

# Methods and Applications of XAFS

## Instructors:

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**Steve Heald**  
**Ayman Karim**  
**Joshua Kas**  
**Syed Khalid\***  
**Yuanyuan Li**  
**Jing Liu**  
**Nebojsa Marinkovic\***  
**Marc Porosoff**  
**Bruce Ravel**  
**Eli Stavitski\***  
**Qi Wang**

## BNL administrators:

**Mercy Baez**  
**Gretchen Cisco**

## Financial support

**Photon Sciences Division,  
Brookhaven National Laboratory**



**Thursday, Nov 13**

# Agenda at a glance

## Session I. XAFS: Present and Future

**A. Frenkel, K. Attenkofer**

NSLS-II tour:

**K. Attenkofer, N. Marinkovic, E. Stavitski,  
S. Khalid, S. Ehrlich, E. Farquhar**



Lunch (12:40-2pm)

## Session II. Basics of EXAFS Data Analysis

**J. Kas, S. Calvin, Q. Wang**

Coffee break (3:50-4:10pm)

**B. Ravel, S. Calvin**

Dinner (6pm)



**Friday, Nov 14**

## Session III. Instrumentation

**J. Kas, D. Haskel**

Coffee break (10:20-10:50am)

**S. Heald, S. Khalid**

Lunch (12:30-2pm)



## Session IV. Theory and Experiment

**A. Frenkel, A. Karim, M. Porosoff**

Coffee break (4-4:15pm)

**N. Marinkovic, E. Farquhar**

Dinner (6pm)



**Saturday, Nov 15**

## Session V. Practicum: Data Processing and Analysis

Applying methods of XAS data analysis to sample projects (provided by the course). Parallel sessions.

A special hands-on session on FEFF9. Lunch (12-1pm)



## History of synchrotrons



**Alfred-Marie LIENARD  
(1869-1958)**

The concept of retarded potentials in the calculation on the effects due to the motion of charged particles



**Edwin Mattison McMillan  
(1907 –1991)**

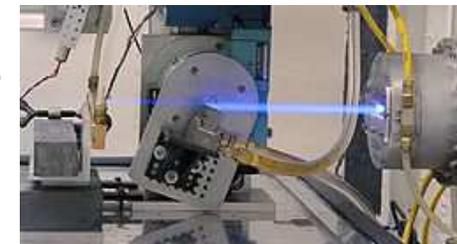
Developed the first synchrotron at Berkeley;  
Built in 1946

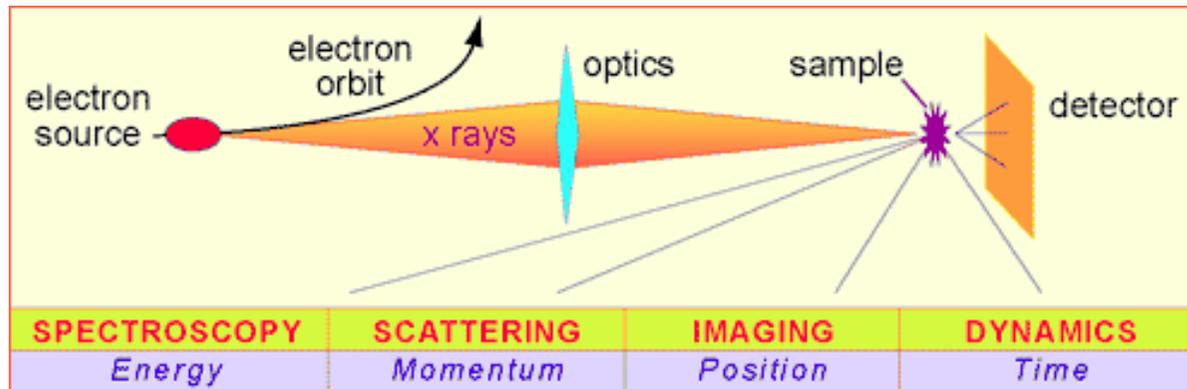


**Vladimir Veksler  
(1907 –1966)**

Developed the principles of synchrotron design

**Synchrotron radiation: 1947**  
GE synchrotron





- SPECTROSCOPY**
- 01 Low-Energy Spectroscopy
  - 02 Soft X-Ray Spectroscopy
  - 03 Hard X-Ray Spectroscopy
  - 04 Optics/Calibration/Metrology

Studies the energies of particles that are emitted or absorbed by samples:

Characteristics of chemical bonding, electron motion.

