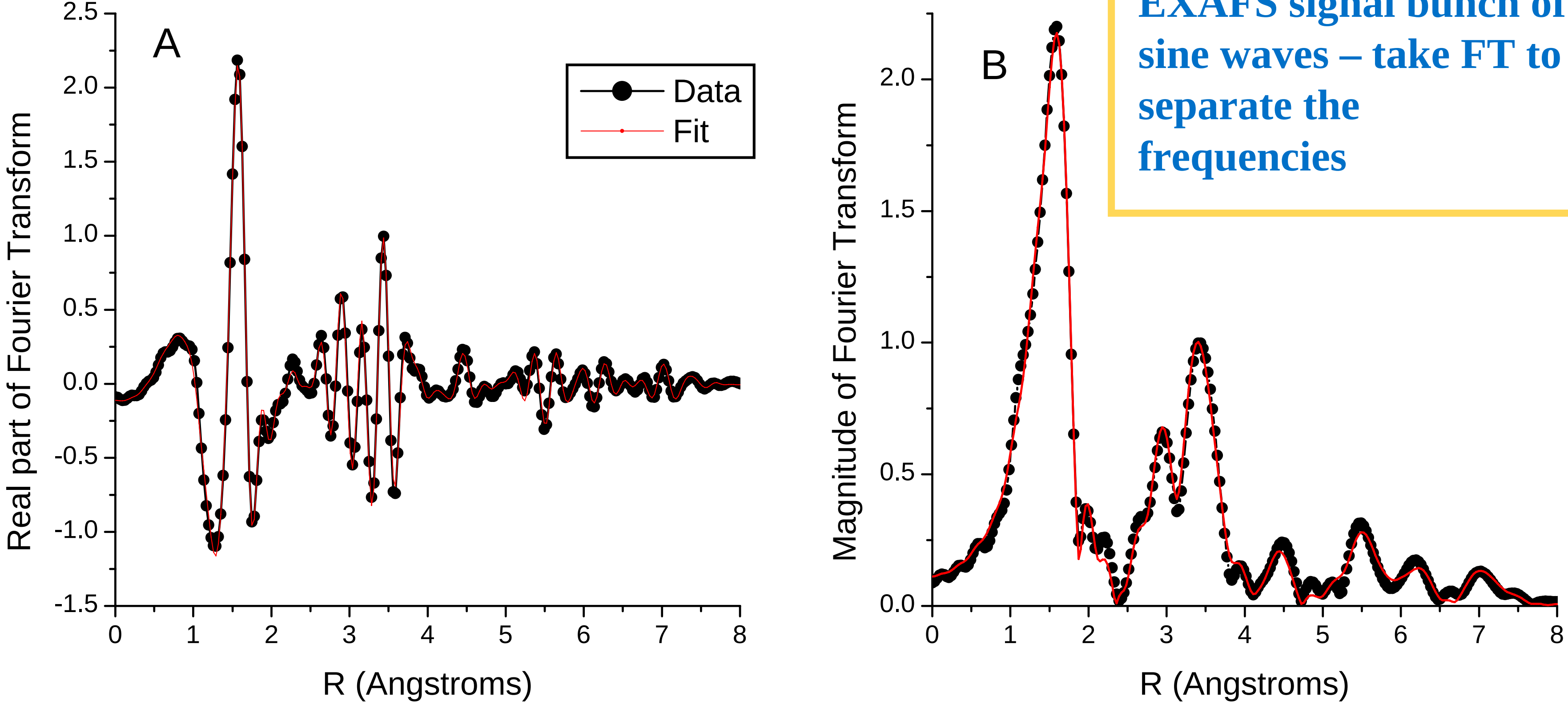
EXAFS Model for Cassiterite



Path	*N*	*reff*	ΔR	σ^2	ΔE
Sn-O1	**4**	**2.0519**	Alpha•**reff**	σ^2o1	ΔEo1
Sn-O2	**2**	**2.0567**	**Alpha•reff**	**σ^2o1**	**ΔEo1**
Sn-Sn1	**2**	**3.1864**	**Alpha•reff**	σ^2sn1	ΔEsn
Sn-O3	**4**	**3.5906**	**Alpha•reff**	σ^2o3	ΔEo2
Sn-Sn2	**8**	**3.7093**	**Alpha•reff**	σ^2sn2	**ΔEsn**
Sn-O5	**8**	**4.2414**	**Alpha•reff**	σ^2o5	**ΔEo2**
Sn-Sn3	**4**	**4.7373**	**Alpha•reff**	σ^2sn3	**ΔEsn**
Sn-O7	**8**	**4.8006**	**Alpha•reff**	σ^2o7	**ΔEo2**
Sn-Sn4	**8**	**5.7092**	**Alpha•reff**	σ^2sn4	**ΔEsn**
Sn-Sn5	**8**	**5.8365**	**Alpha•reff**	**σ^2sn4**	**ΔEsn**
Sn-Sn7	**4**	**6.6995**	**Alpha•reff**	σ^2sn7	**ΔEsn**
Sn-Sn8	**8**	**7.4187**	**Alpha•reff**	σ^2sn8	**ΔEsn**
Sn-Sn9	**16**	**7.6578**	**Alpha•reff**	σ^2sn9	**ΔEsn**

