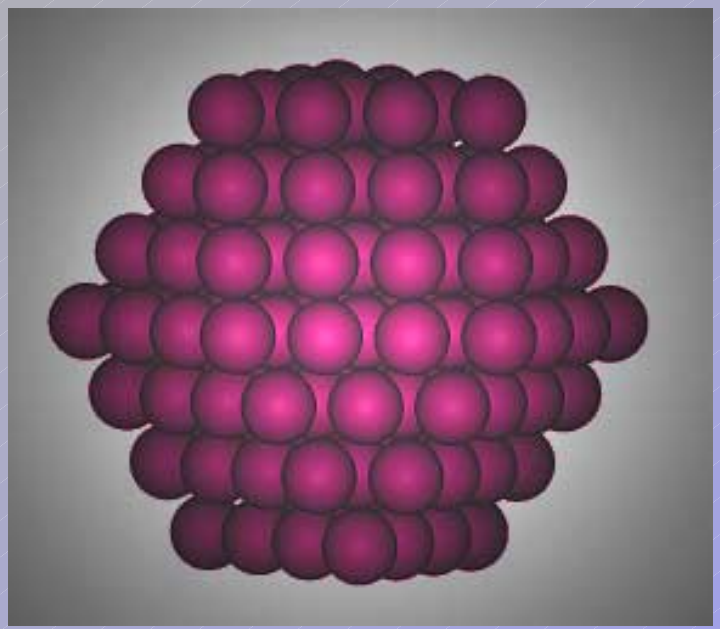
Atomic Scale Ordering in Metallic Nanoparticles



Structure:

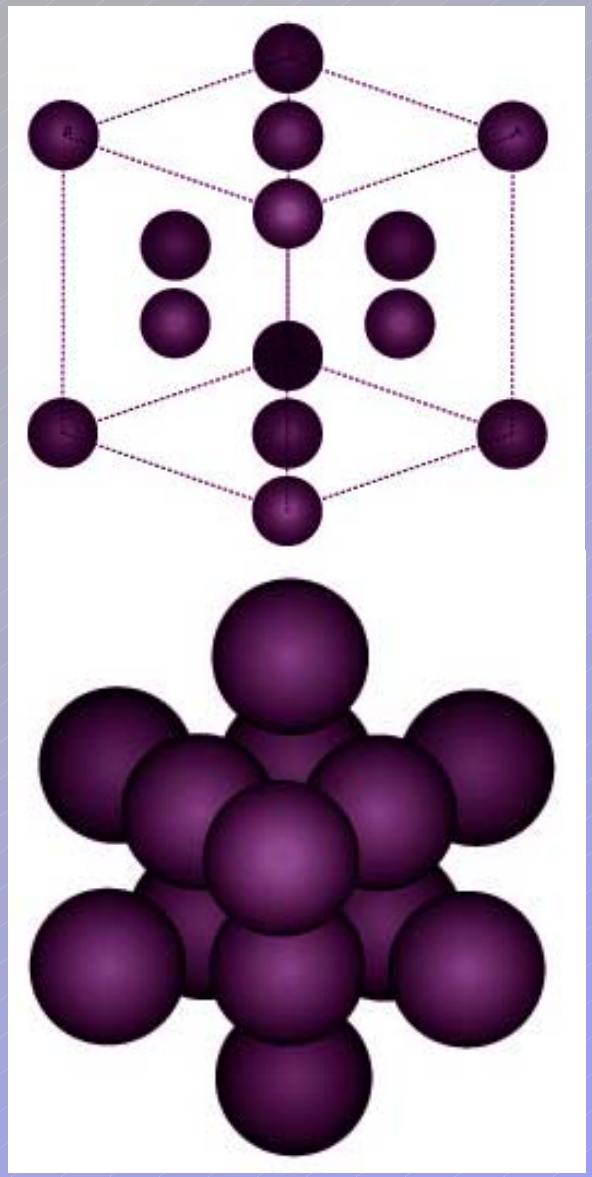
- Atomic packing: microstructure?
- Cluster shape?
- Surface structure?
- Disorder?

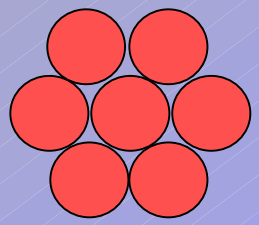
Characterization

- **Electron Microscopy**
  - Scanning Transmission Electron Microscopy (STEM)
  - Electron Diffraction

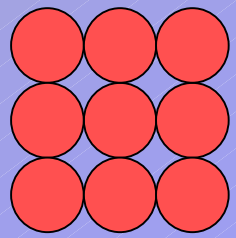
- **X-ray Absorption Spectroscopy**
  - X-ray Absorption Near Edge Spectroscopy (XANES)
    - Provides information on chemical states
      - Oxidation state
      - Density of states
  - Extended X-ray Absorption Fine Structure (EXAFS)
    - Provides local (~10 Å) structural parameters
      - Nearest Neighbors (coordination numbers)
      - Bond distances
      - Disorder

Face Centered Cubic Structure

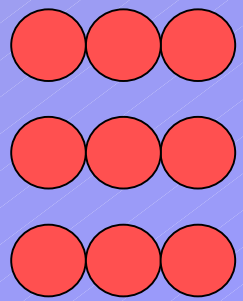




(111)

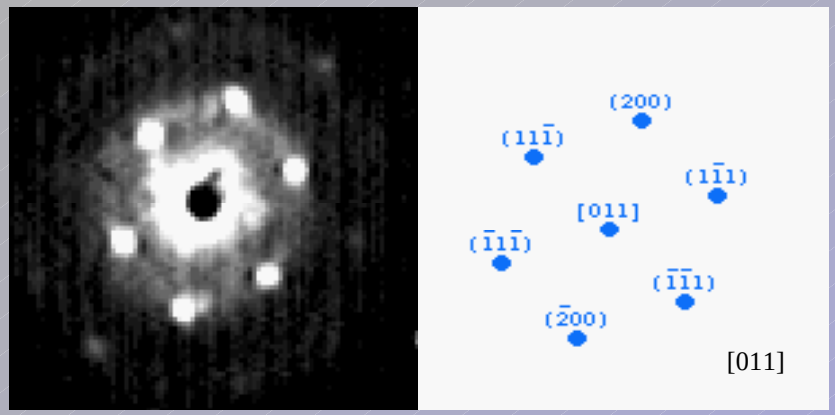


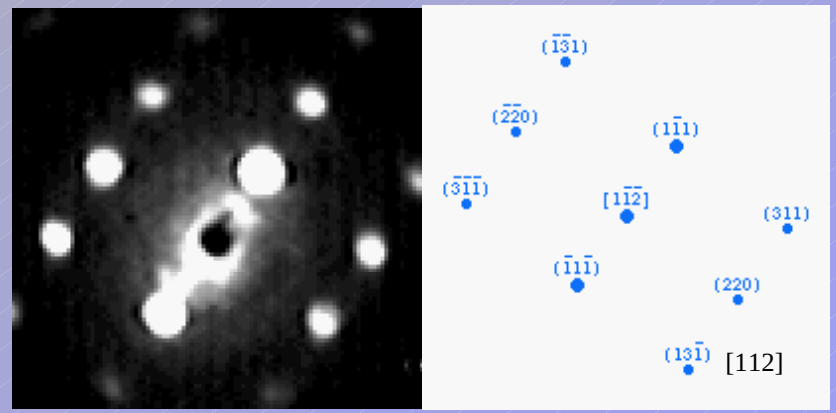
(001)

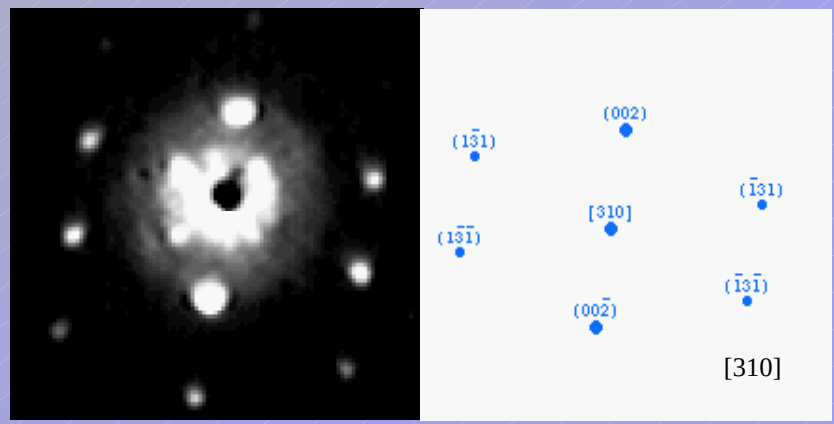


(110)

