X-RAY ABSORPTION SPECTROSCOPY (XAS)

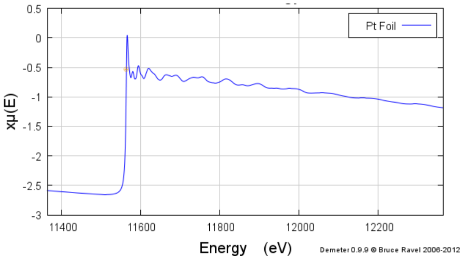
DR. SHELLY D KELLY
Group Leader
Advanced Photon Source

July 11, 2022
24th National School on Neutron and X-ray Scattering

OUTLINE

- Background X-ray absorption spectroscopy
- Fundamentals of atoms and electronic transitions
- X-ray absorption near edge spectra (XANES) process
- XANES examples
- Extended X-ray absorption fine structure (EXAFS) fundamentals
- EXAFS examples

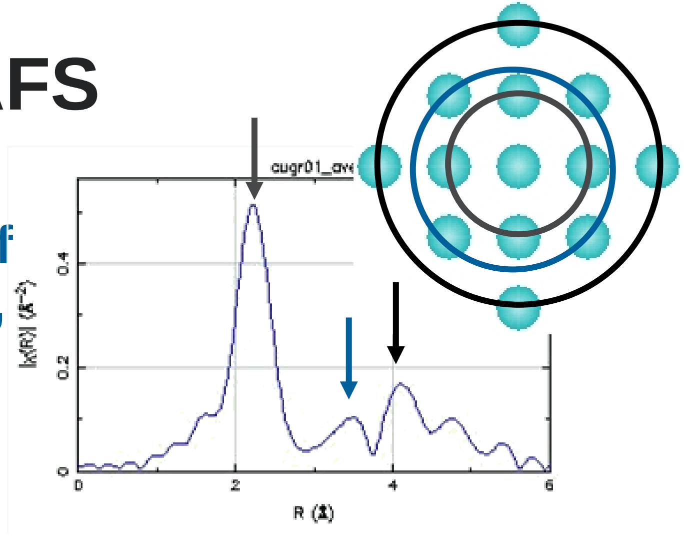
1920 PUBLISHED ABSORPTION EDGES



The K-characteristic absorption frequencies for the chemical elements magnesium to chromium H. Fricke Physical Review, 1920

- Absorption of X-Rays.-This paper contains an account of an experimental investigation concerning the discontinuity in the X-ray absorption corresponding to the K-series for the chemical elements from magnesium to chromium inclusively. The method followed was the same as that devised and employed by de Broglie. A specially designed vacuum spectrograph was used. Fine Structure of Absorption.-The spectrograms show that the discontinuity has a rather complex structure, a result in advance of those obtained by earlier investigators. A photometric study of the plates was made in order to obtain a more accurate knowledge of the detailed structure of the absorption limits. Results. These are recorded in tables which give for each element the wave-lengths of the different remarkable points in the structure of the discontinuities. The theoretical bearing of the new observations is briefly discussed. © 1920 The American Physical Society.

1971 UNDERSTANDING OF EXAFS

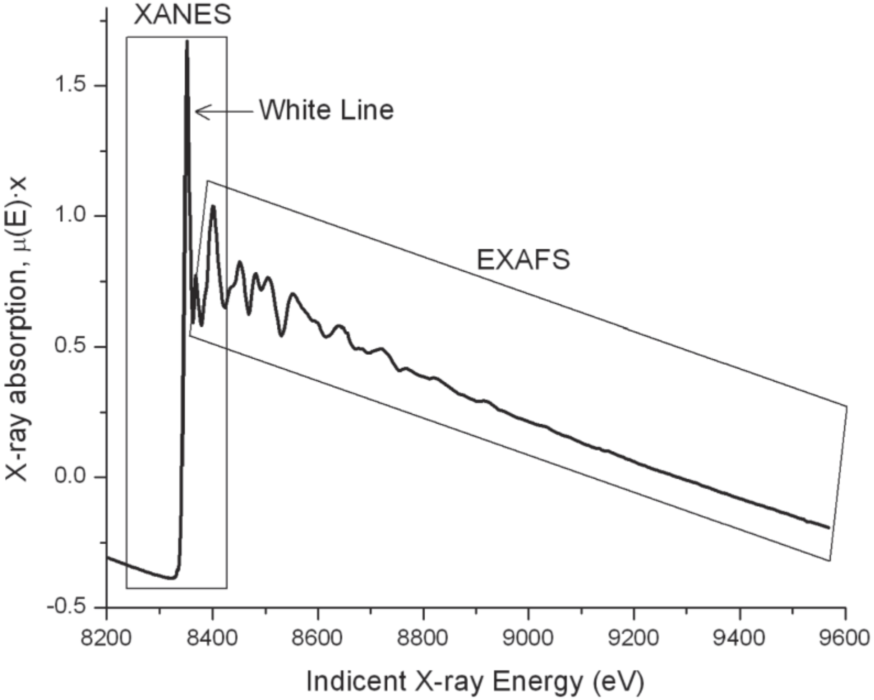


New technique for investigating noncrystalline structures: Fourier analysis of the extended x-ray-absorption fine structure, Sayers, D.E., Stern, E.A., Lytle, F.W., Physical Review Letters , 1971

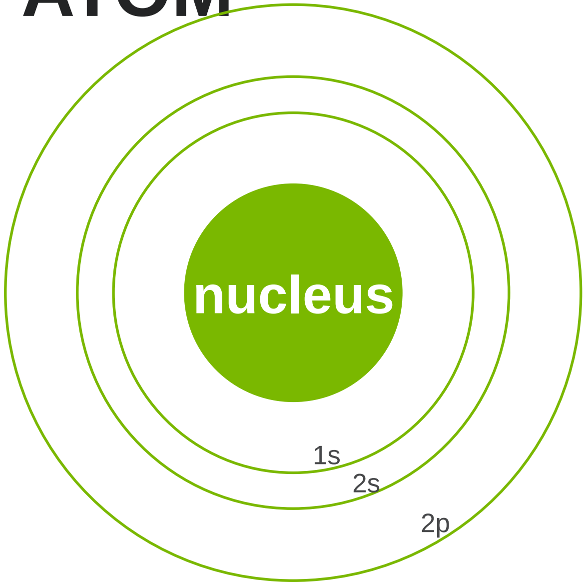
We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).