- SCATTERING**
- 05 Hard X-Ray Diffraction
  - 06 Macromolecular Crystallography
  - 07 Hard X-Ray Scattering
  - 08 Soft X-Ray Scattering

Obtains patterns of light produced when x-rays are deflected :

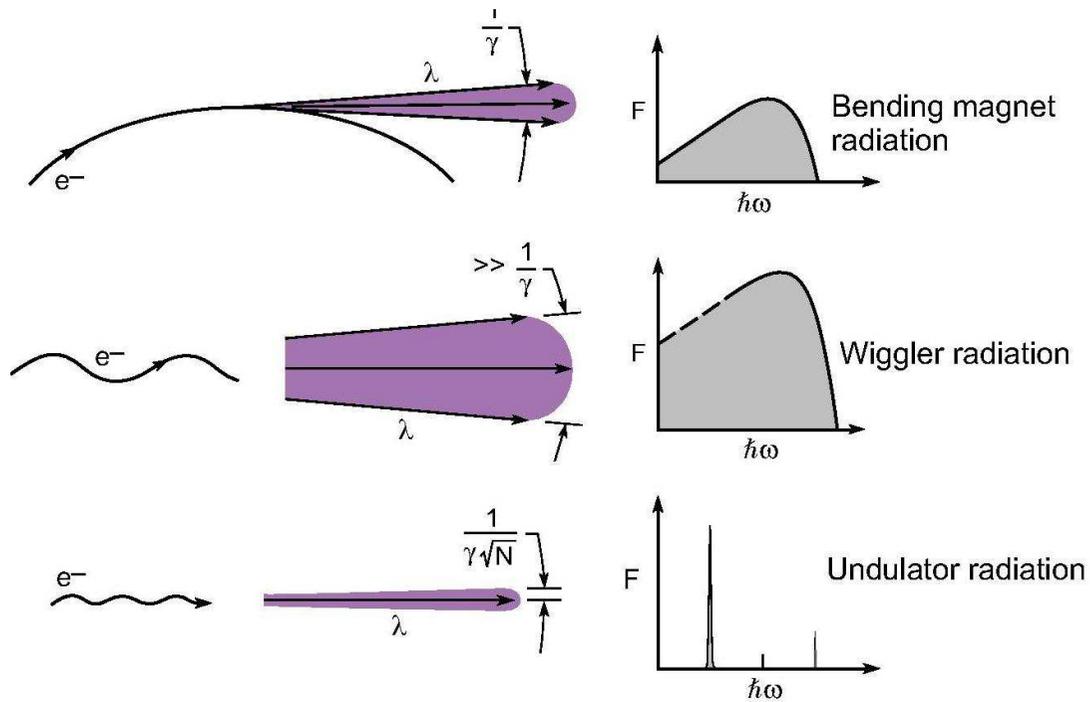
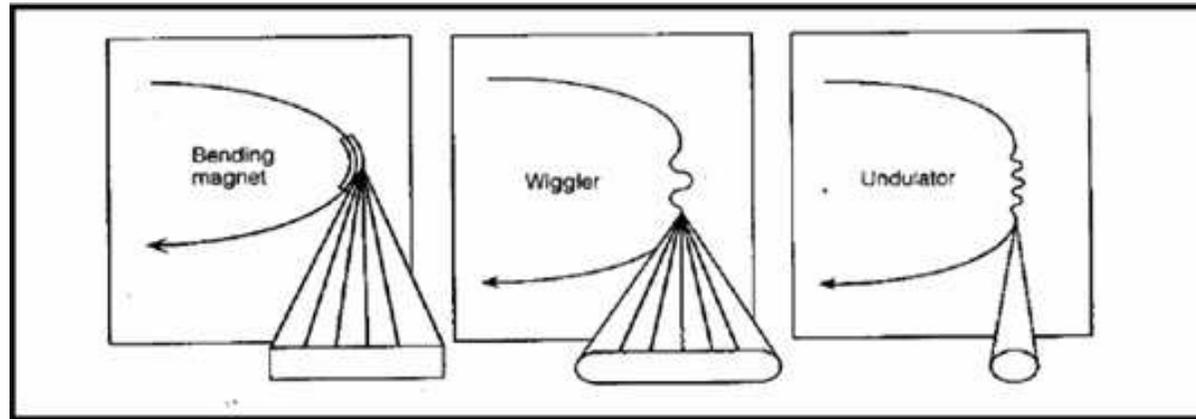
Structures of crystals, large molecules, proteins.

- IMAGING**
- 09 Hard X-Ray Imaging
  - 10 Soft X-Ray Imaging
  - 11 Infrared Imaging
  - 12 Lithography