- **Used to determine S_0^2 for Sn.**
- **The model is described by 18 parameters**

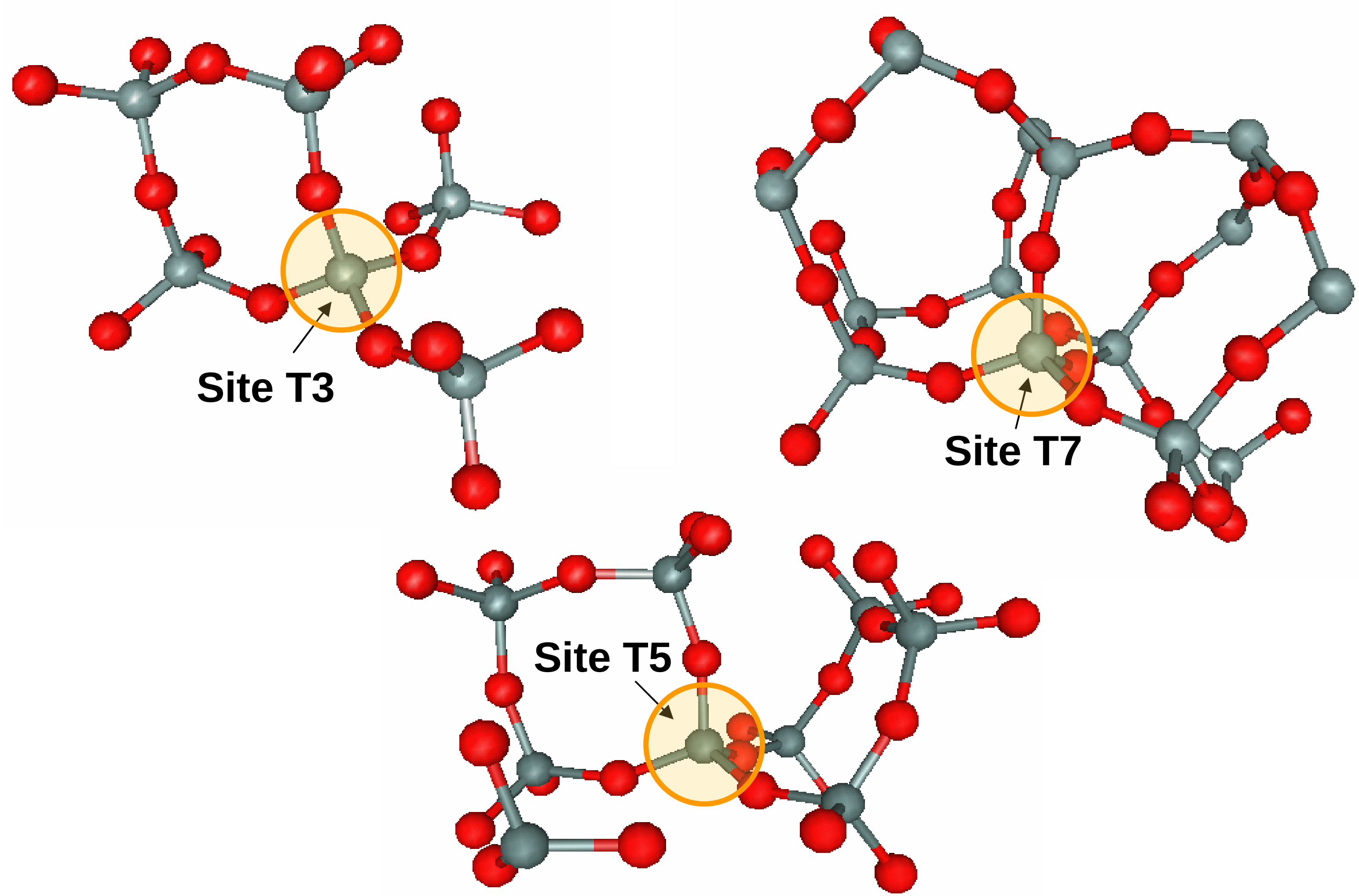
EXAFS Model and Cassiterite data



EXAFS signal bunch of sine waves – take FT to separate the frequencies

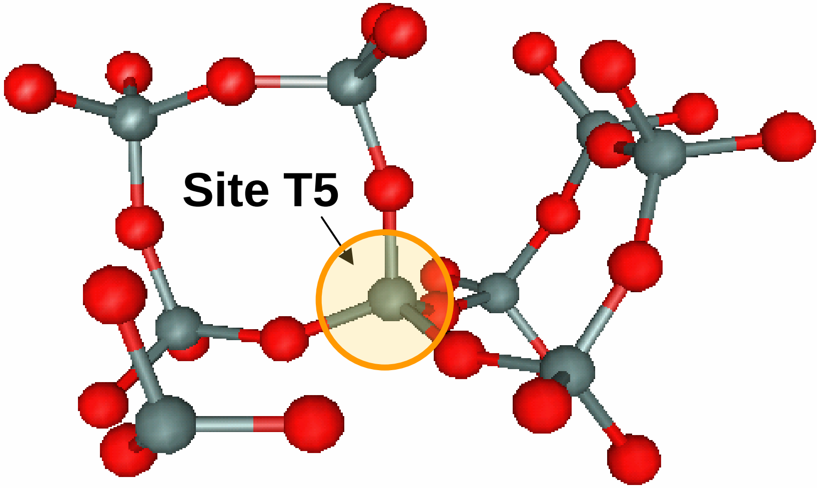