ACRONYMS

- General terms:
  - XAS: X-ray absorption spectroscopy
  - XAFS: X-ray absorption fine structure
- Specific terms:
  - EXAFS: Extended x-ray absorption fine structure
  - XANES: x-ray absorption near edge structure



ELECTRONIC STRUCTURE OF AN ATOM



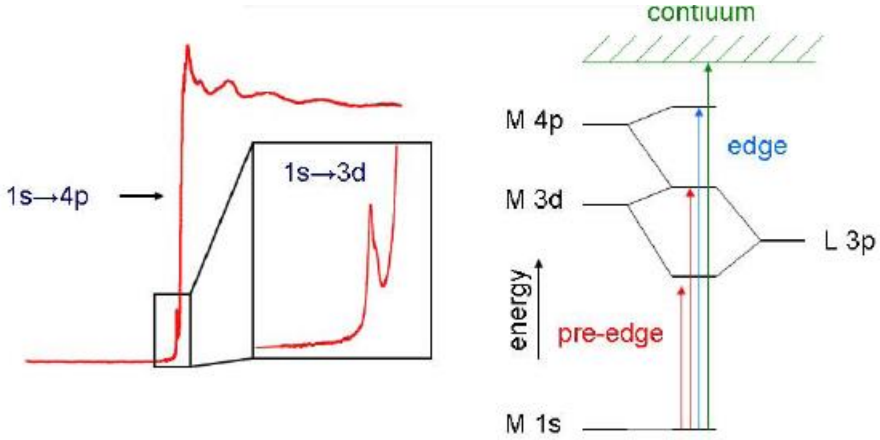
- Electronic structure described by 4 quantum numbers:
  - Principal: n
  - azimuthal: ℓ = 0, 1, 2,…n-1 = s, p, d, f
  - total angular momentum: $j=\ell+s$, spin = +1/2 or -1/2
- K shell, n=1; 1s
- L shell, n=2; 2s, $2p_{1/2}$, $2p_{3/2}$
- M shell, n=3; 3s, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, and $3d_{5/2}$
- Electronic transitions due to X-ray absorption must follow dipole selection rule requires conservation of angular momentum
  - Transitions are allow for ℓ = +/- 1

XANES: ELECTRONIC 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*: $\Delta l = \pm 1$
- 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.

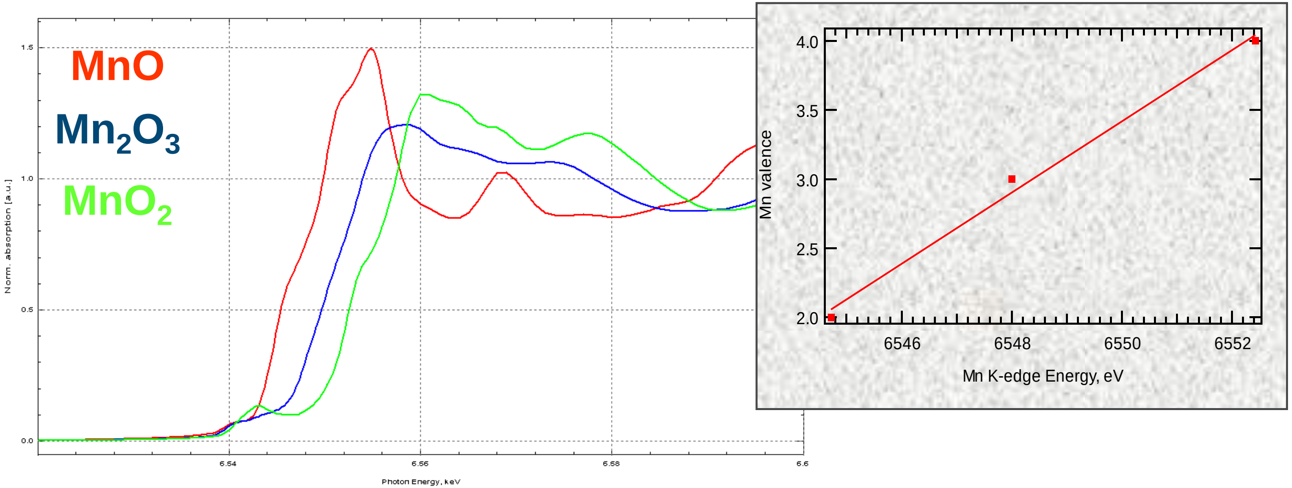
METAL K-EDGE XANES



- Absorption edge: dipole 1s → 4p transition (Δl = ±1)
- Pre-edge: mixing of 3d-4p opens 1s → 3d transition

OXIDATION STATE OF MN OXIDES

Mn K-edge XANES

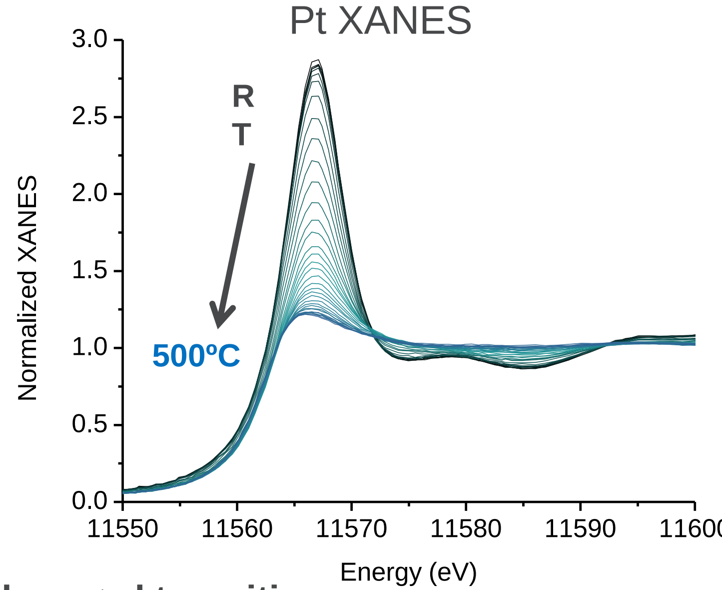


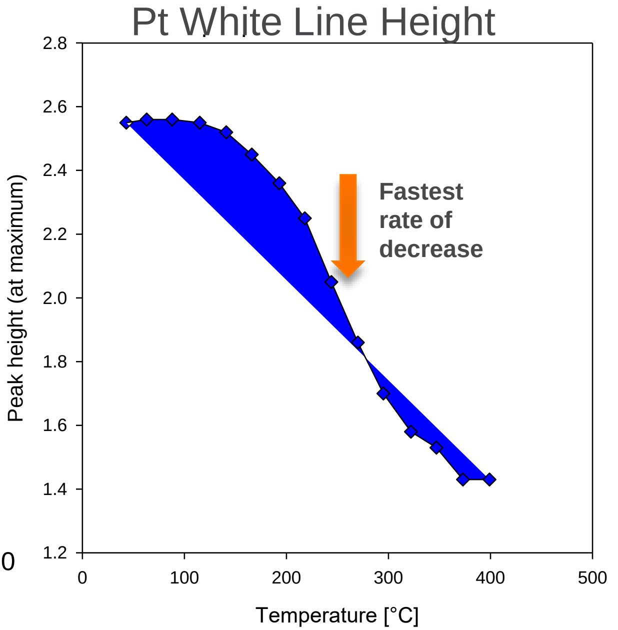
- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
- First observation was by Berengren for phosphorus in 1920*!