Electron Microdiffraction



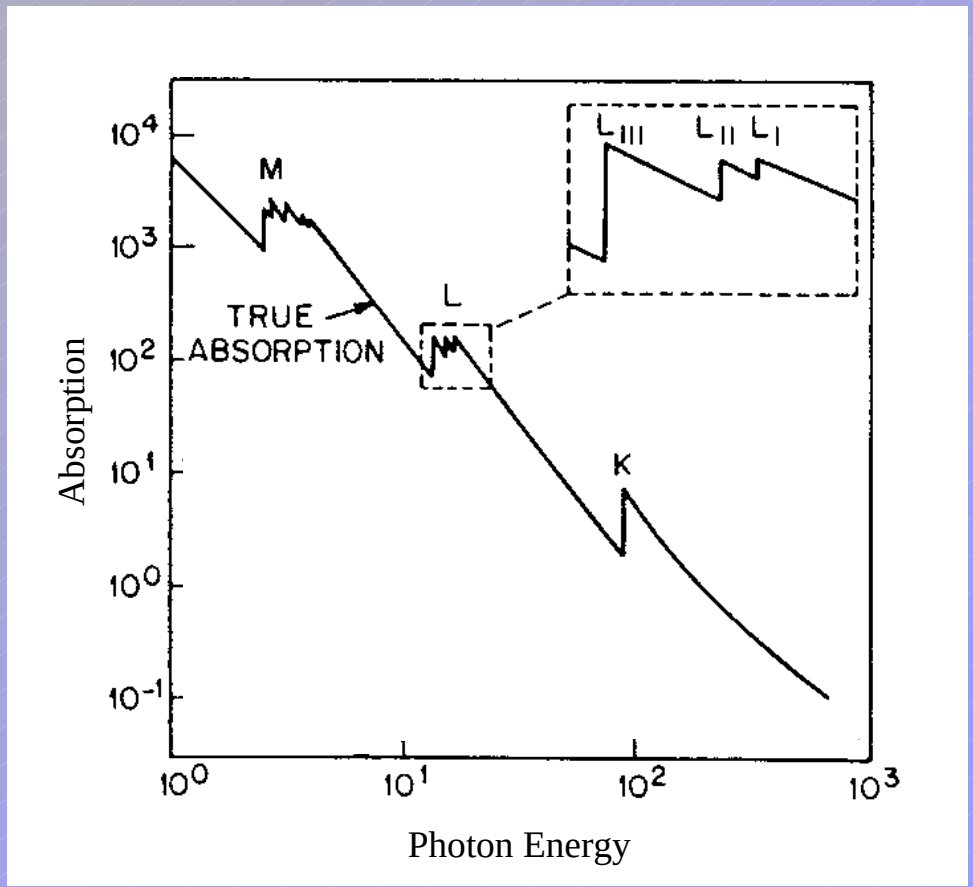




Electron diffraction probes the ordered microstructure of the nanoparticles. Above are 3 sample diffraction patterns for ~ 20 Å Pt nanoparticles. All are indexed as face-centered cubic (fcc).

X-Ray Absorption Spectroscopy

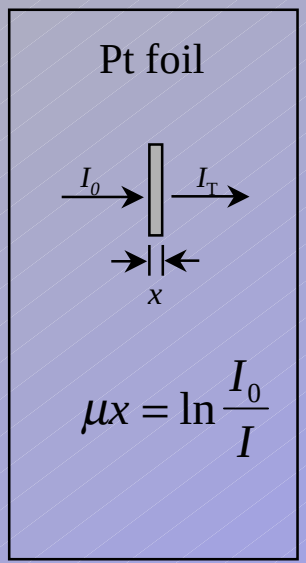
- Absorption coefficient (μ) *vs.* incident photon energy
- The photoelectric absorption decreases with increasing energy
- "Jumps" correspond to excitation of core electrons

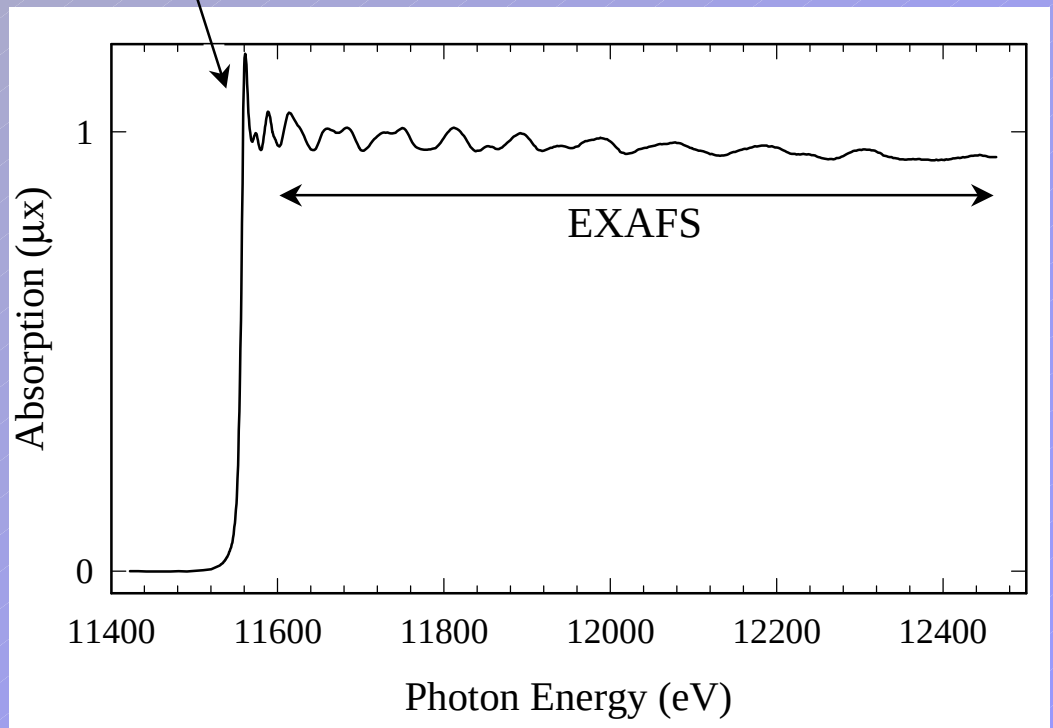


Adapted from Teo, B. K. *EXAFS: Basic Principles and Data Analysis;* Springer-Verlag: New York, 1986.

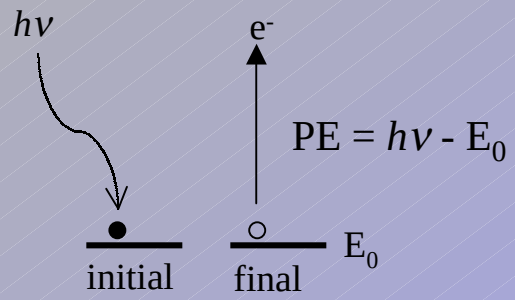
Extended X-ray Absorption Fine Structure

- oscillation of the X-ray absorption coefficient near and edge
- **local** (<10 Å) structure surrounding the absorbing atom

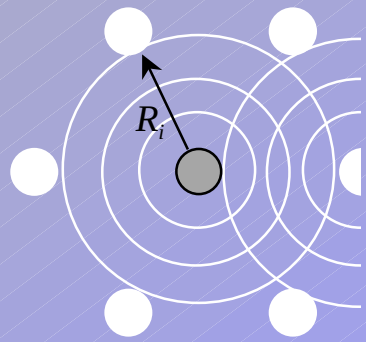




Basics of EXAFS



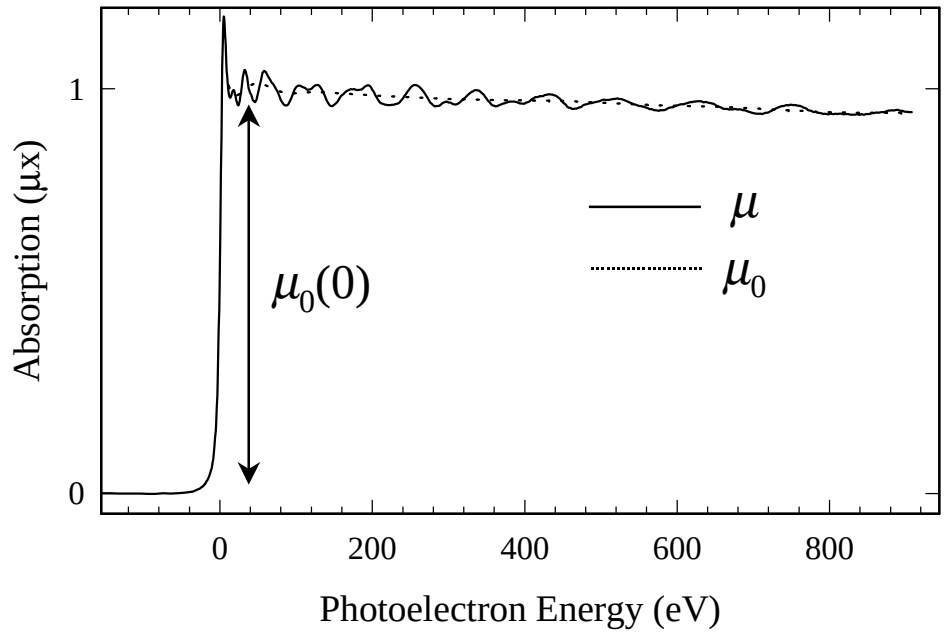
- Excitation of a photoelectron with wavenumber $k = 2\pi/\lambda$