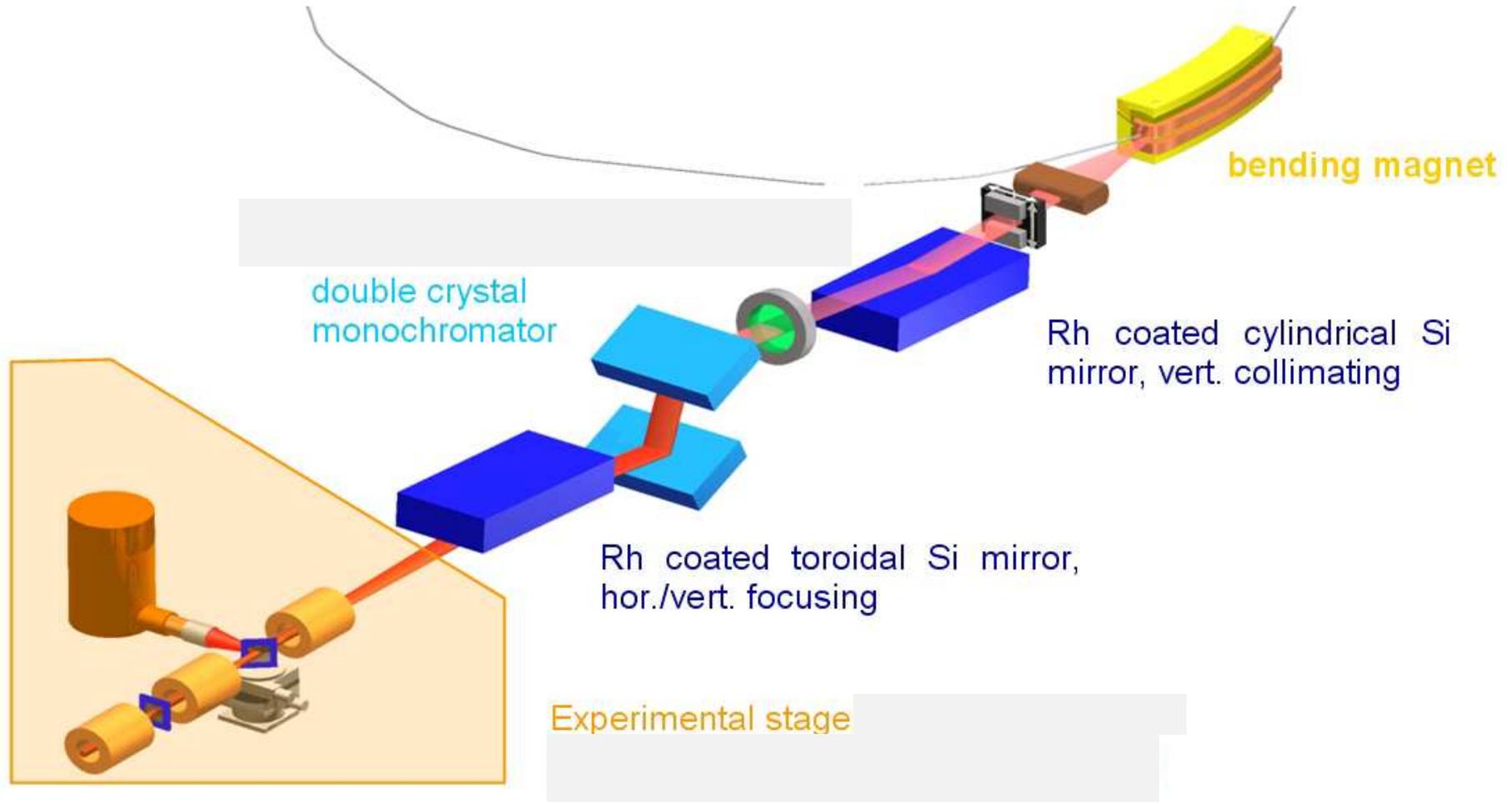
Obtain pictures of the samples:

cell biology, lithography, infrared microscopy, radiology, x-ray tomography.

# X-ray sources: bending magnet, wiggler, undulator



# Synchrotron beamline layout:



(ANKA Synchrotron at KIT)