- **The model reproduces the data to 7.7 Å**

Local Structure about the Si Sites in Beta



- There are three groupings of the framework sites in β-zeolite.

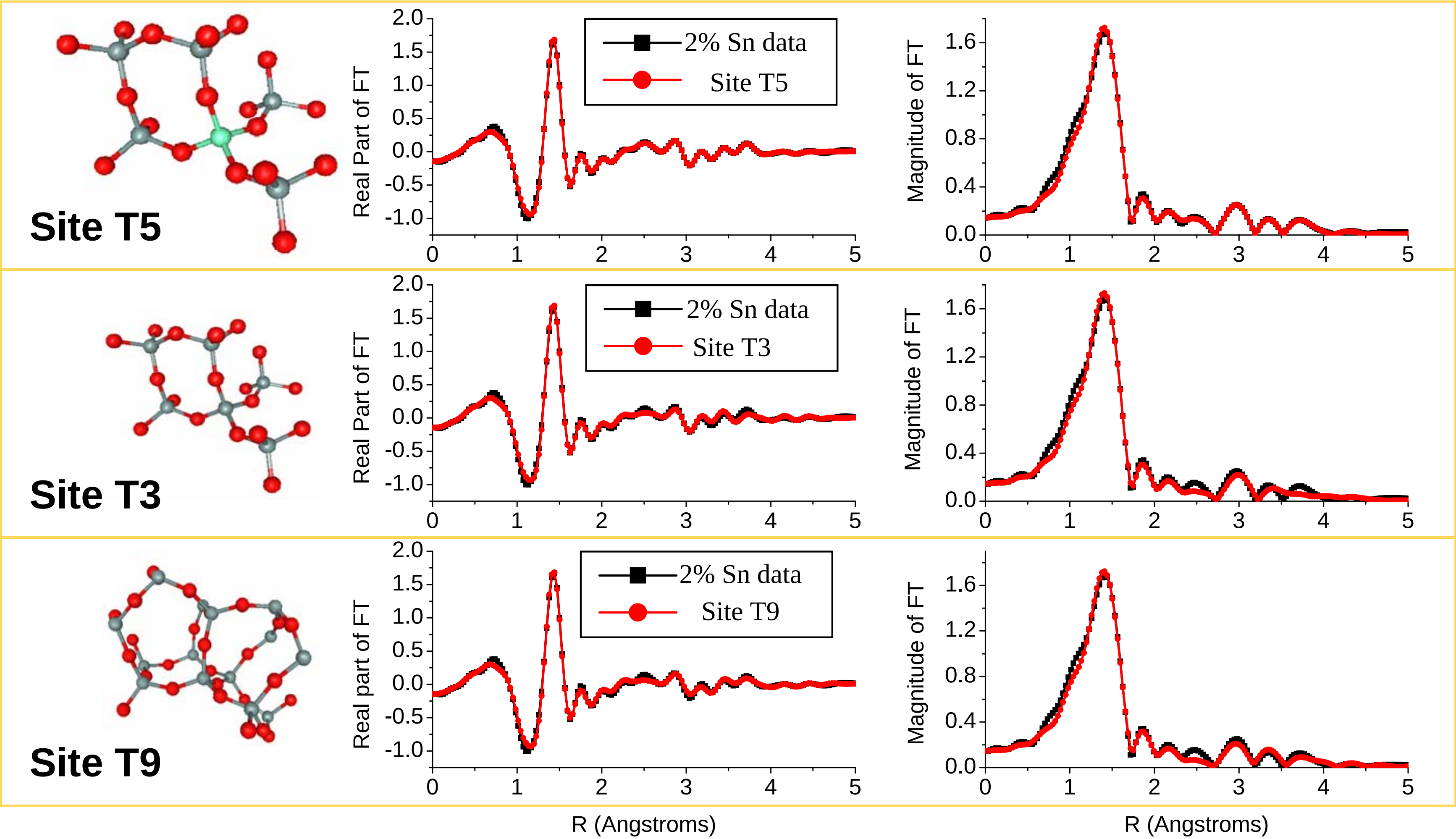
EXAFS Models for Sn-Beta Zeolite, Site T5