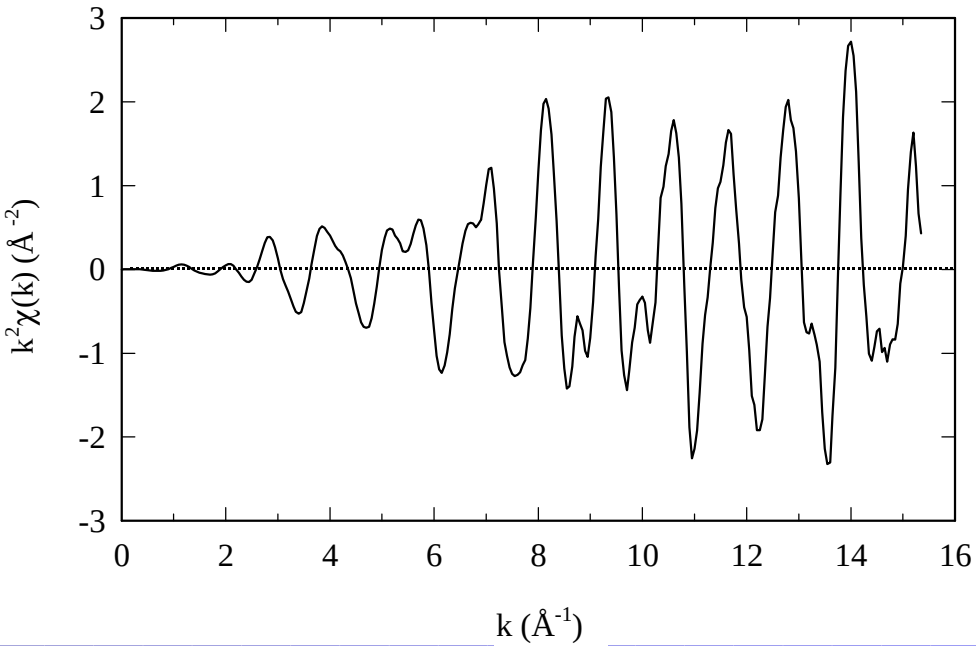


- Oscillations, $\chi_i(k)$: final state interference between outgoing and backscattered photoelectron

$$\chi_i(k) = A_i(k)\sin(2kR_i)$$

R_i - distance to shell-i
$A_i(k)$ - backscattering amp.





Data Analysis

Convert to wave number

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

Subtract background and normalize

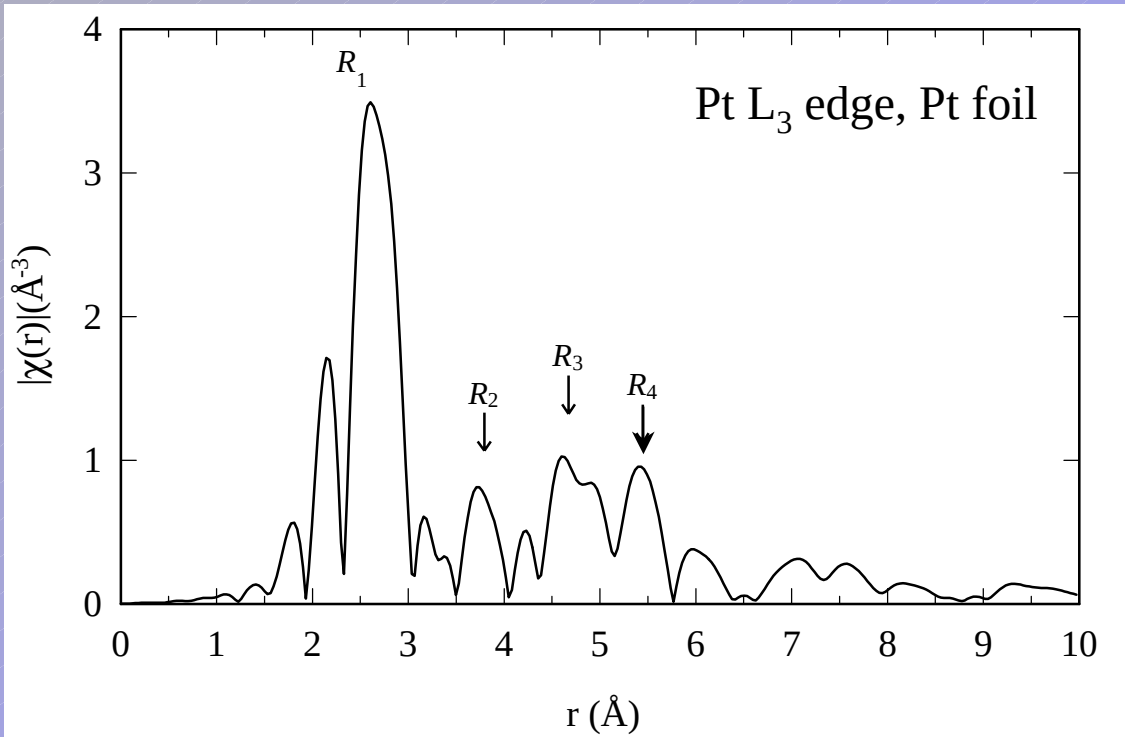
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0(0)}$$

Resulting data is the sum of scattering from all shells

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

Fourier Transform

Resolve the scattering from each distance (R_i) into *r*-space

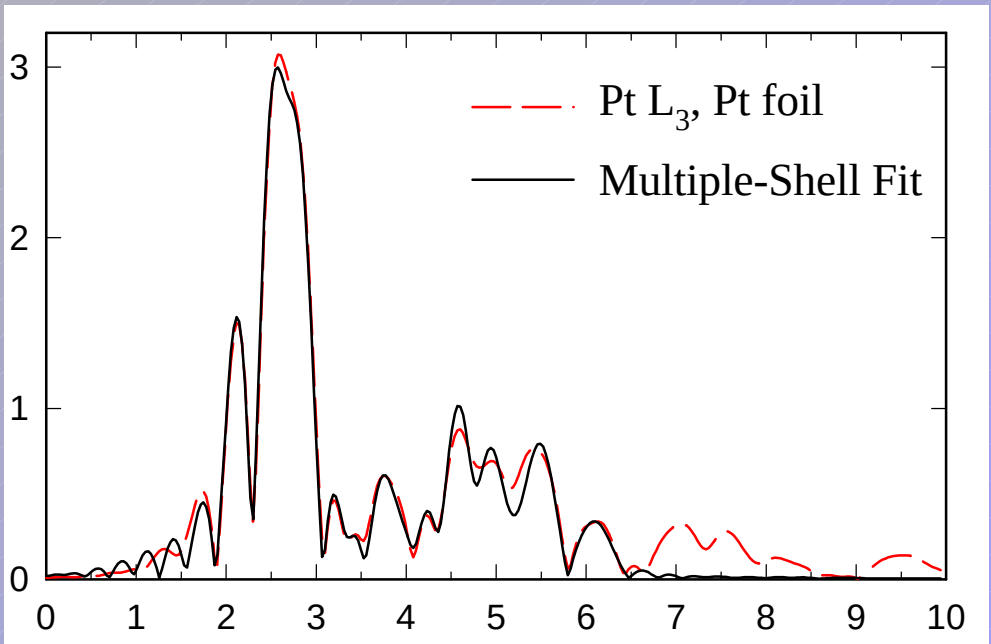


Multiple-Shell Fit

Calculate $F_i(k)$ and $\delta_i(k)$ for each shell-i (i = 1 to 6) using the **FEFF** computer code