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

PT XANES DURING IN SITU REDUCTION

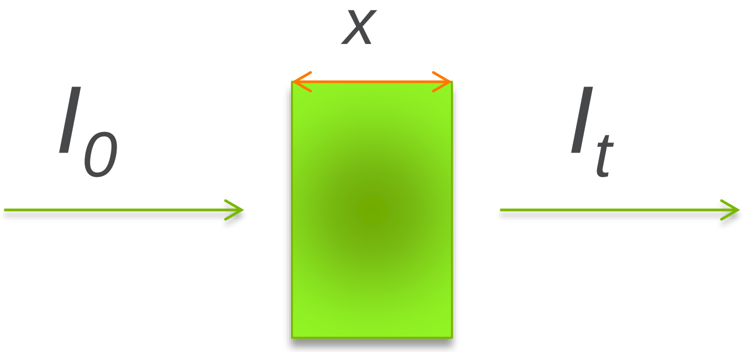
Direct in situ measurement of Pt reduction





- Pt L_3-edge p->d transition
- Pt electrons: $[Xe]4f^{14}5d^6s^1$
- Pt white line intensity decreases as temperature increases due to 5d electrons filling
- Rate of decrease is fastest at ~270°C.

BEER'S LAW: ABSORPTION OF X-RAYS BY MATTER



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

- μ x is the absorption length of a material
- One absorption length, I_t = 37% I_0
- Two absorption lengths, I_t = 13% I_0

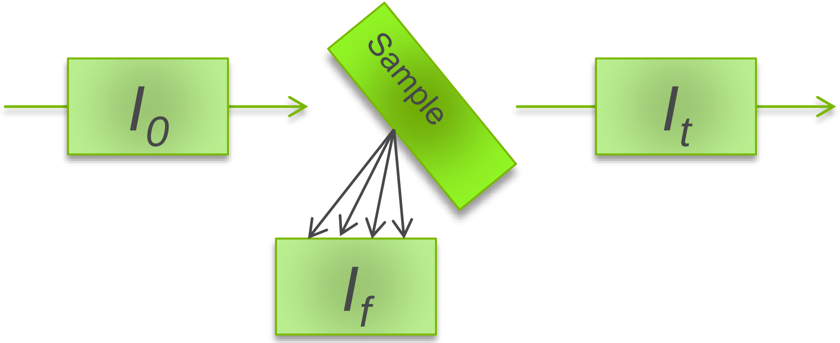
MEASUREMENT OF X-RAY ABSORPTION COEFFICIENT