# Absorption Coefficient and Fine Structure

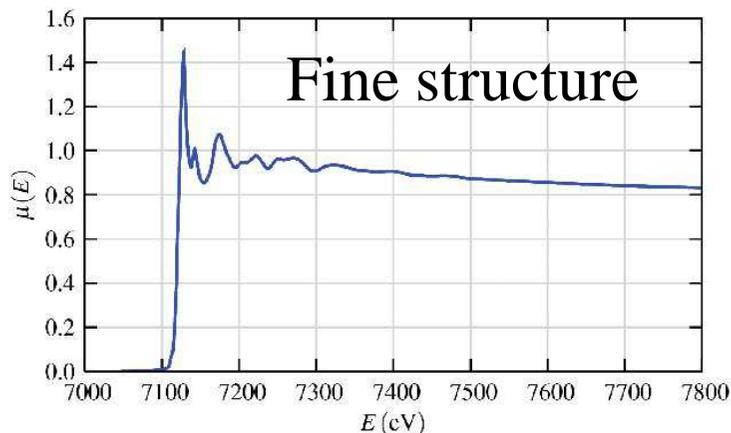
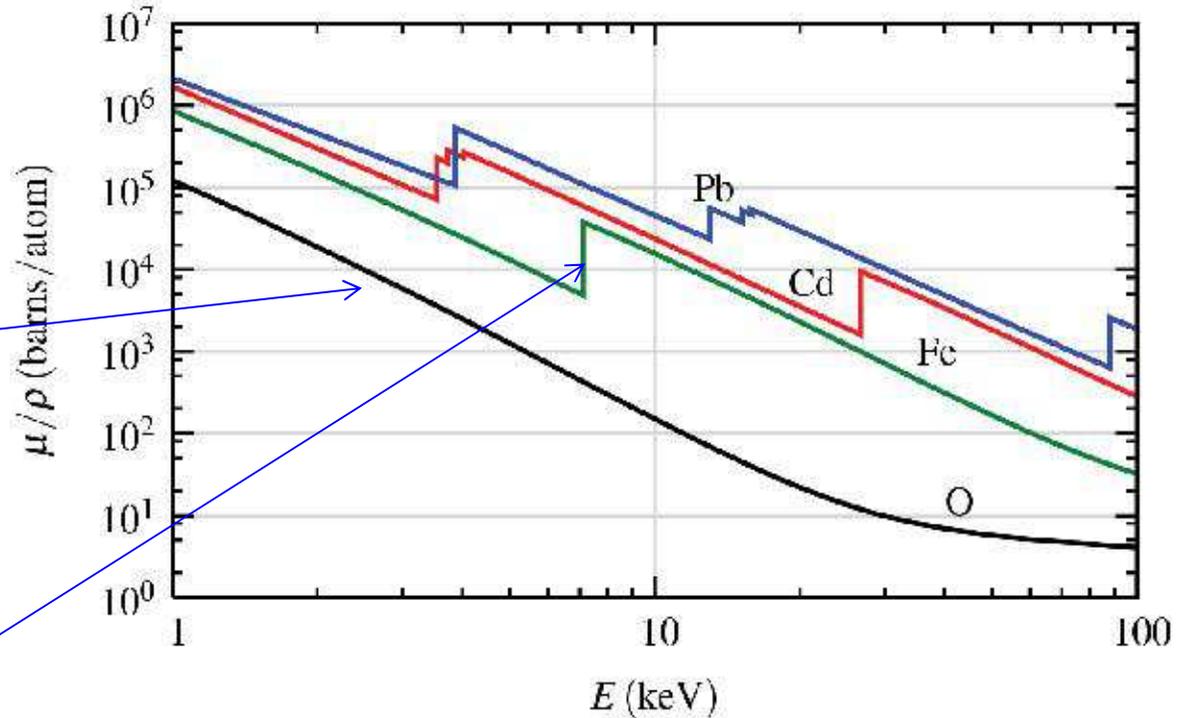
Beer – Lambert Law:

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

Victoreen formula:

$$\mu(E) = aE^{-3} + bE^{-4}$$

Absorption edges:  
(M. de Broglie, 1913)



Friscche and Hertz, 1920

(observed)

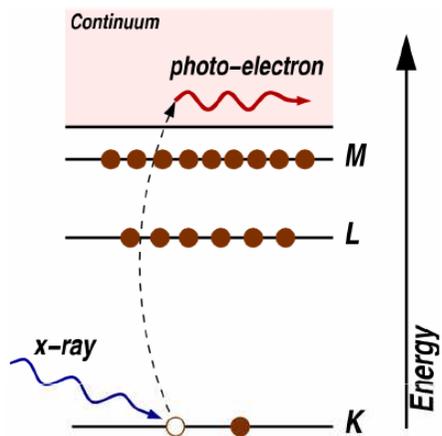
Kronig: LRO, 1931

Stern, Sayers, Lytle, SRO, 1971

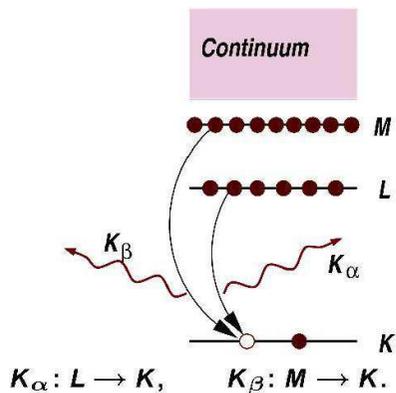
# Theory of EXAFS and XANES

Fermi's Golden Rule  
in one-electron approximation:

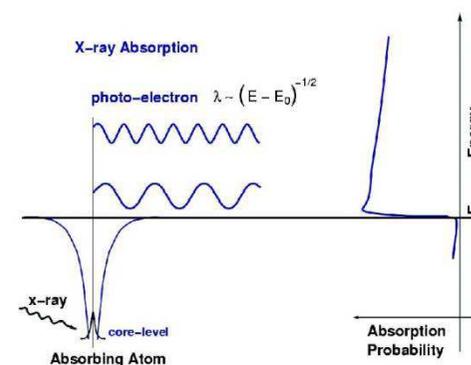
$$\mu(E) \propto \sum_f^{E_f > E_F} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E - E_f + E_i)$$