Path	N	Reff (Å)	ΔR	σ^2
Sn in Si SiteT5of beta-zeolite structure				
Sn-O1	4	1.86	ΔRo1	σ^2o1
Sn-O1a-O1b triangle	12	3.38	ΔRo1o1	σ^2o1o1
Sn-Si1	3	3.57	ΔRsi1	σ^2si1
Sn-O1-Si1	6	3.65	ΔRsi1	σ^2si1
Sn-O1-Si1-O1	3	3.72	ΔRsi1	σ^2si1
Sn-Si2	1	3.66	ΔRsi2	σ^2si2
Sn-O1-Si2	2	3.70	ΔRsi2	σ^2si2
Sn-O1-Si2-O1	1	3.72	ΔRsi2	σ^2si2
Sn-O1-Sn-O1	4	3.72	2·ΔRsi1	4·σ^2o1
Sn-O2	2	4.24	ΔRo2	σ^2o2
Sn-O3	2	4.30	ΔRo2	σ^2o2
Sn-O4	2	4.40	ΔRo2	σ^2o2
Sn-Si3	3	4.28	ΔRsi3	σ^2si3

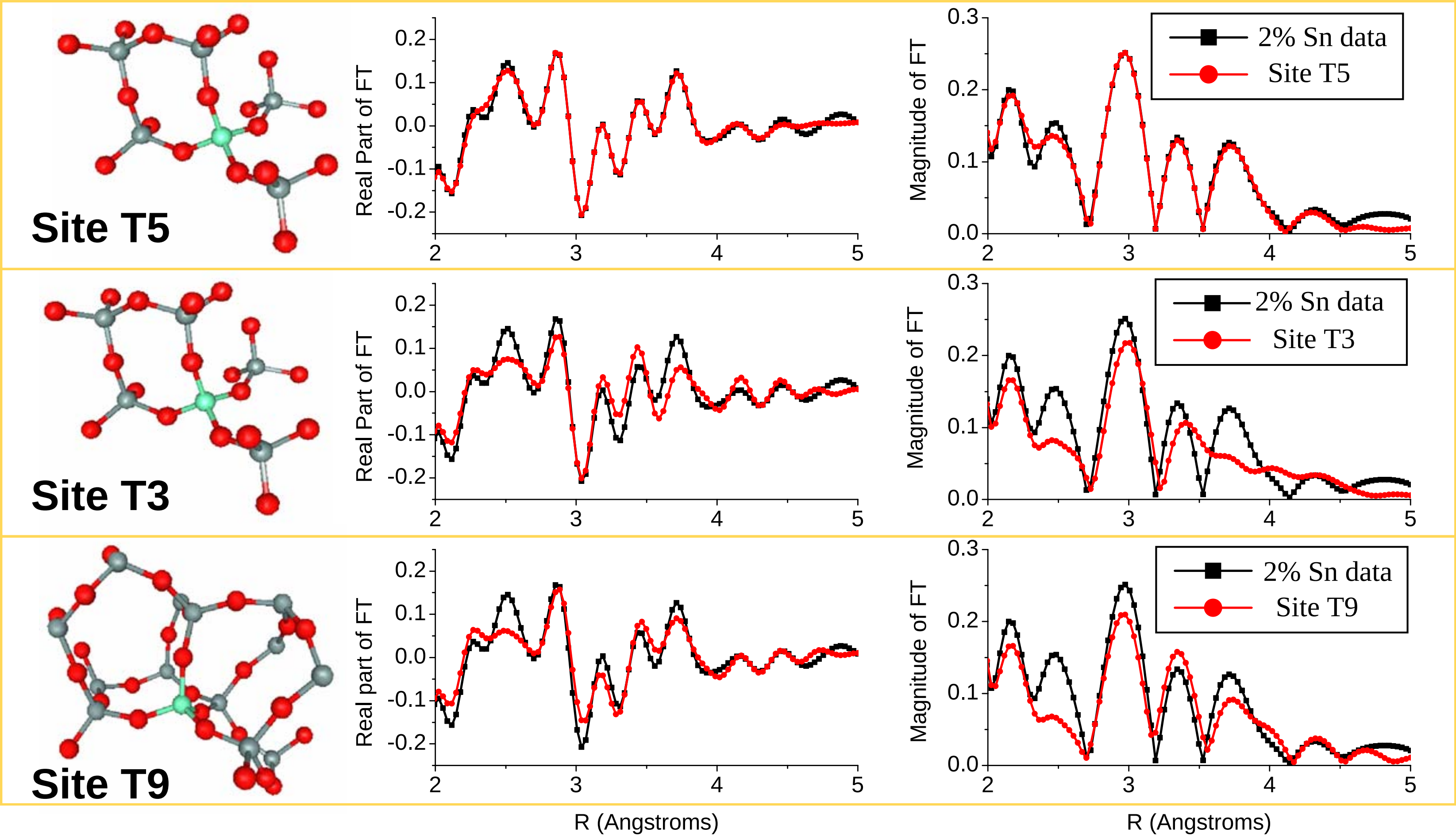
- **The model is described with 13 parameters**