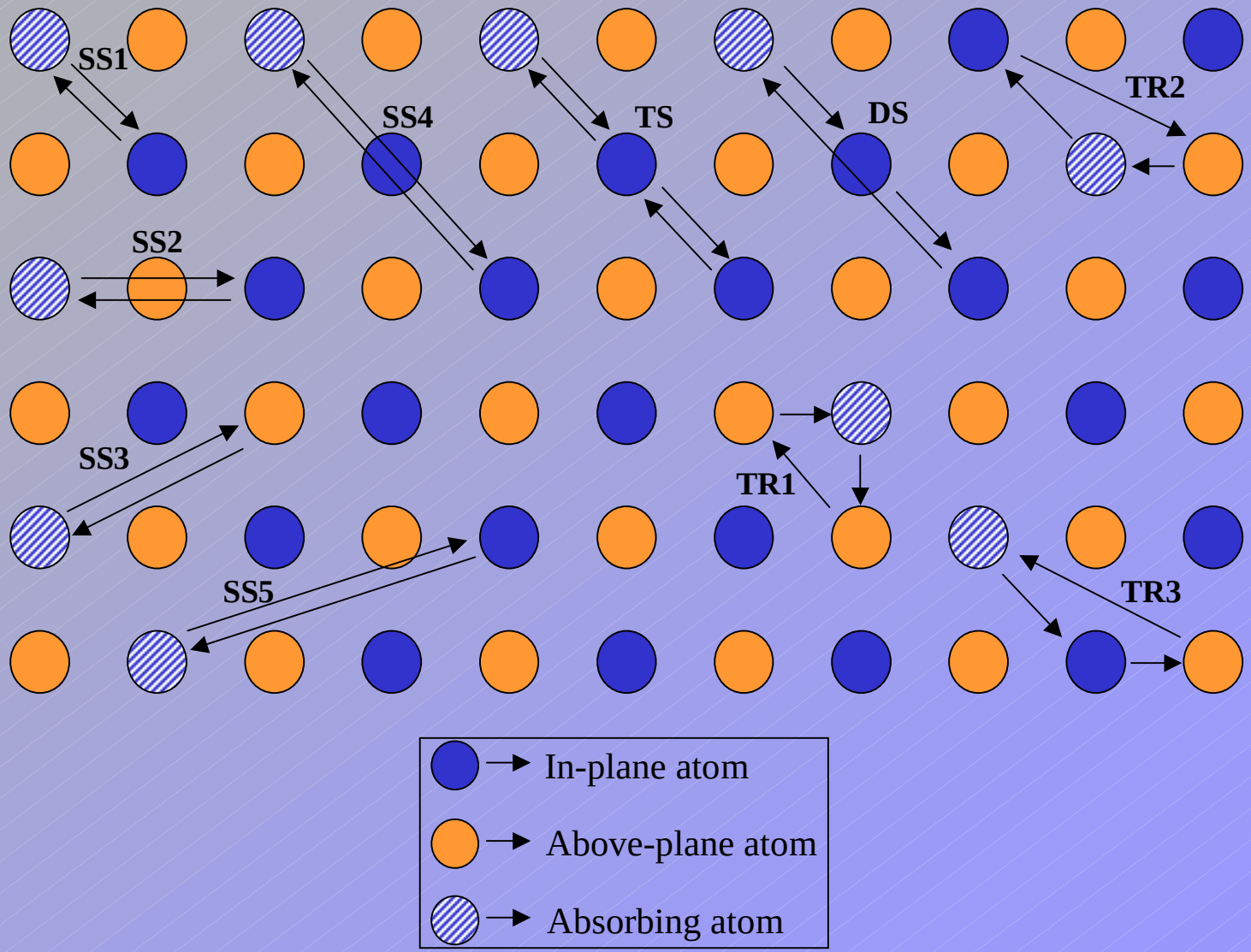
Non-linear least-square refinement: vary N_i, R_i, σ^2_i using the EXAFS equation

$$\chi_i(k) = N_i \frac{F_i(k)}{kR_i^2} e^{-2k^2\sigma^2} \sin(2kR_i + \delta_i(k))$$

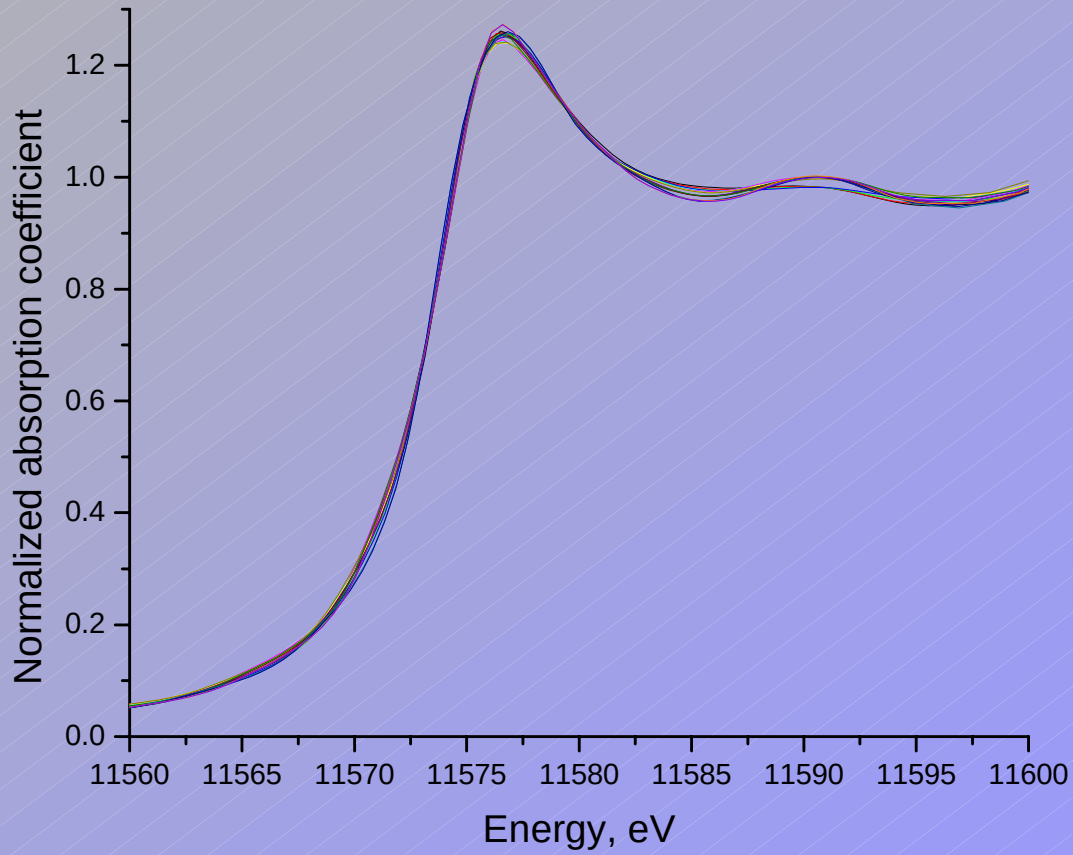


	Bond distance, R_i (Å)				
	R_1	R_2	R_3	R_4	R_5
fit	2.768(3)	3.914(4)	4.794(4)	5.535(5)	6.189(6)
actual	2.7719	3.9200	4.8010	5.5437	6.1981