Transmission mode



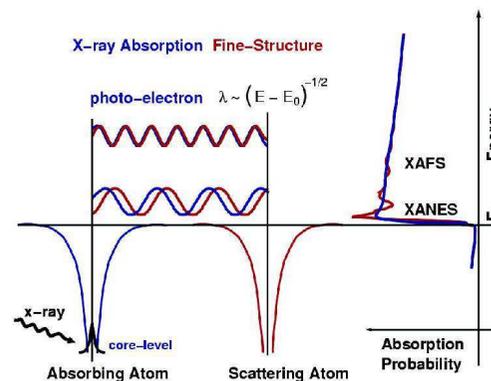
Fluorescence mode



$$E = E_0 + \frac{p^2}{2m}$$

$$p = \hbar k = \frac{h}{\lambda}$$

Absorption in the isolated atom



Absorption in the atom with neighbors

$$\mu(E) \propto \sum_f^{E_f > E_F} \left| \langle f | H_{\text{int}} | i \rangle \right|^2 \delta(E - E_f + E_i)$$

$$H \sim \vec{A} \cdot \vec{p}$$

$$\mu \sim \left| \langle \psi_f | \vec{\epsilon} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} | \psi_i \rangle \right|^2 \delta(E - E_f + E_i)$$

Initial states are highly localized; hence,  
only final state matters for EXAFS



Edward Stern, Dale Sayers, Farrel Lytle

$$\langle \psi_f | \vec{\epsilon} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} | \psi_i \rangle \approx \langle \psi_f | \vec{\epsilon} \cdot \vec{r} | \psi_i \rangle \quad (\text{dipole approximation})$$

$$\psi_f = \psi_{\text{out}} + \psi_{\text{sc}}$$

$$\psi_{\text{sc}} \sim f(k) \frac{e^{ikr_j}}{r_j} \frac{e^{ik|\vec{r}-\vec{r}_j|}}{|\vec{r}-\vec{r}_j|}$$

VOLUME 27, NUMBER 18

PHYSICAL REVIEW LETTERS

1 NOVEMBER 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray-Absorption Fine Structure\*

Dale E. Sayers† and Edward A. Stern‡

*Department of Physics, University of Washington, Seattle, Washington 98105*

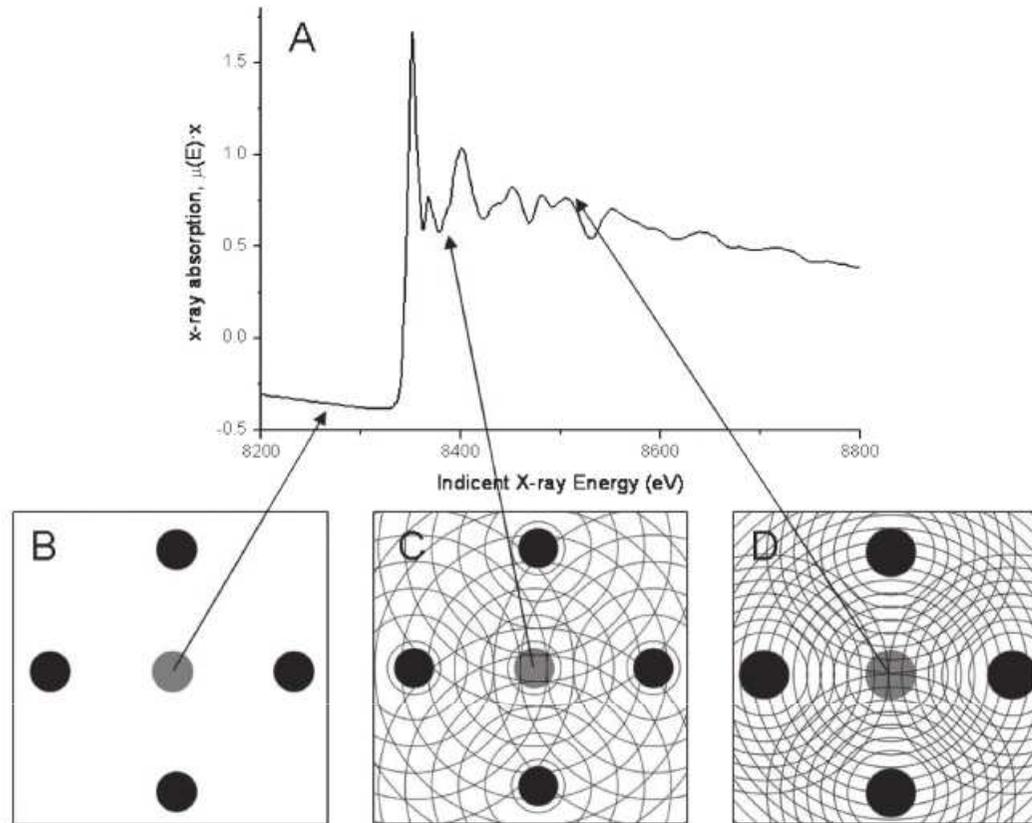
and

Farrel W. Lytle

*Boeing Scientific Research Laboratories, Seattle, Washington 98124*

(Received 16 July 1971)