Comparison of Models for Beta-Zeolite



- **All models give Sn-O = 1.91Å, consistent with tetrahedral Sn(IV), and CN = 4. Thus, Sn is in the beta framework.**

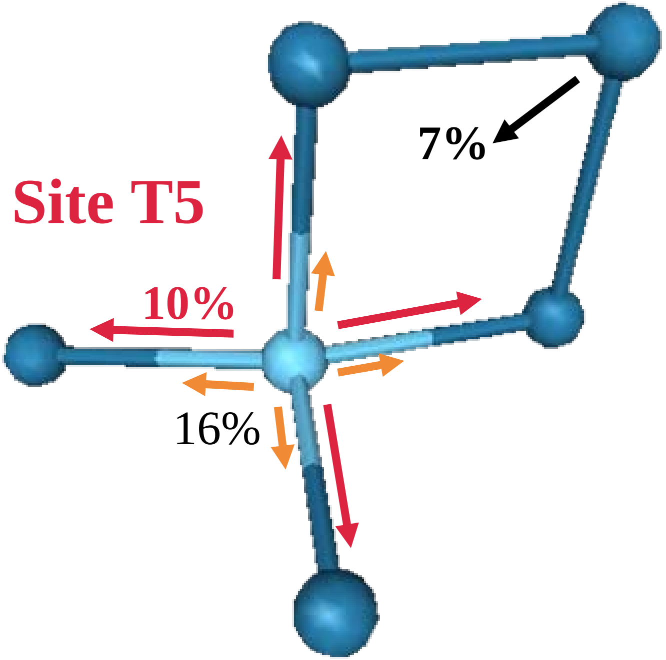
Comparison of Models for Beta-Zeolite



- **Model for Site T5 clearly better fit to the data. Sn preferentially occupies T5 sites in beta framework**
- **Supported statistically by value of χ^2. Value ~20 times less than other 2 sites.**