Multiple Scattering Paths

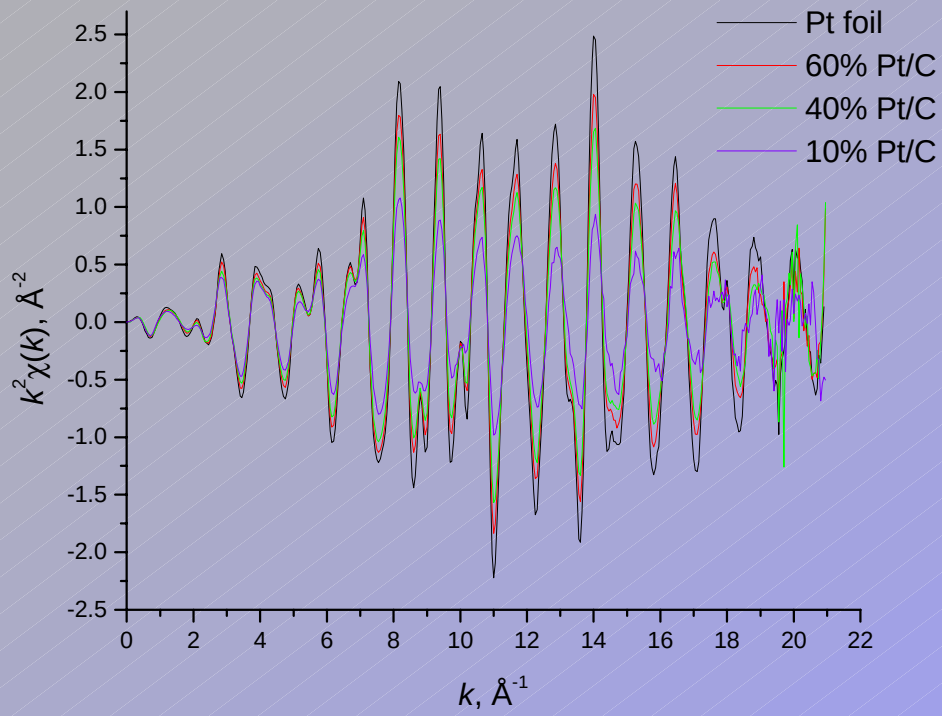


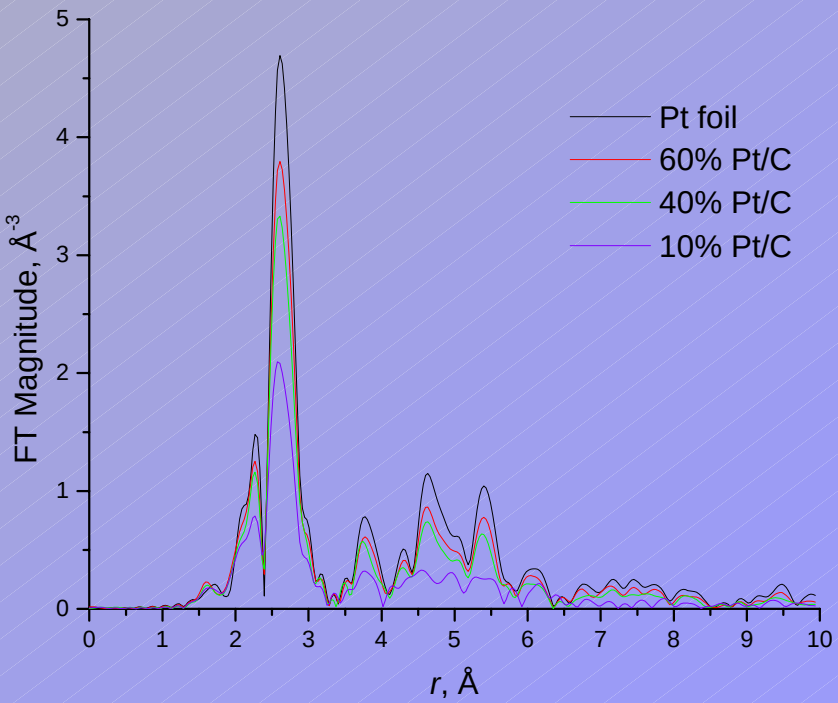
X-Ray Absorption Near Edge Spectroscopy (XANES)



XANES measurements for reduced 10%, 40% Pt/C, 60% Pt/C Pt/C, and Pt foil at 200, 300, 473 and 673 K. A total of 16 measurements are shown. All overlay well with bulk Pt (Pt foil); therefore, the samples are reduced to their metallic state.

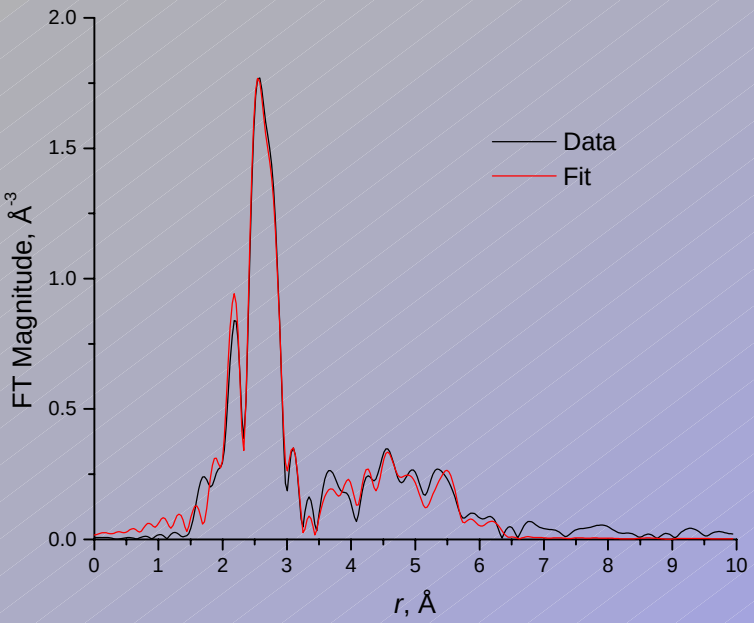
Size Dependence



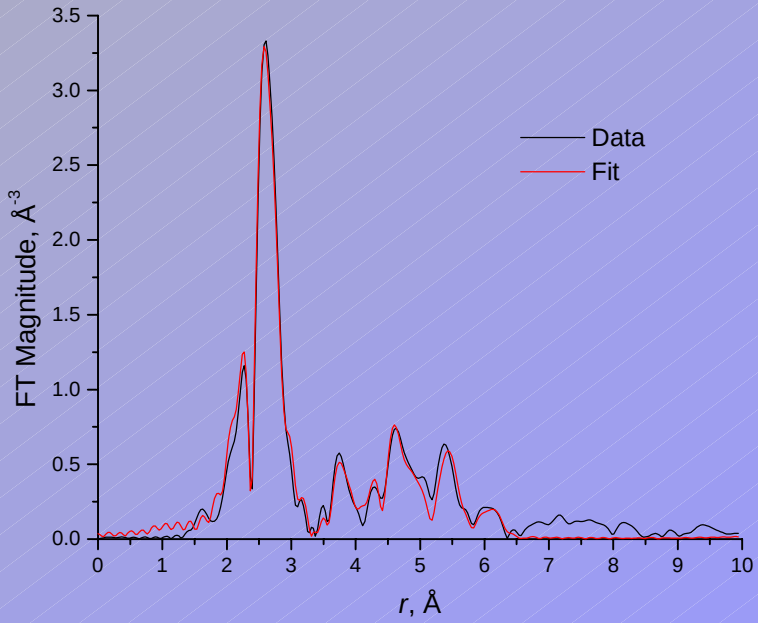


Size dependence on the extended x-ray absorption spectra. The amplitude of the EXAFS signal is directly proportional to the coordination numbers for each shell; therefore, as the cluster size increases, the amplitude also will increase.

Multiple Shell Fitting Analysis



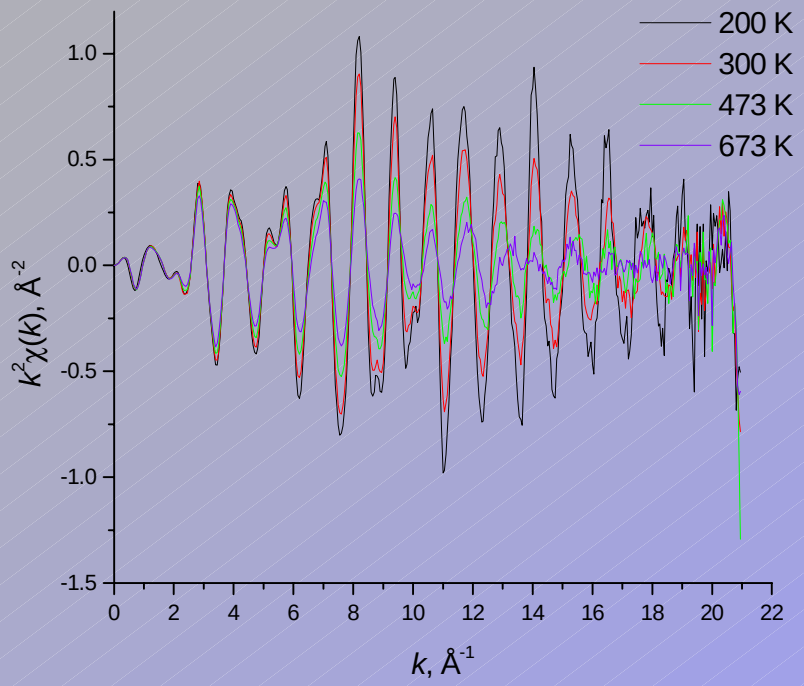
10% Pt/C

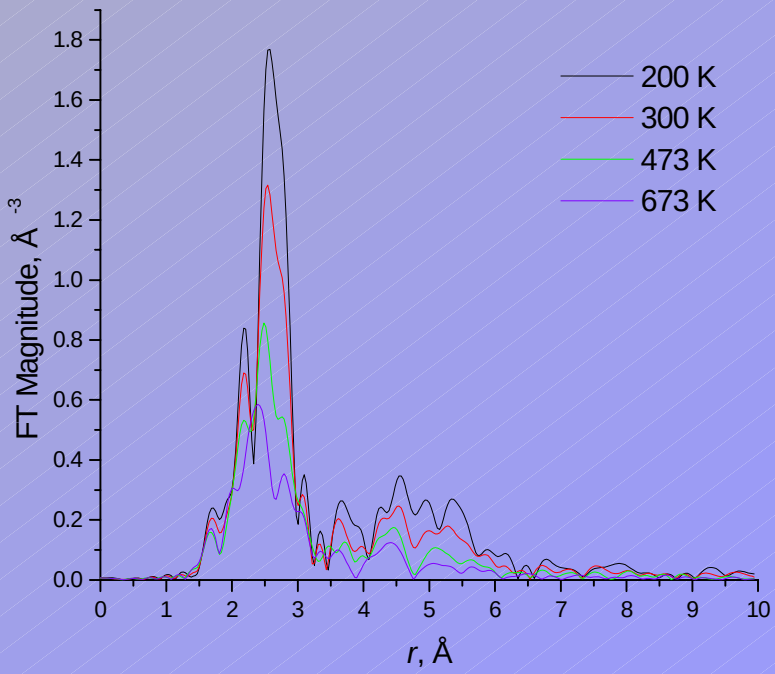


40% Pt/C

i	10% Pt/C	40% Pt/C	60% Pt/C	Pt foil	Bulk fcc
1	8.3(5)	10.5(5)	11.4(6)	12.6(7)	12
2	2.3(1.1)	4.0(1.3)	4.7(1.7)	5.9(2.0)	6
3	10.9(3.2)	16.8(3.5)	19(4)	23(5)	24
4	5.5(1.4)	7.6(1.4)	8.5(1.6)	11(2)	12
5	5.4(3.4)	10(4)	11(4)	14(5)	24