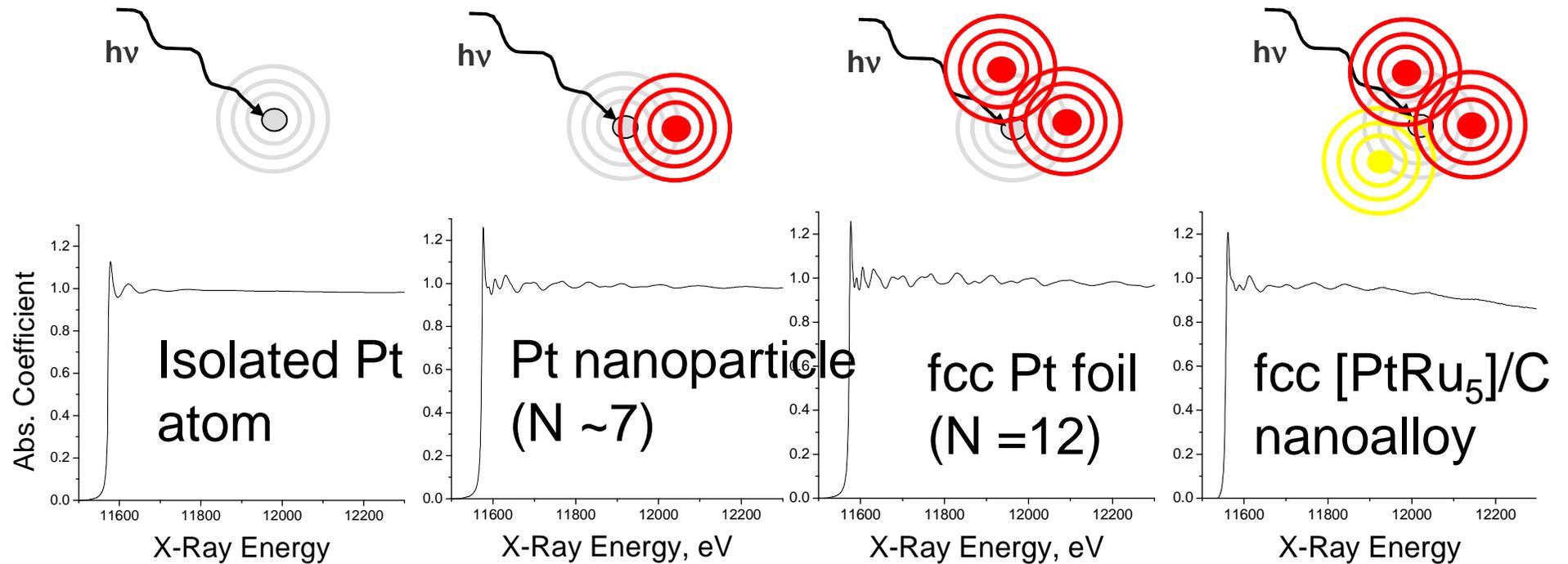
We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The 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%).



**Fig. 14–7.** Illustration of the X-ray absorption process. (A) Nickel K-edge X-ray absorption spectrum of NiO. (B–D) Nickel absorber atom (gray filled circle) and four of six neighboring oxygen atoms (black filled circles). The crests of photoelectron waves produced by X-ray absorption by the absorber atom (Ni) and by scattering from neighboring oxygen atoms are shown as concentric circles about Ni and O atoms, respectively. (B) At X-ray energies below the absorption edge no photoelectron is produced. (C) At energies close to but above the absorption edge, the photoelectron wavelength is longer than at higher energies. This particular wave produces a minimum in the oscillatory part of the absorption coefficient because the outgoing and scattered parts of the photoelectron meet at a minimum at the absorbing atom; that is, the peak crests are completely out of phase at the center of the absorber atom. (D) At higher X-ray energies the wavelength of the photoelectron is shorter than shown in C. This particular wave produces a maximum in the oscillatory part of the absorption coefficient because the outgoing and scattered parts of the photoelectron are in phase and meet at a maximum at the absorber atom.