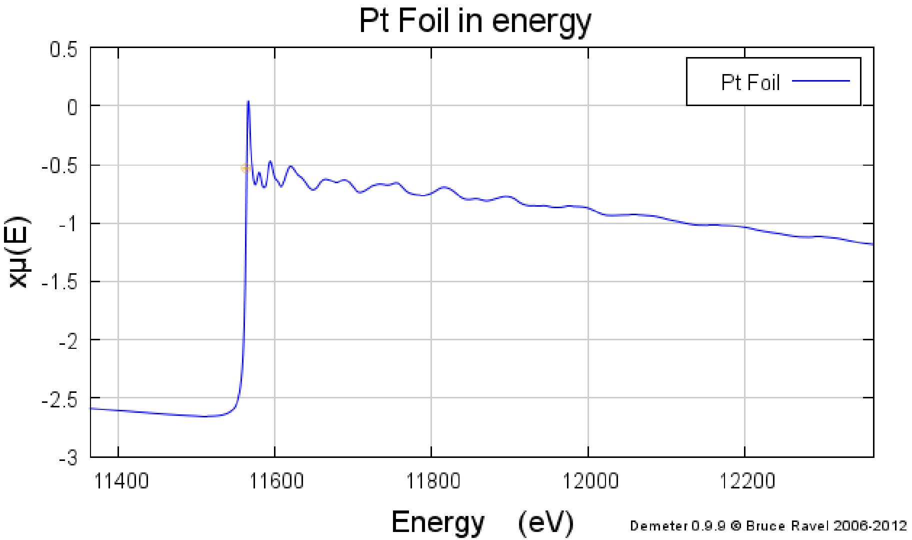
Transmission

$$\mu = \log \frac{I_0}{I_t}$$

Fluorescence

$$\mu \propto \frac{I_f}{I_0}$$





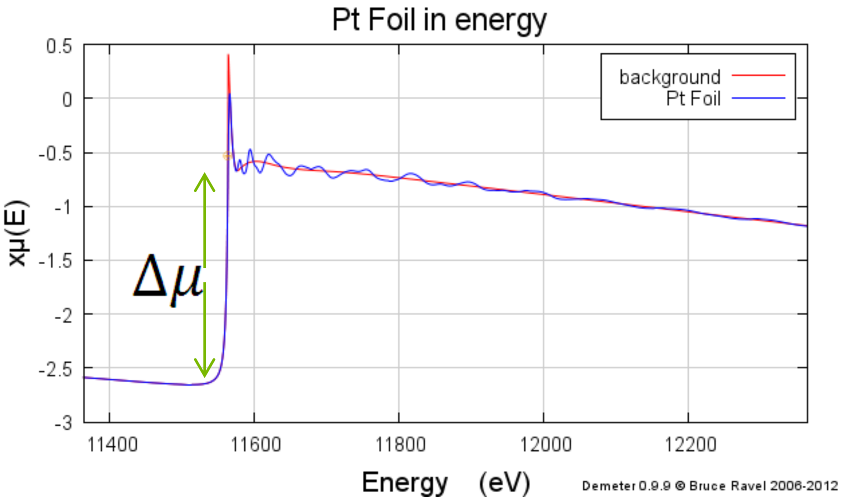
Demeter 0.9.9 © Bruce Ravel 2006-2012

DEFINITION OF EXAFS

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

Background

Edge Step



Demeter 0.9.9 © Bruce Ravel 2006-2012

FERMI’S GOLDEN RULE

$$\mu(E) \propto |\langle i|H|f\rangle|^2$$

$\langle i|$ Initial State: atom with core electron

H Interaction term: incident x-ray

$|f\rangle$ Final State: atom with core hole, photo-electron

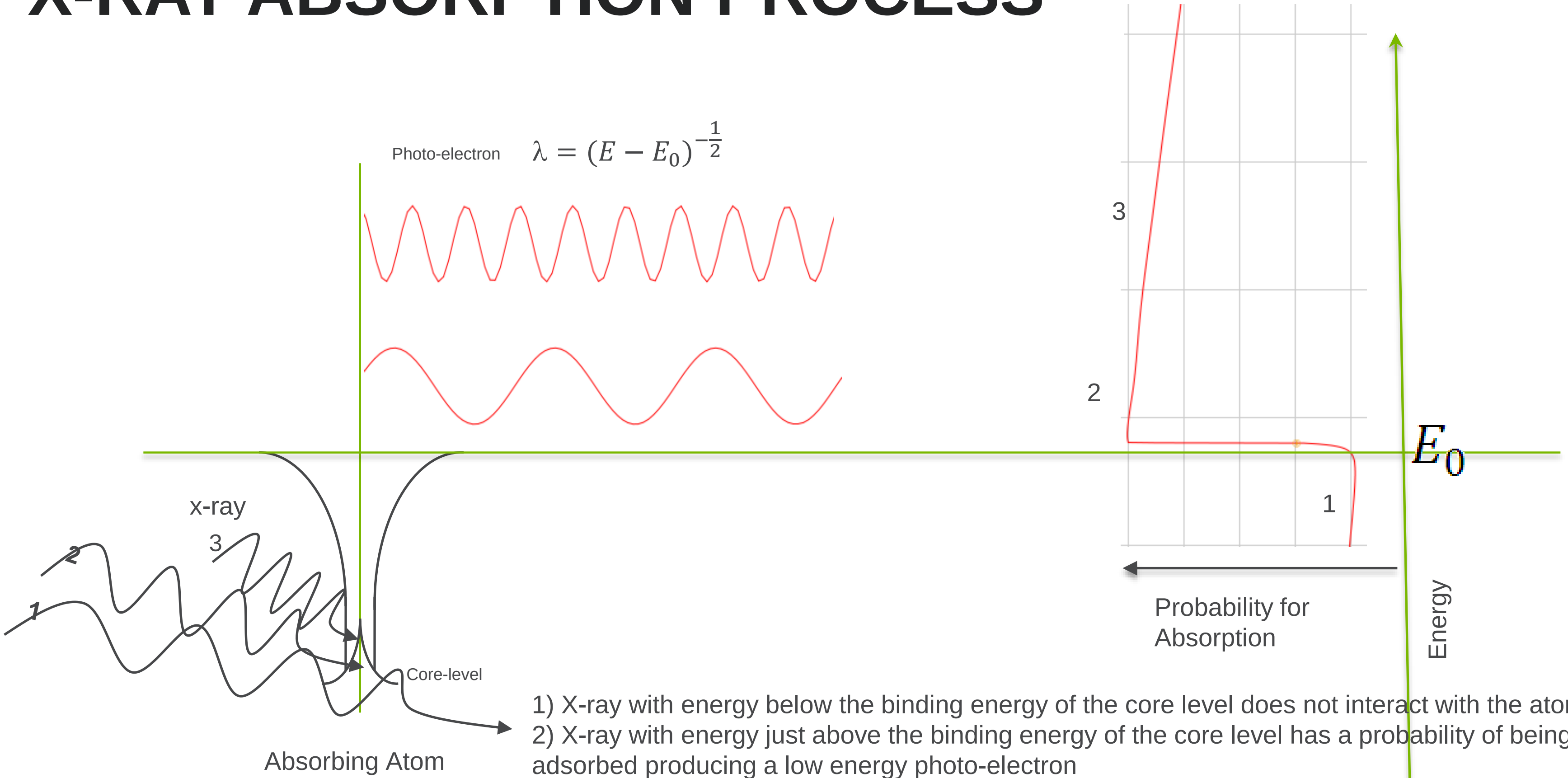
- Transition between two quantum states
- Initial state is well localized at the absorbing atom
- Final state is not, but can be written in terms of two parts