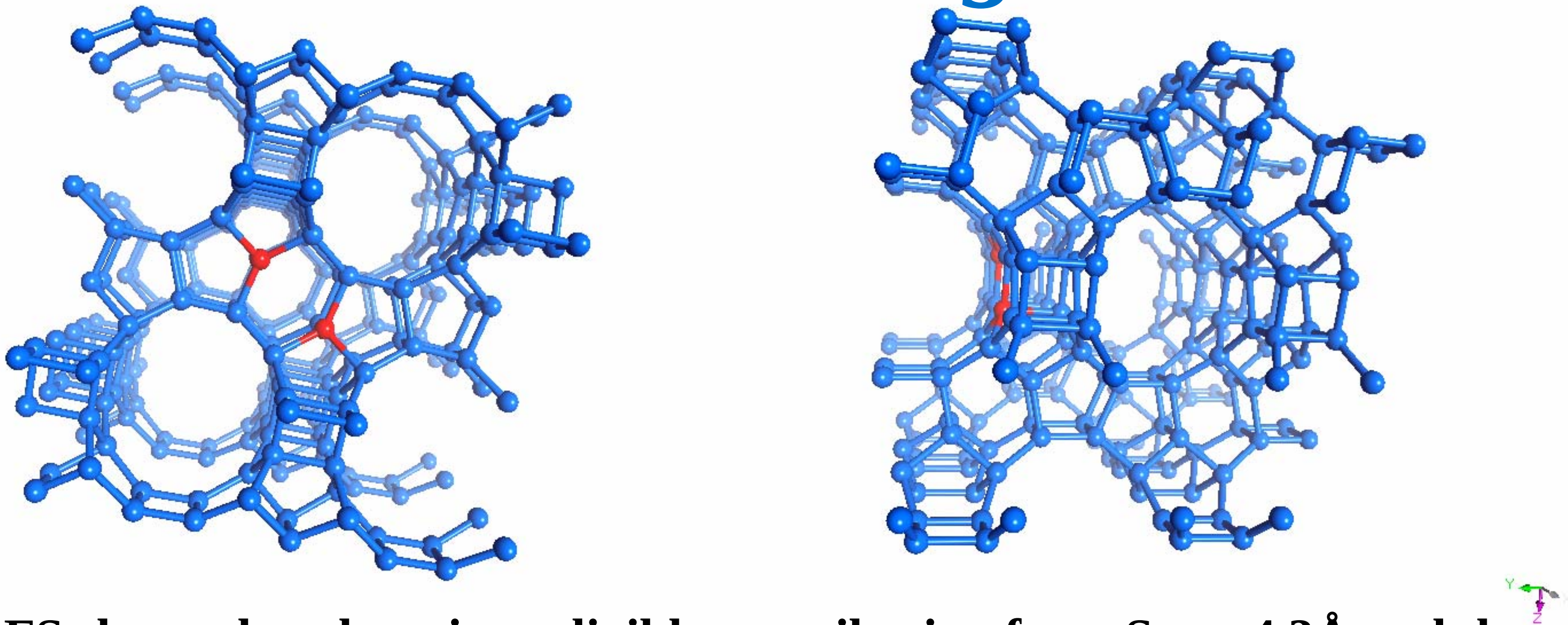
Best Fit Values for Sn in Site T5

Path	N	R_{eff} (Å)	R (Å)	ΔR (Å)
		XRD for Si in site T5	EXAFS for Sn in site T5	% Change
Sn-O1	4	1.62	1.906 ± 0.001	16
Sn-Si1	3	3.15	3.50 ± 0.01	10
Sn-Si2	1	3.20	3.86 ± 0.10	17
Sn-O2	2	3.70	4.48 ± 0.02	19
Sn-O3	2	3.75	4.53 ± 0.02	19
Sn-O4	2	3.83	4.63 ± 0.02	19
Sn-Si3	3	4.31	4.03 ± 0.05	-6.7
Sn-Sn	1	5.01	4.99 ± 0.04	-0.4



- First neighbor oxygen atom distances are expanded by 16%
- First neighbor Si atom distances are expanded by 10%
- Second neighbor Si atom distance is contracted by 7%

Sn-Sn Pairing



- **EXAFS shows that there is negligible contribution from Sn at 4.3Å and that positions at 5.1Å are 100% occupied by Sn.**
- ***Thus, substitution of Sn is always paired!***
- ***If T5 site is occupied by Sn then T5 site on opposite side of 6-ring is always occupied by Sn.***
- **Sn loading is 0.5 Sn per unit cell, so on average only 1 of 8 BEA unit cells occupied by pair of Sn atoms.**

Summary: EXAFS

- **Provides quantitative element specific 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 neighboring atoms (σ_j^2)**
- **Can be performed on all forms of matter.**
- **Can be performed on all elements (>H).**
- **Can be performed in situ.**
- **Can provide time-resolved, and spatially resolved information.**

Summary: XANES

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…..

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- *Basic Principles and Applications of EXAFS*, **Chapter 10 of Handbook of Synchrotron Radiation, pp 995--1014. E. A. Stern and S. M. Heald, edited by E. E. Koch, North-Holland, 1983.**
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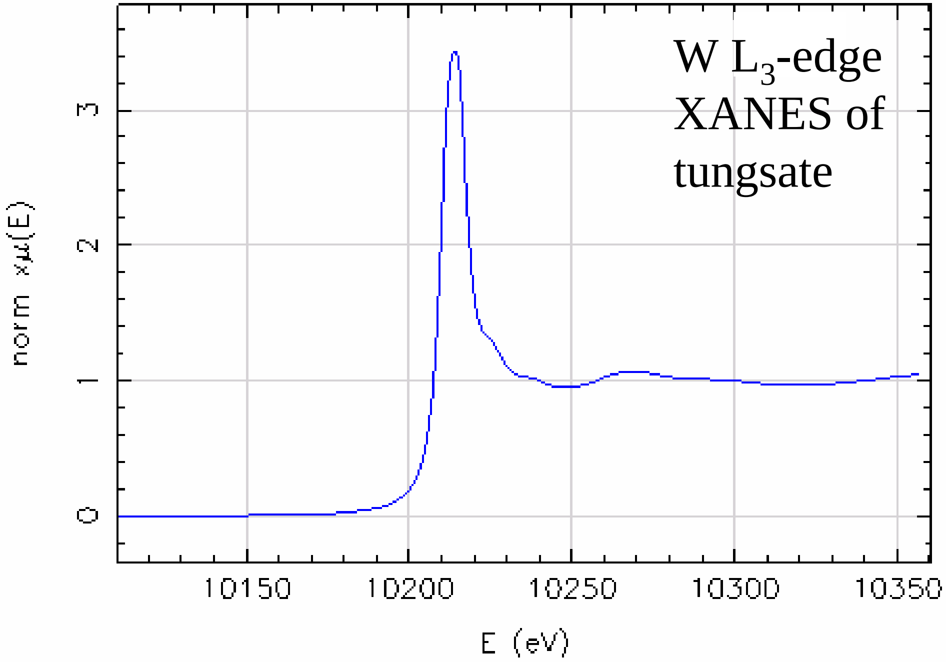
- *Theoretical approaches to x-ray absorption fine strucure* **J. J. Rehr and R. C. Albers, Reviews of Modern Physics Vol 72, pp. 621-892 (2000).**
- **McMaster compilation of x-ray cross sections. http://www.csrri.iit.edu/mucal.html**
- **Many websites: e.g. http://www.xafs.org and http://www.i-x-s.org/**