S. Kelly, D. Hesterberg, B. Ravel,  
 In: *Methods of Soil Analysis*, 2008, Ch. 14, p. 394

# Extended X-Ray Absorption Fine Structure (EXAFS)



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

EXAFS from a single diatomic molecule

$$\chi(k) \sim N e^{-2k^2\sigma^2} f(k) \sin(2kr + \delta)$$

EXAFS from an atom in a condensed substance

# Parameters in EXAFS Equation

$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} |f^{\text{eff}}(k)| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin\left[2kR - \frac{4}{3}C_3 k^3 + \delta(k)\right]$$

Amplitude

FEFF

Same parameterization for single and multiple-scattering paths.

$$E_0 = E_0^{\text{bkg}} + \Delta E_0$$

$$R = R_{\text{model}} + \Delta R$$

$$\chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k)$$

IFEFFIT  
(GUI: Demeter)

- Easy and transparent parameterization of structural models for EXAFS data fitting
- FEFF theory
- Error analysis

# FEFF

FEFF6,8, 9:

Spherically symmetric potentials (muffin tin approximation)

Input: (xyz) coordinates and atomic numbers

Mean free path

Imaginary part of interstitial potential and life time broadening

Self Energy

Metals – Hedin-Lundqvist

Insulators – Hedin-Lundqvist or Dirac-Hara

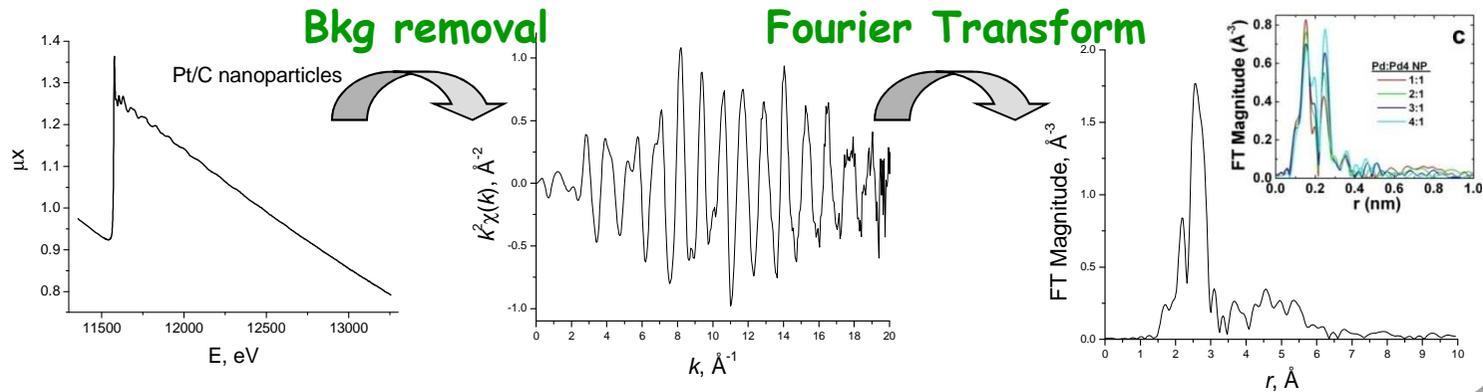
Molecules – Dirac-Hara or ground state

Multiple scattering expansion

Each photoelectron path with its  $f(k)$ ,  $\delta(k)$ ,  $\lambda(k)$   
is saved as a file

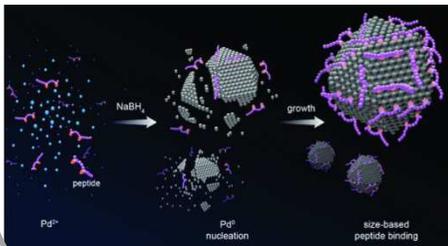
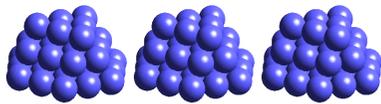
# EXAFS data analysis and modeling

## I. Processing and visual examination of the data

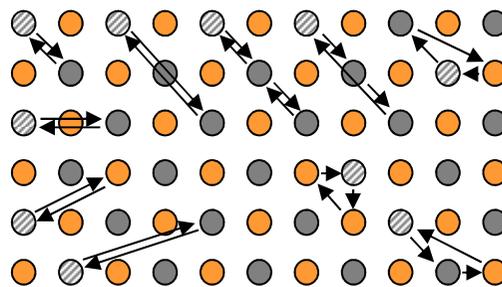


## II. Deciding on the model and refinement parameters

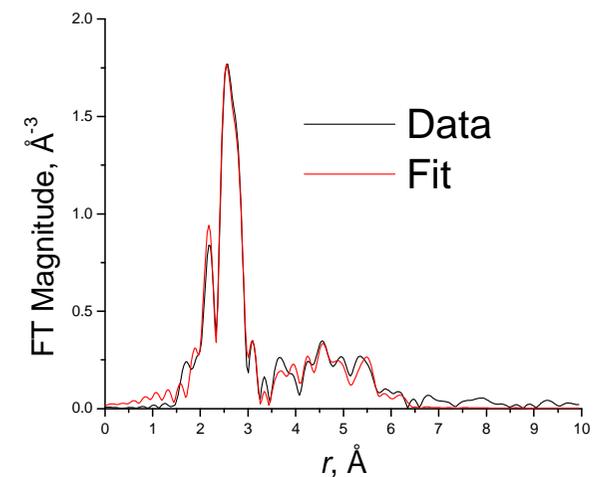
**Structural modeling**  
(different for homogeneous and heterogeneous systems)