$$|f\rangle = |f_0\rangle + |\Delta f\rangle$$

depends on neighboring atoms

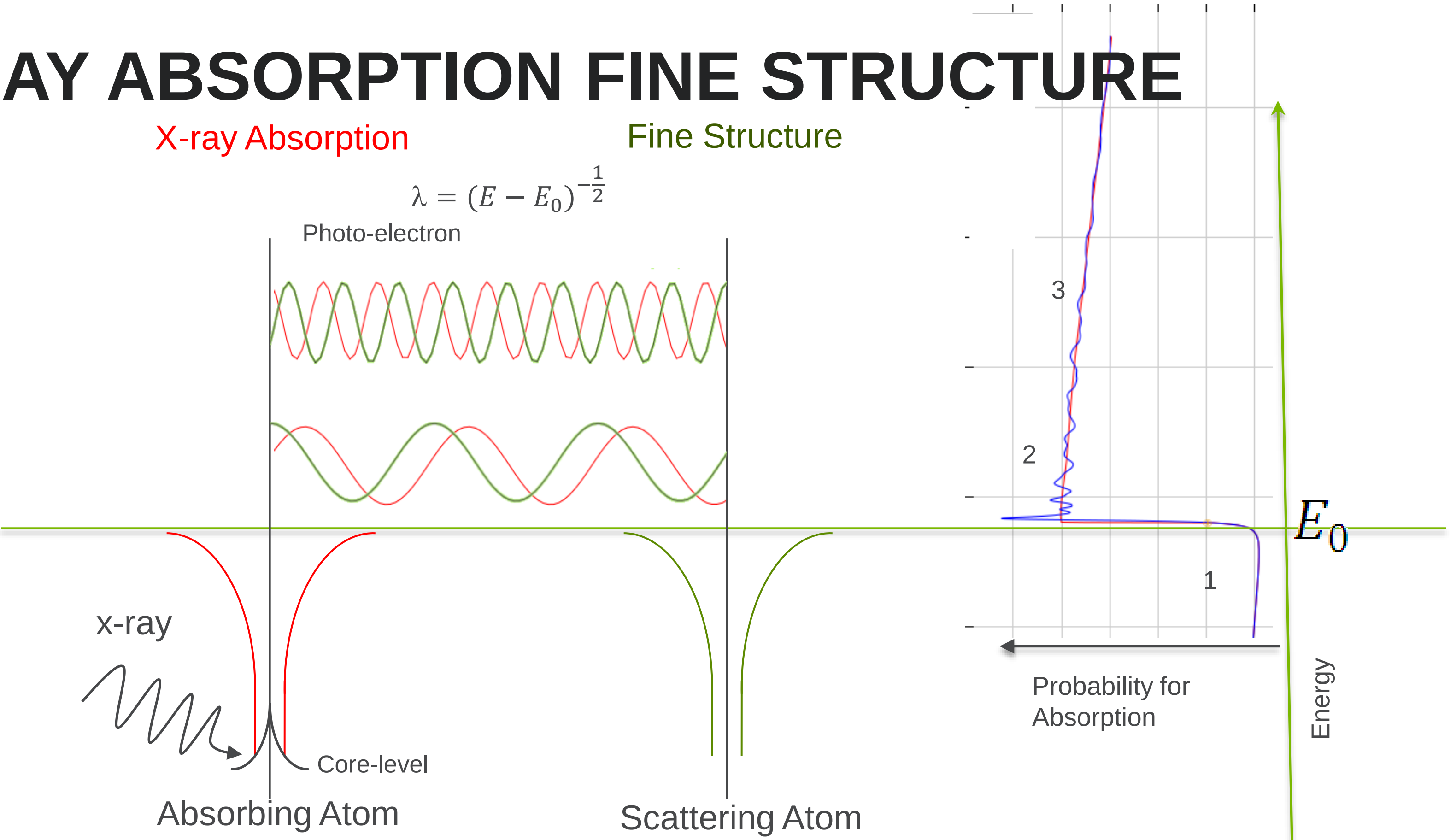
depends on adsorbing atom

X-RAY ABSORPTION PROCESS



1) X-ray with energy below the binding energy of the core level does not interact with the atom
2) X-ray with energy just above the binding energy of the core level has a probability of being adsorbed producing a low energy photo-electron
3) X-ray with higher energy have a probability of being adsorbed and producing higher energy photo-electron

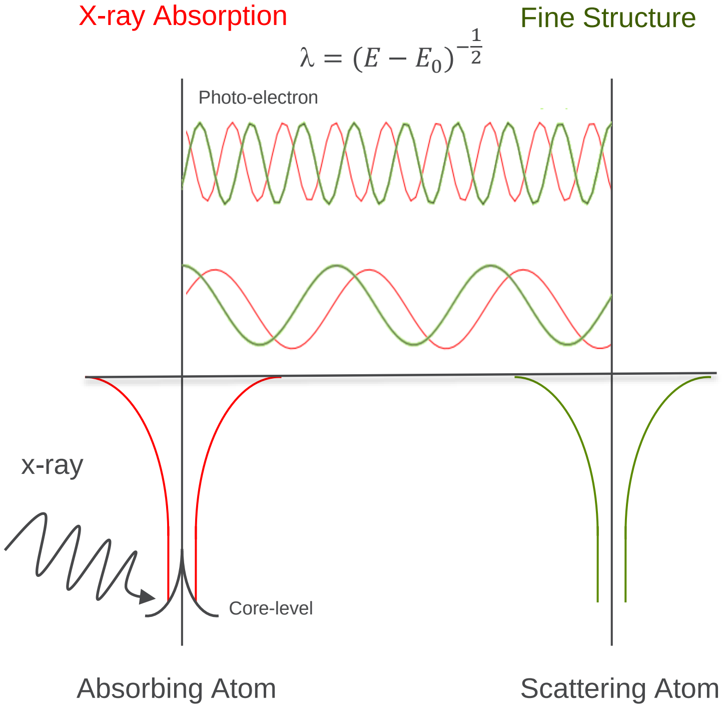
X-RAY ABSORPTION FINE STRUCTURE



$$\lambda = (E - E_0)^{-\frac{1}{2}}$$

Interference between outgoing and scattered photoelectron at the absorbing atom causes modulations in the probability for absorption.

ATOMIC PHASE SHIFT $\delta(k)$



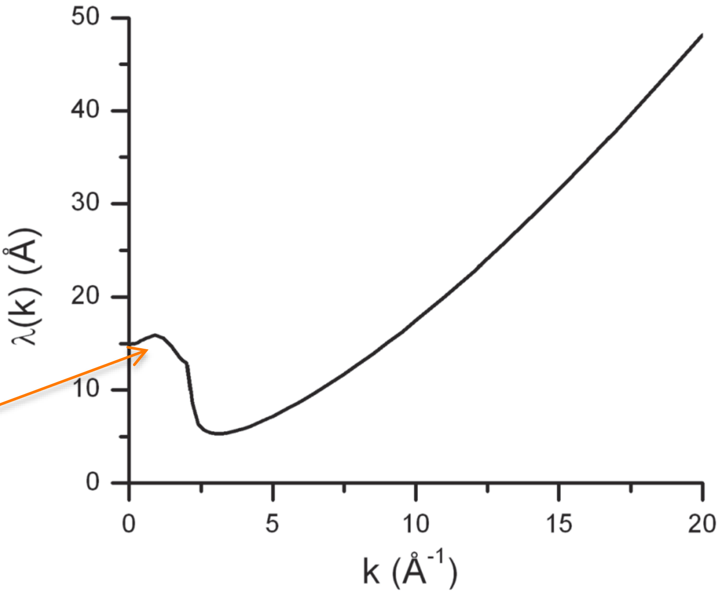
$$\chi(k) \propto \psi_{scatt}(k, r = 0)$$

$$\propto \frac{e^{ikR}}{kR}\left[F(k)e^{-i\delta(k)}\right]\frac{e^{ikR}}{kR}$$

$$\chi(k) \propto \frac{F(k)}{k^2R^2}\sin(2kR + \delta(k))$$

- Atomic Phase shift has two parts. One part from the absorbing atom and another part from the scattering atom.
- Typically corrections to the FT for atomic phase shift takes into account only the absorbing atom component

LIFETIME OF PHOTOELECTRON AND CORE HOLE



λ is large for low wavenumbers indicates that the XANES region contains contributions with long path lengths