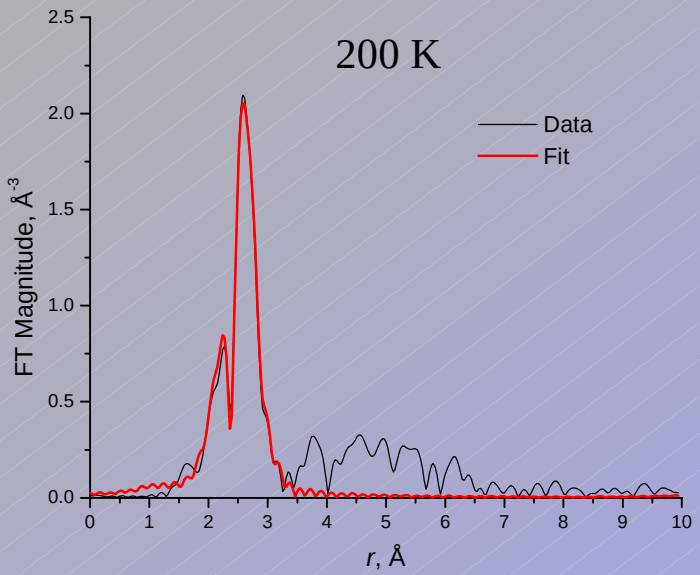
Temperature Dependence

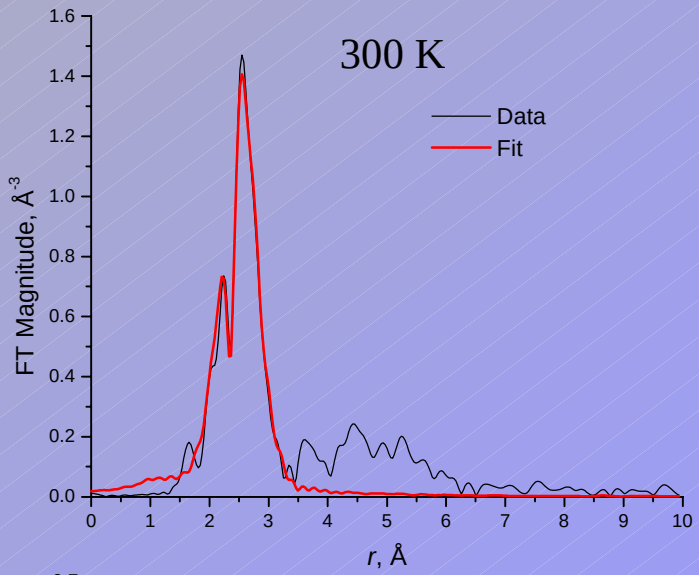


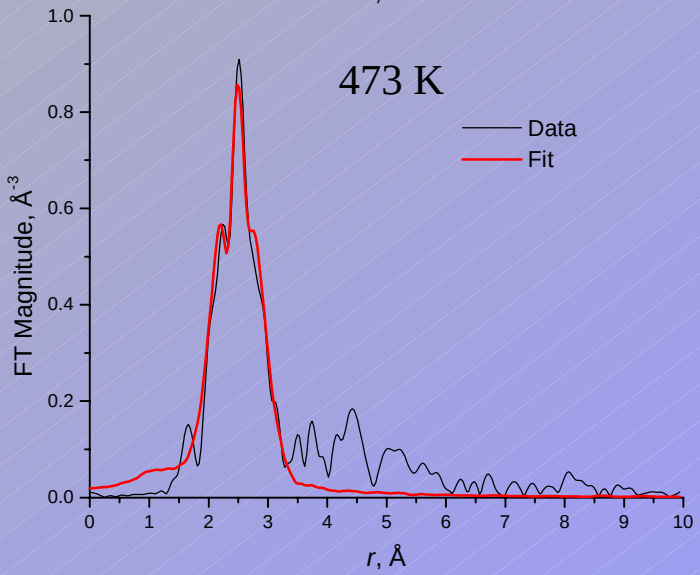


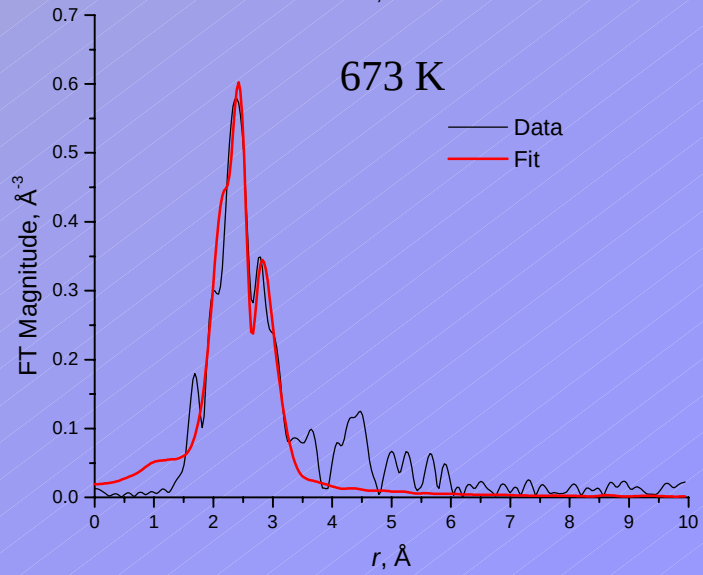
Temperature dependence on the extended x-ray absorption spectra for 10% Pt/C. As the temperature increases, the dynamic disorder (σ_D^2) increases, causing the amplitude to decrease.

First Shell Fitting: 10% Pt/C



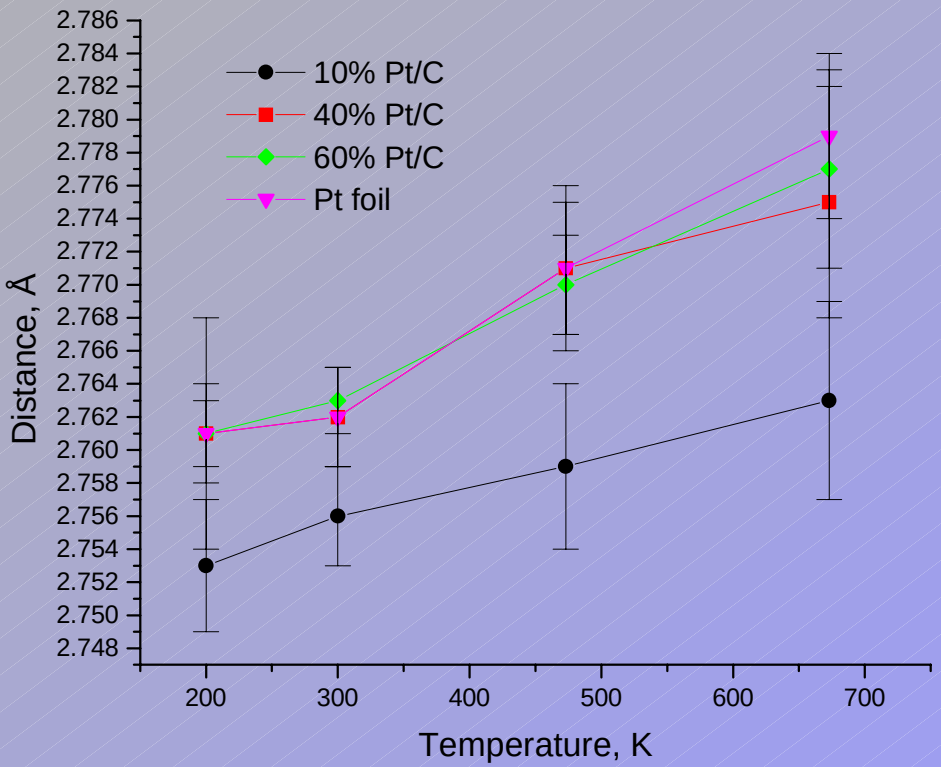






Size Dependent Scaling of Bond Length and Disorder

$$\chi_i(k) = N_i \frac{F_i(k)}{kR_i^2} e^{-2k^2\sigma^2} \sin(2kR_i + \delta_i(k))$$



The EXAFS Disorder, σ^2, is the sum of the static, σ_s^2, and dynamic, σ_d^2, disorder as follows:

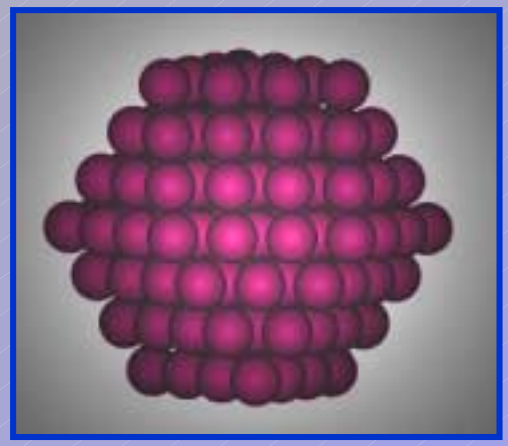
$$\sigma^2 = \left\langle \left(r - \langle r \rangle\right)^2 \right\rangle = \sigma_s^2 + \sigma_d^2$$

The dynamic disorder, σ_d^2, can be separated by using the following relationship:

$$\sigma_d^2 = \frac{\hbar}{2\omega\mu} \frac{1 + \exp(-\Theta_E / T)}{1 - \exp(-\Theta_E / T)}$$

Structure and Morphology

- Determining shape and texture
  - Electron microscopy
  - X-Ray absorption spectroscopy
  - Molecular modeling

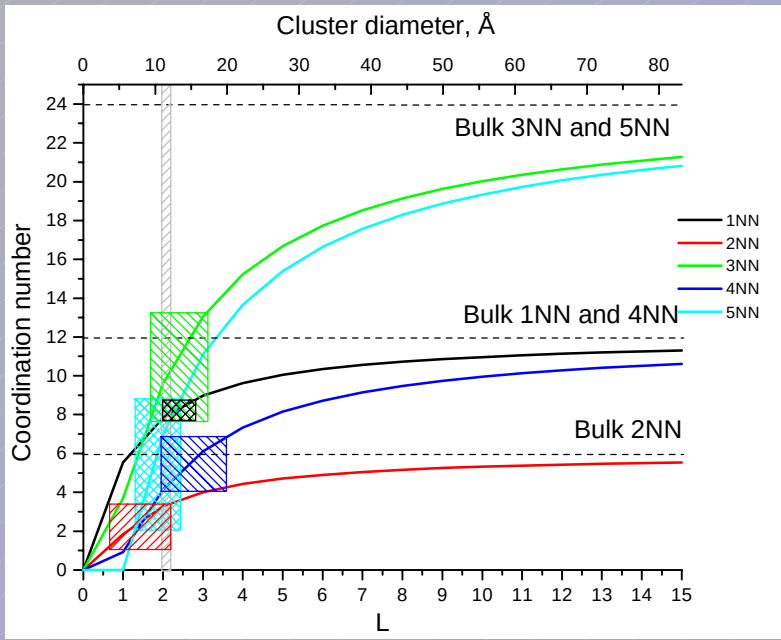


Spherical cuboctahedron

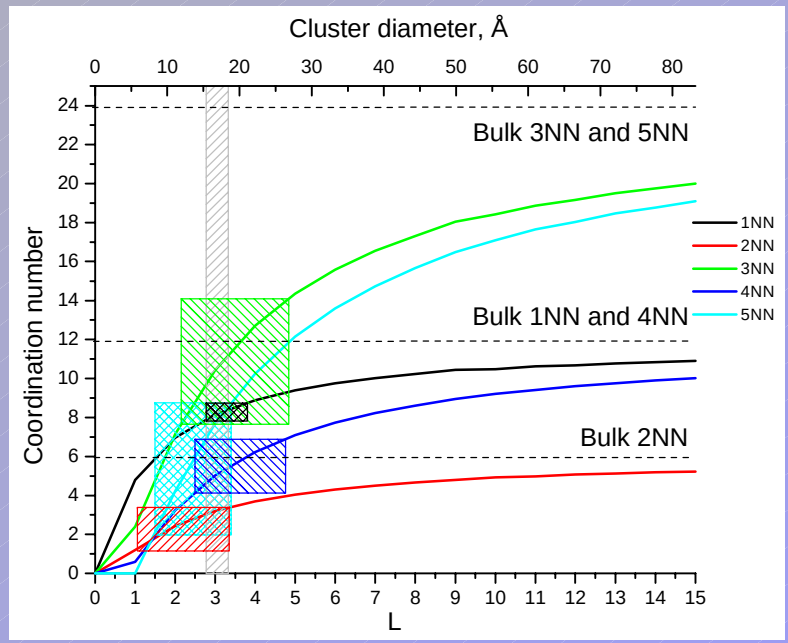
Hemispherical cuboctahedron, (111) basal plane

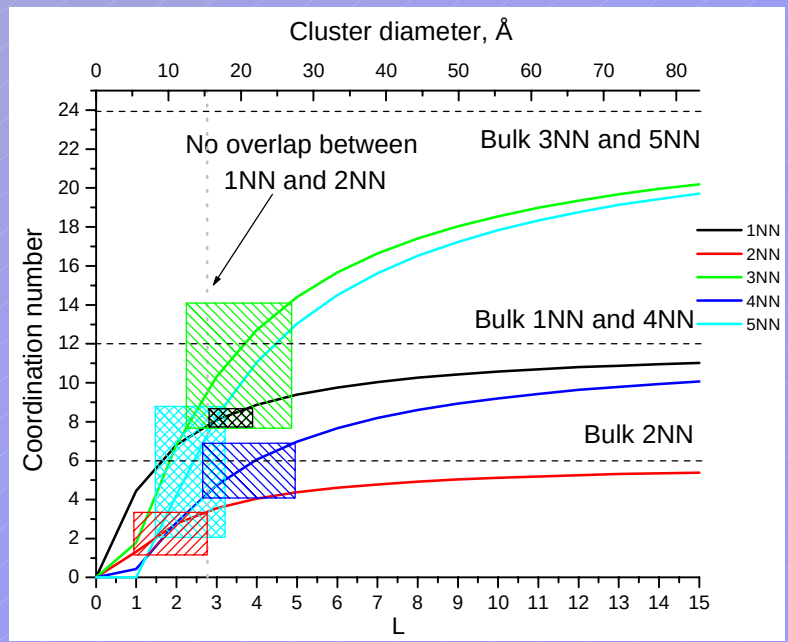
Hemispherical cuboctahedron, (001) basal plane

Theoretical vs. Experimental



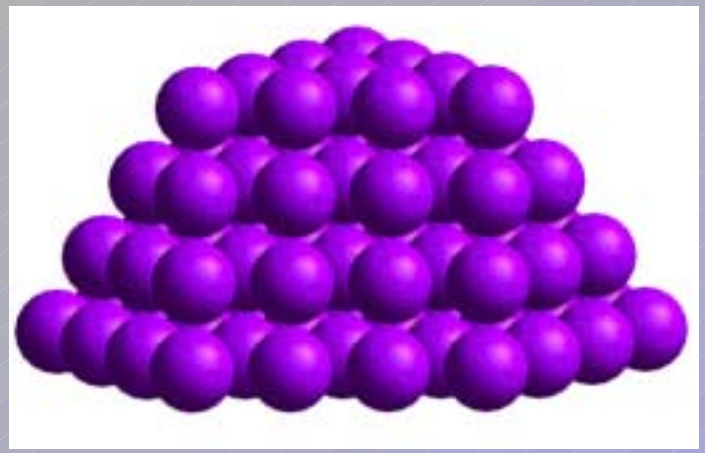
Spherical

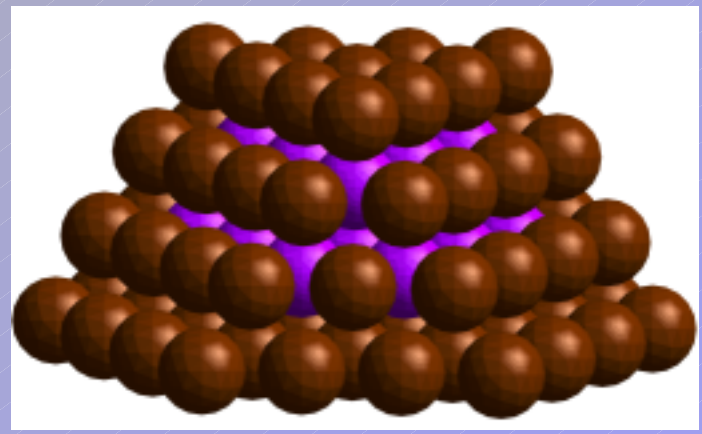




Hemispherical

Molecular Modeling: Understanding Disorder





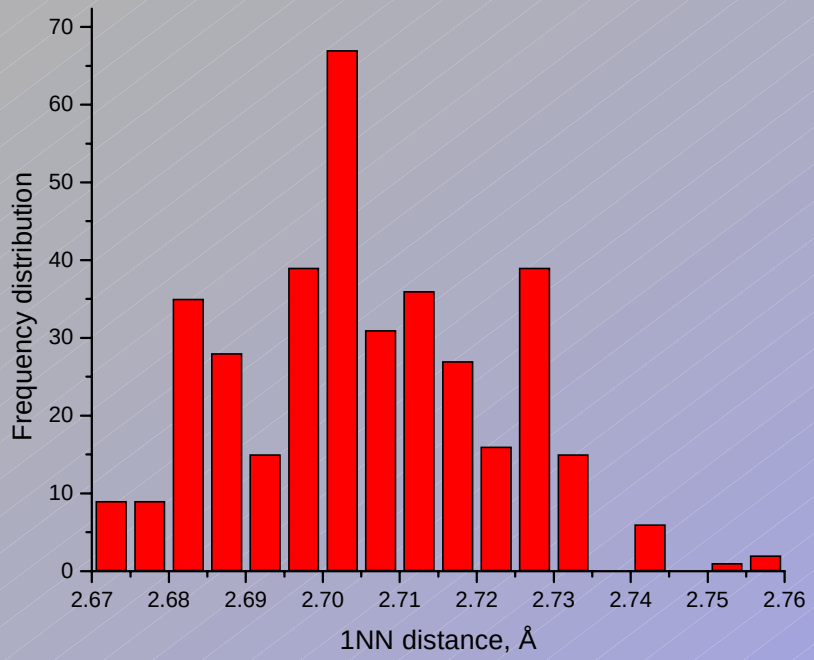
- Probe bulk vs. surface relaxation.
  - Bulk:

    Allow relaxation of entire structure.