Additional Slides

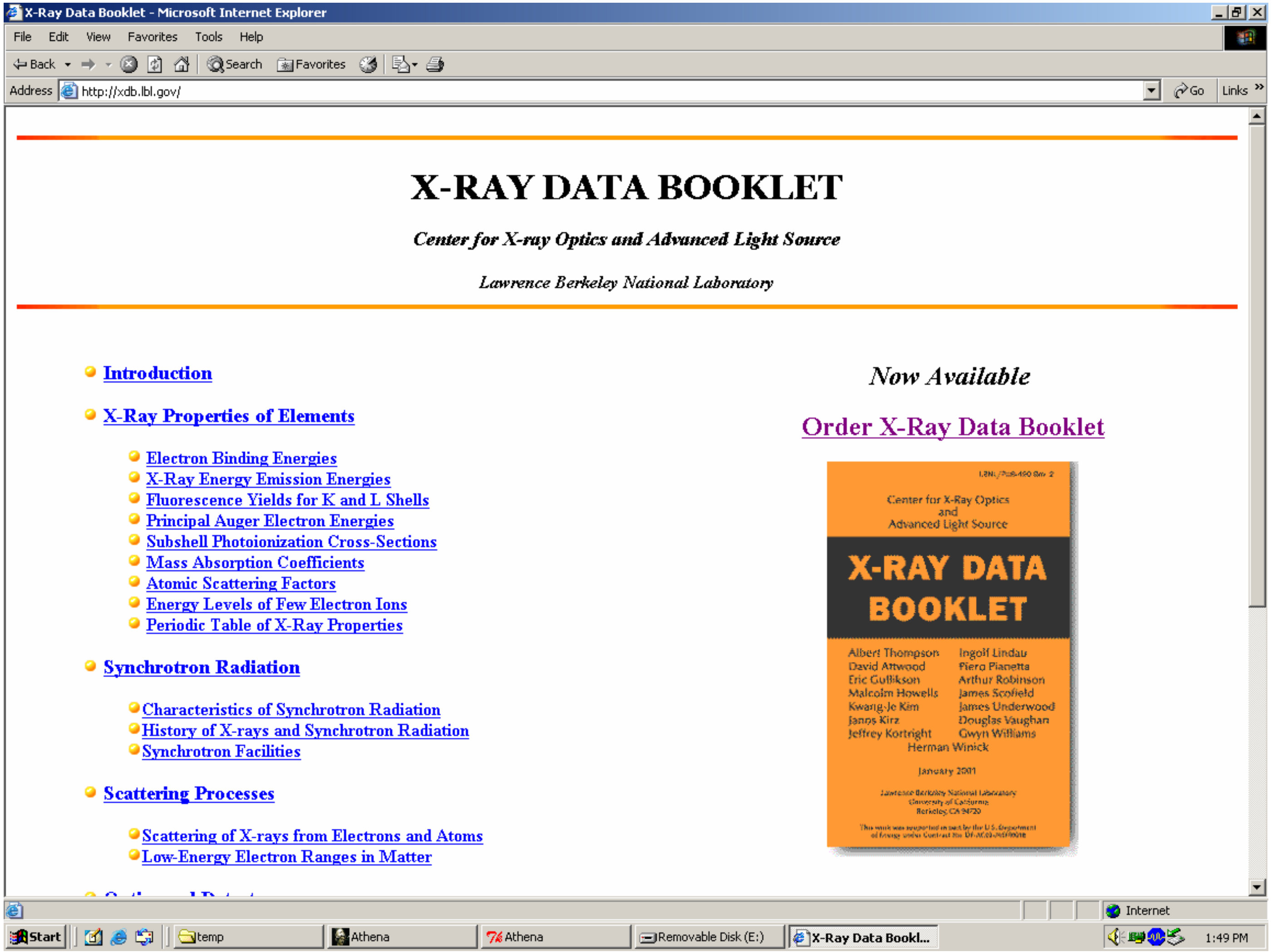
Miscellaneous: E to k

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



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

Miscellaneous: “Yellow book”