Probability for a coherent photoelectron to travel the distance 2R is given by

$$e^{-\frac{2R}{\lambda_j}}$$

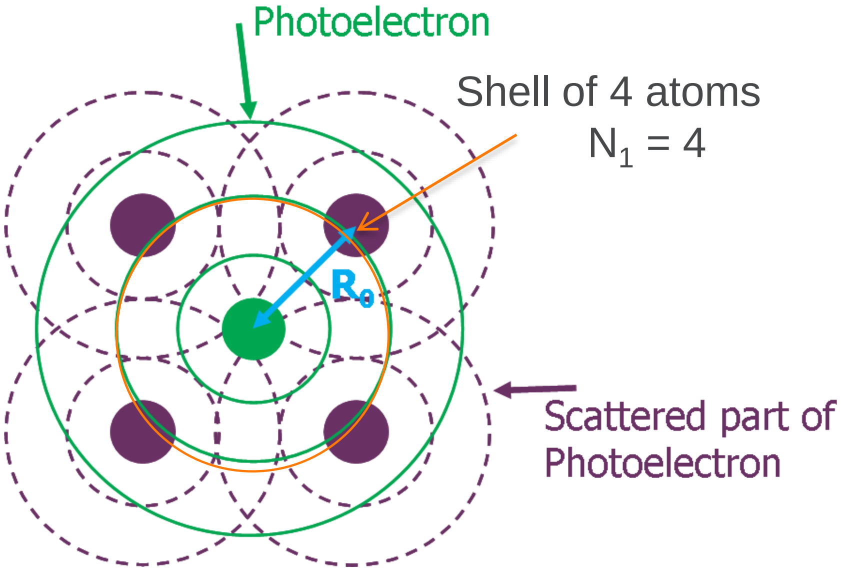
- X-ray absorption fine structure requires a core hole and a coherent photoelectron.
- The mean free path λ of the photoelectron limits the contributions to EXAFS to the first few neighbors

PASSIVE ELECTRON REDUCTION FACTOR

$$S_0^2 = \left|\langle \phi_f^{N-1} | \phi_i^{N-1} \rangle\right|^2$$

- The initial and final states include all the passive electrons of the absorbing atom.
- If the electrons do not react to the creation of the core hole, then there is no difference in these passive electrons and the initial and final states are identical giving S_0^2= 1, indicating a screened potential.
- If the electrons do react (they only have 10^{-15} seconds to do so) then the final state will be slightly different from the initial state. The final state will have the electrons pulled in slightly due to the core hole and the value for S_0^2 can be as small as ~ 0.7, indicating an unscreened potential.
- Value for S_0^2 depends only on the adsorbing atom and can be transferred from a standard material such as a foil.
- S_0^2 often contains experimental affects such as energy resolution so it is best to measure a foil under the same experimental conditions as the unknown sample.

MANY SINGLE SCATTERING PATHS



Shell of 4 atoms
$N_1 = 4$

Summing over scatting events

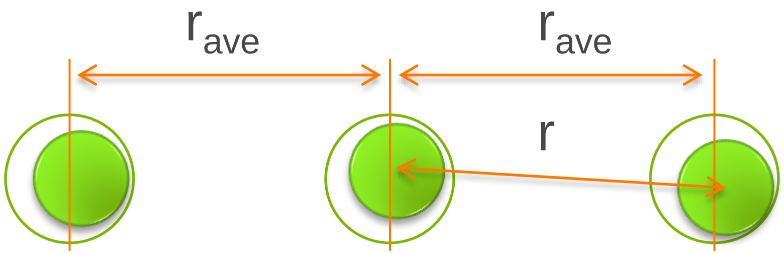
$$\chi(k) = \sum_j \chi_j(k)$$

Summing over shells of atoms

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

- EXAFS signal is the sum of many individual scattering events j.
- It is convenient to group scattering events from shells of atoms, i, of the same type at the same radial distance from the adsorbing atom. Then we need to multiply the scattering contribution by the number of atoms in each shell (N_i).

MEAN SQUARE DISPLACEMENT

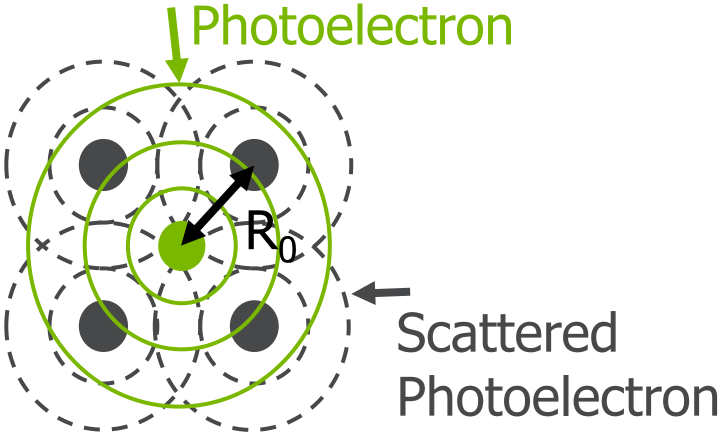


$$\int P(r) e^{i2k\Delta r}\, d\Delta r = exp\left[\sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} C_n\right]$$

$$= e^{2ik\Delta r} + e^{-2k\sigma^2} + e^{-\frac{4}{3}ik^3 C_3} + \cdots$$

- Summing over shells introduces an error because not all of the atoms in a shell are at exactly the same radial distance from the adsorbing atom.
- The scattering process takes place in 10^{-15} seconds. Atomic vibrations occur in 10^{-12} to 10^{-13} seconds.
- Neighboring atoms are frozen at some position about their equilibrium position.

THE EXAFS EQUATION



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

with

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k) e^{-2k^2\sigma_j^2} e^{-\frac{2R}{\lambda}}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2 m_e(E-E_0)/ \hbar$$

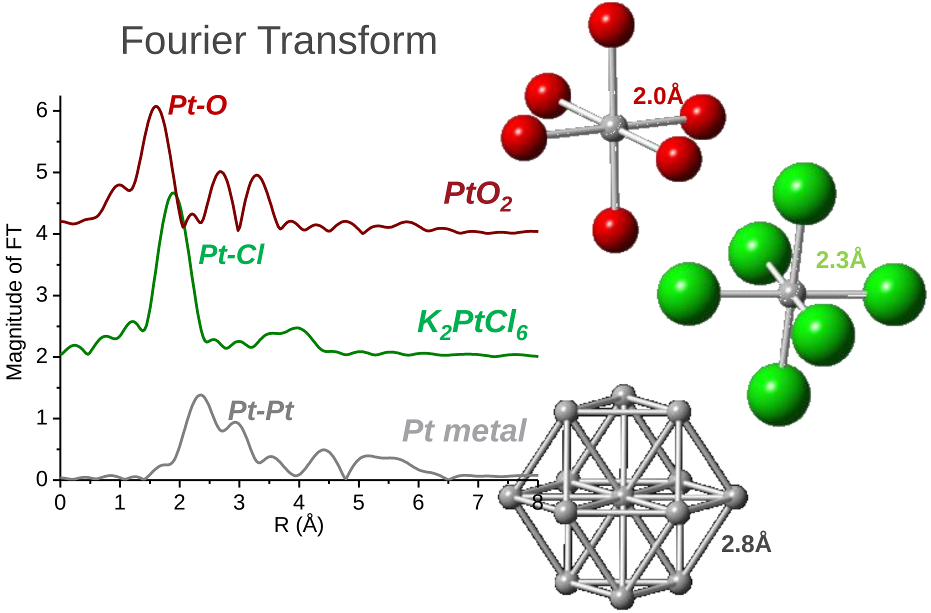
Theoretically calculated values	
$F_i(k)$	effective scattering amplitude
$\varphi_i(k)$	effective scattering phase shift
$\lambda(k)$	mean free path