  - Surface:

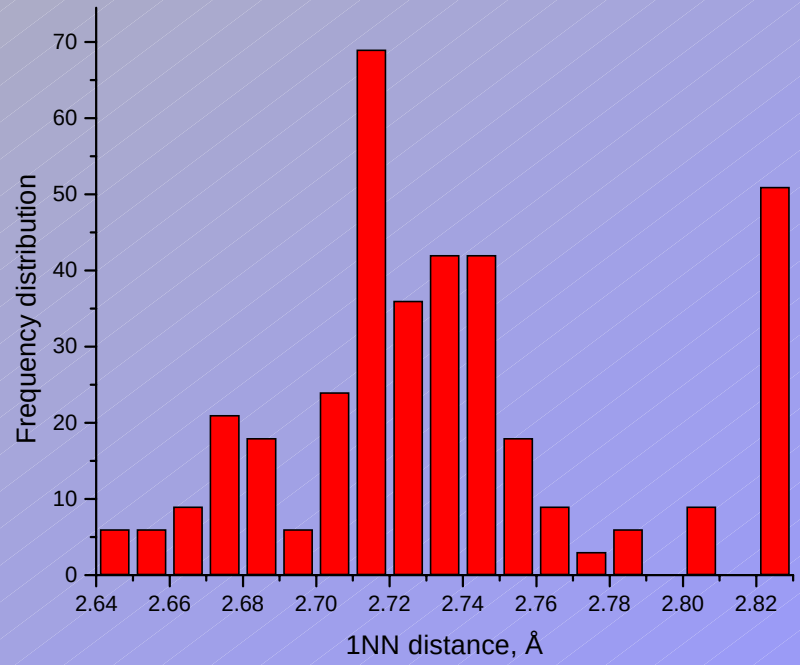
    Allow relaxation of atoms bound in surface sites only.

Bond Length Distributions: 10% Pt/C



Bulk Relaxation

- Theoretical:
  $\langle d_{1NN} \rangle = 2.706$ Å
  $\sigma^2 = 0.0003$ Å^2
- Experimental:
  $\langle d_{1NN} \rangle = 2.753(4)$ Å
  $\sigma^2 = 0.0017(2)$ Å^2



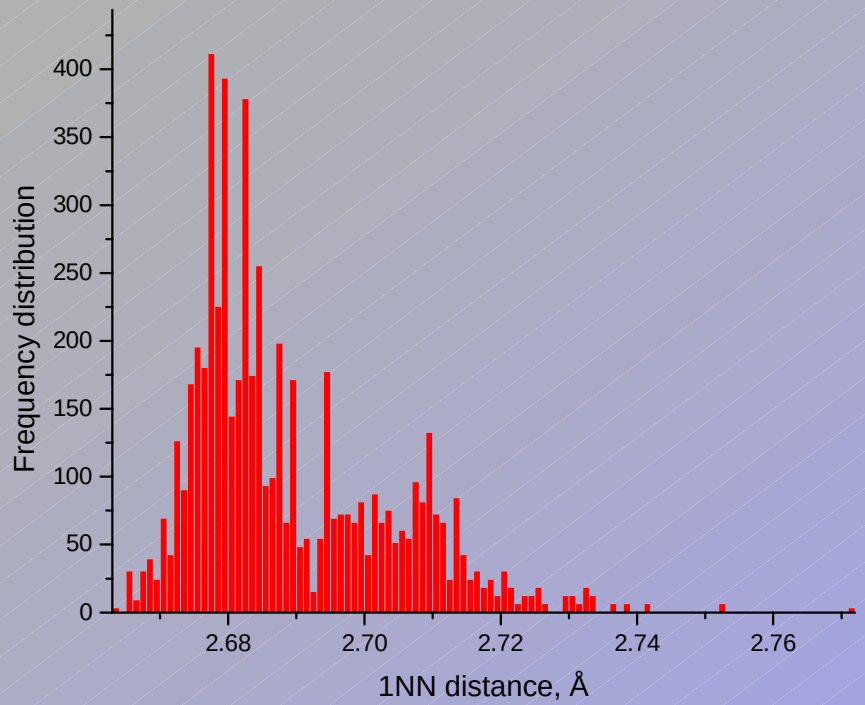
Surface Relaxation

- Theoretical:
  $\langle d_{1NN} \rangle = 2.74$ Å
  $\sigma^2 = 0.0022$ Å^2
- Experimental:
  $\langle d_{1NN} \rangle = 2.753(4)$ Å
  $\sigma^2 = 0.0017(2)$ Å^2

$\langle d_{1NN} \rangle_{BULK} = 2.77$ Å

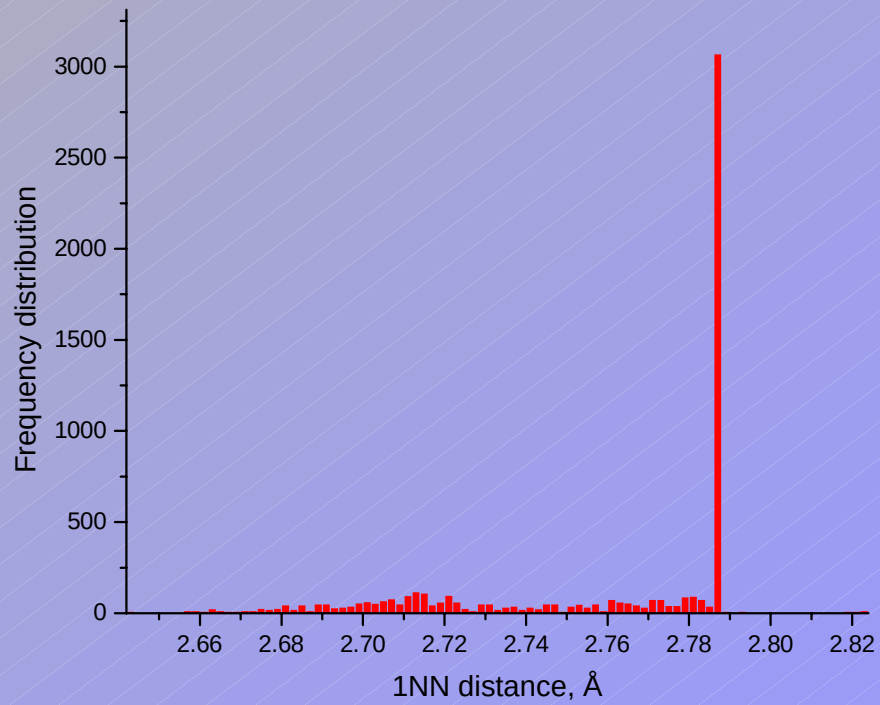
$\langle d_{1NN} \rangle_{FOIL} = 2.761(2)$ Å

Bond Length Distributions: 40% Pt/C



Bulk Relaxation

- Theoretical:
  $<d_{1NN}>$ = 2.689 Å
  σ^2 = 0.0002 Å^2
- Experimental:
  $<d_{1NN}>$ = 2.761(7) Å
  σ^2 = 0.0010(2) Å^2



Surface Relaxation

- Theoretical:
  $<d_{1NN}>$ = 2.76 Å
  σ^2 = 0.0013 Å^2
- Experimental:
  $<d_{1NN}>$ = 2.761(7) Å
  σ^2 = 0.0010(2) Å^2

$<d_{1NN}>_{BULK}$ = 2.77 Å

$<d_{1NN}>_{FOIL}$ = 2.761(2) Å

Future Directions

- In-depth modeling of relaxation phenomena.
- Further understanding the “nano-phase” behavior of bimetallic particles.
- Polymer matrices as supports and stabilizers for nanoparticles.
  - Silanes
  - Hydrogels

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