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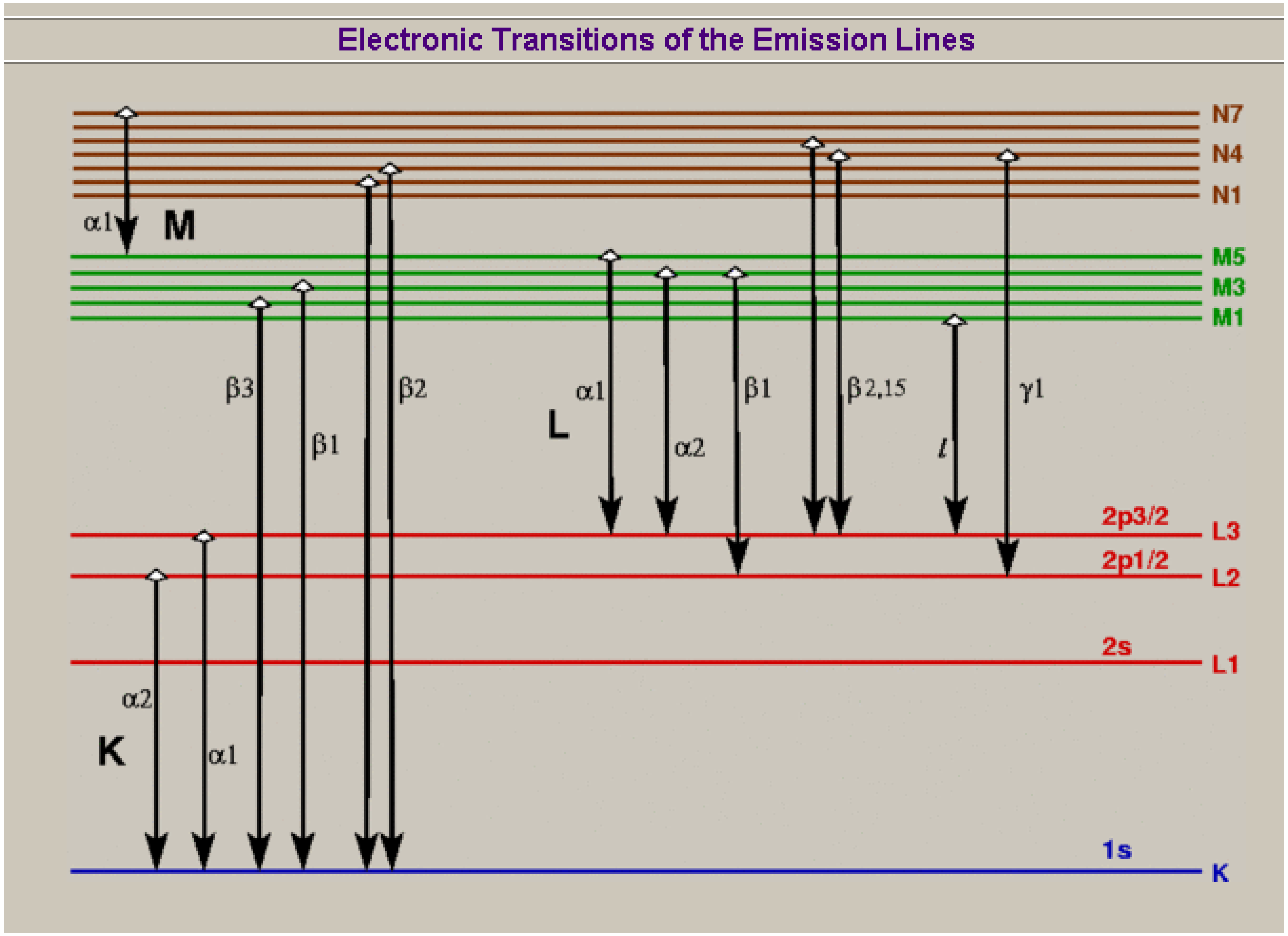

Energy Resolution

- Depends on divergence and intrinsic resolution.
- From derivative of Bragg equation, divergence results in: $\Delta E/E = \cot(\theta)\Delta\theta$
- $\Delta\theta$ determined by slits (or collimating mirror if present).

- Example: 1mm slit 30m from source at 10 keV with Si(111) monochromator

  $\Delta\theta = 1/30000 = 3.3\text{x}10^{-5}$, $\theta = 11.4$ or $\cot(\theta) = 4.9$

  From divergence: $\Delta E/E = 3.3\text{x}10^{-5}(4.9) = 1.6 \text{ x } 10^{-4}$

- Add divergence term and intrinsic term in quadrature to get approximate final resolution:

  $\Delta E/E = \sqrt{}(1.6\text{x}10^{-4})^2 + (1.3\text{x}10^{-4})^2 = 2.1\text{x}10^{-4}$ or 2.1 eV