Starting values	
R_0	initial path length

Parameters determined from a fit to data	
N_i	degeneracy of path
S_0^2	passive electron reduction factor
σ_i^2	mean squared displacement of half-path length
E_0	energy shift
ΔR	change in half-path length

PT EXAFS OF REFERENCE MATERIALS

Pt EXAFS: unique information about the average local atomic environment of Pt



PtO_2

Neighbor	Number	Distance (Å)
Pt-O	6	2.07
Pt-Pt	6	3.10

K_2PtCl_6

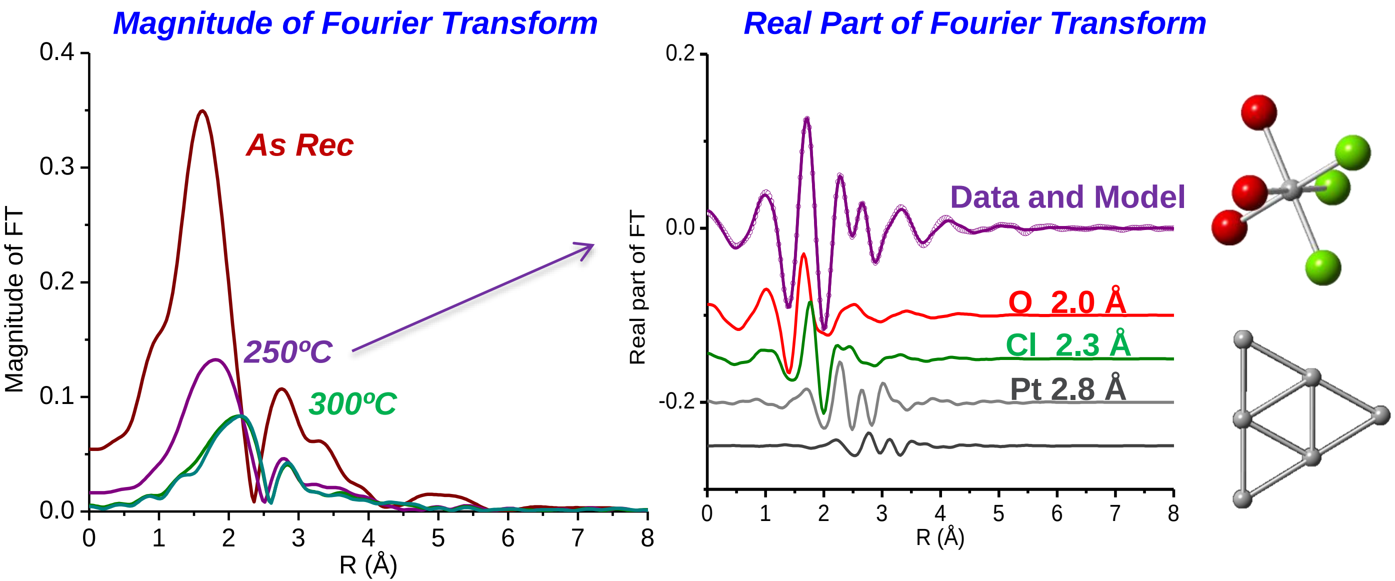
Neighbor	Number	Distance (Å)
Pt-Cl	6	2.32
Pt-K	4	4.22

Pt metal

Neighbor	Number	Distance (Å)
Pt-Pt	12	2.77
Pt-Pt	6	3.92

- Pt-O, Pt-Cl , and Pt-Pt signals are unique and are readily distinguished.

LOW TEMPERATURE REGION



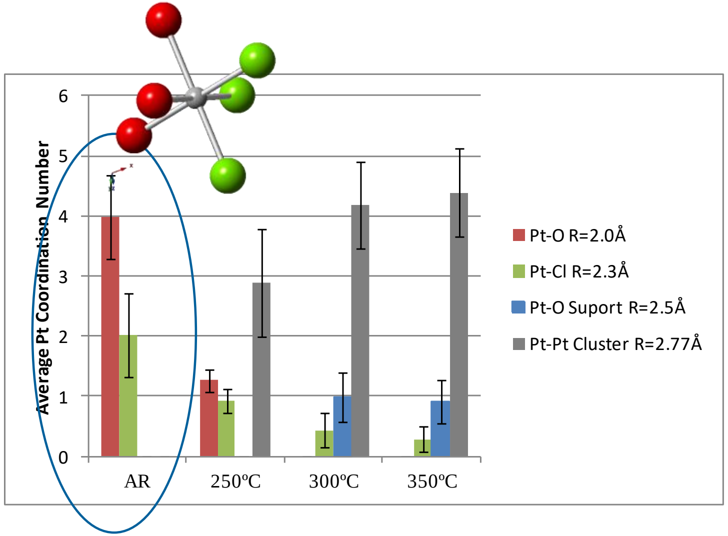
Magnitude of Fourier Transform

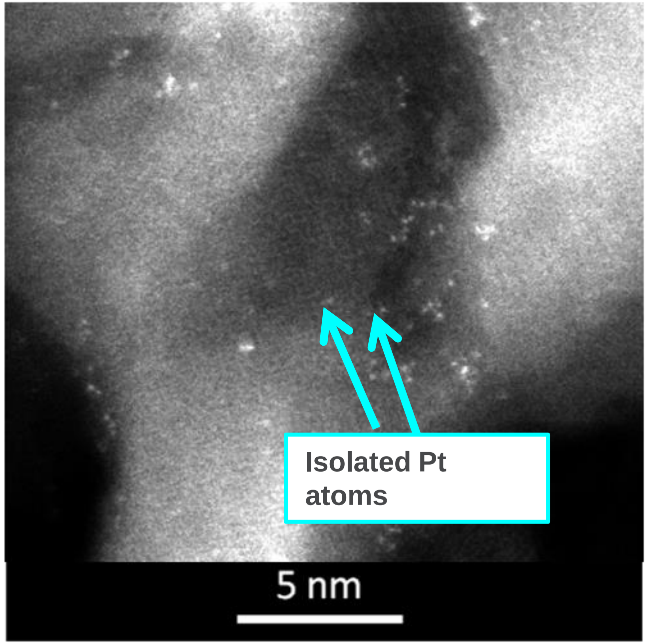
Real Part of Fourier Transform

- Large changes in Pt EXAFS with reduction temperature
- Pt-O and Pt-Cl bonding readily distinguished
- Pt-Pt cluster formation observed by 250ºC

EXAFS AND STEM: AS RECEIVED

Direct in situ measurement of Pt reduction





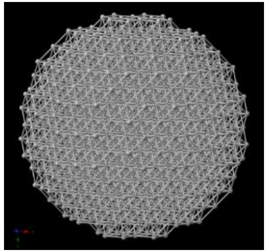
* Bradley et al, Catalysis Letters 142 (2012) pp. 176-182

- STEM Images show isolated atoms and few dimers*
- Good agreement with EXAFS

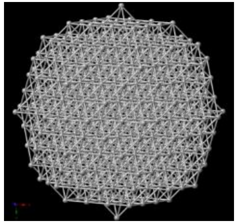
PT CLUSTER SIZE AND EXAFS PT-PT CN

Pt-Pt Coordination Number is related to Pt cluster size

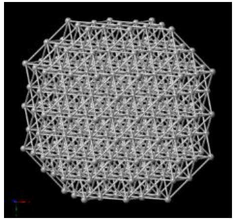
3 nanometer
959 atoms
Pt-Pt1 CN 10.4



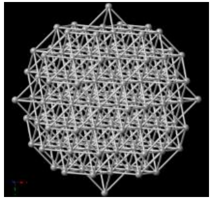
2.4 nanometer
459 atoms
Pt-Pt1 CN 9.83



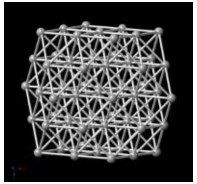
2 nanometer
321 atoms
Pt-Pt1 CN 9.64



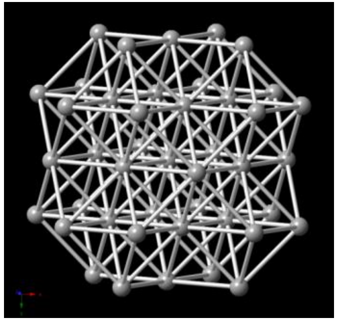
1.6 nanometer
141 atoms
Pt-Pt1 CN 8.85



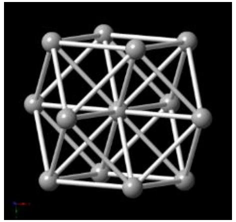
1.2 nanometer
67 atoms
Pt-Pt1 CN 6.33



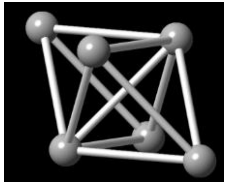
1.0 nanometer
43 atoms
Pt-Pt1 CN 5.4



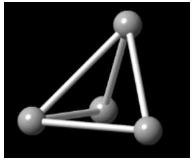
0.6 nanometer
13 atoms
Pt-Pt1 CN 4.8



6 atoms
Pt-Pt1 CN 4.0

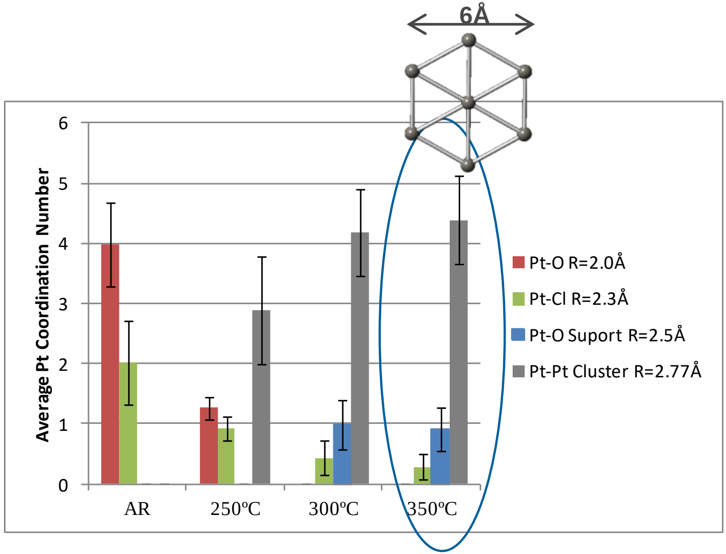


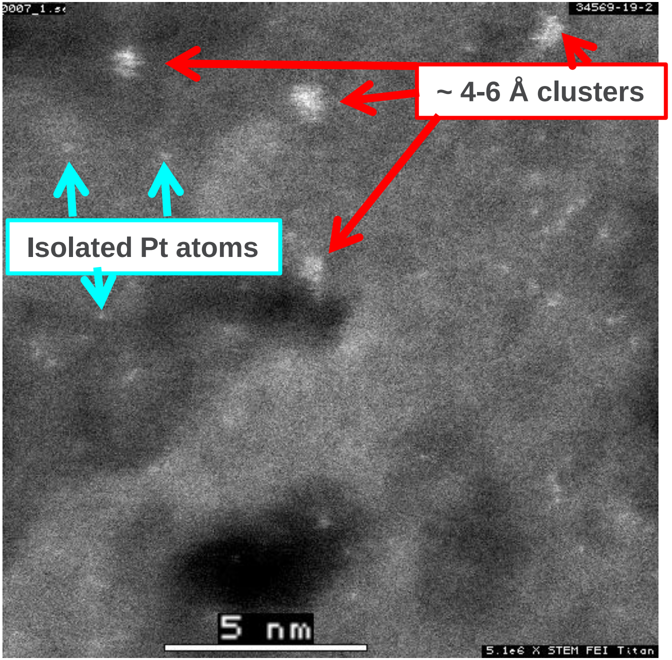
4 atoms
Pt-Pt1 CN 3



EXAFS AND STEM: 350ºC REDUCTION

350ºC Reduced: Isolated atoms and 6Å clusters





~ 4-6 Å clusters

Isolated Pt atoms

- STEM Images:
  - Isolated Pt atoms
  - Small groups of Pt atoms
  - ~ 4 Å – 6 Å diameter Pt clusters
- EXAFS: ~ 6 Å diameter Pt clusters

Q & A