**Path expansion and FEFF modeling**  
 $f(k)$ ,  $\alpha(k)$ ,  $\lambda(k)$



## III. Fitting theoretical EXAFS signal to the data



# Treatment of bond length distribution

$$\chi(k) = NB(k) \int \frac{\rho_1(r)}{r^2} e^{-2r/\lambda(k)} \sin[2kr + \delta(k)] dr.$$

Defining the "effective" distribution [9,11]

$$P(r, \gamma) \equiv \frac{\rho_1(r)}{r^2} e^{-2\gamma r}, \quad (2a)$$

and its Fourier transform

$$\tilde{P}(\bar{r}, \gamma; k) = \int P(r, \gamma) e^{2ik(r-\bar{r})} dr, \quad (2b)$$

where  $\gamma \equiv \lambda^{-1}$  and  $\bar{r}$  is a parameter to be chosen later, we may trivially rewrite eq. (1) as

$$\chi(k) = NB(k) \operatorname{Im} \left[ e^{i[2k\bar{r} - \delta(k)]} \tilde{P}(\bar{r}, \gamma; k) \right]. \quad (3)$$

$$C_0 = \ln P_0,$$

$$C_1 = 0,$$

$$C_2 = p_2,$$

$$C_3 = p_3,$$

$$C_4 = p_4 - 3p_2^2,$$

$$C_5 = p_5 - 10p_3p_2,$$

$$C_6 = p_6 - 15p_4p_2 - 10p_3^2 + 30p_2^3.$$

*The cumulant expansion*

The cumulant expansion is defined by the relation [13]

$$\langle e^{\xi x} \rangle = \exp \left[ \sum_{n=0}^{\infty} \frac{\xi^n C_n}{n!} \right], \quad (n \geq 0), \quad (11)$$

where  $\langle \rangle$  indicates an average over any distribution of the variable  $x$  that vanishes sufficiently rapidly at infinity \*\*. Evidently  $C_0 = 0$  if the distribution is normalized. Here we define the cumulants by the relation

$$\int P(r; \gamma) e^{i2k(r-\bar{r})} dr \equiv \exp \left[ \sum_{n=0}^{\infty} \frac{(2ik)^n}{n!} C_n(\bar{r}, \gamma) \right].$$

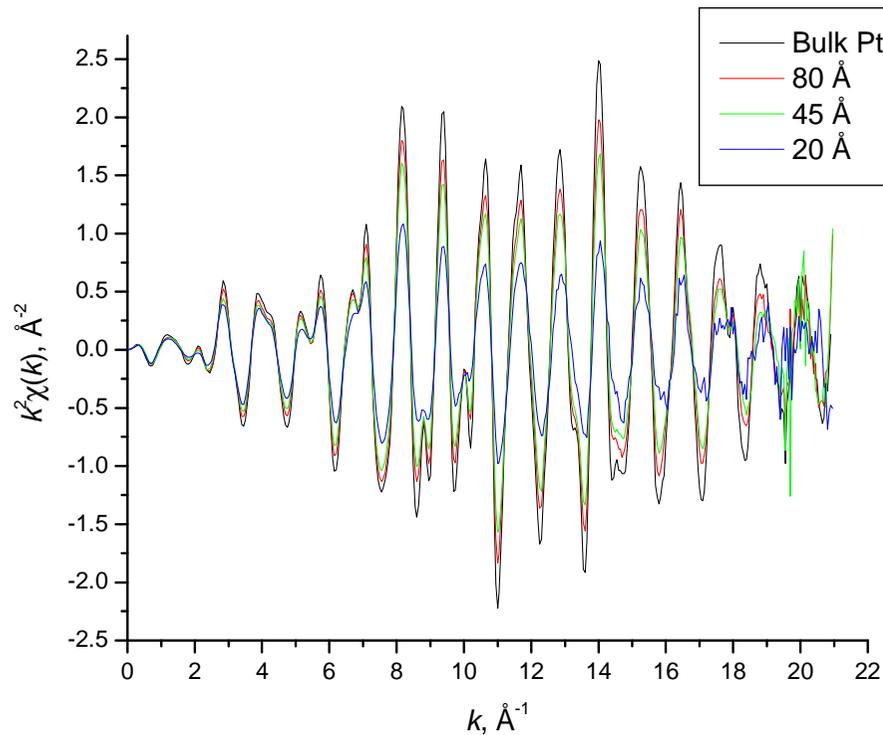
$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} \left| f^{\text{eff}}(k) \right| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin \left[ 2kR - \frac{4}{3} C_3 k^3 + \delta(k) \right]$$

G. Bunker

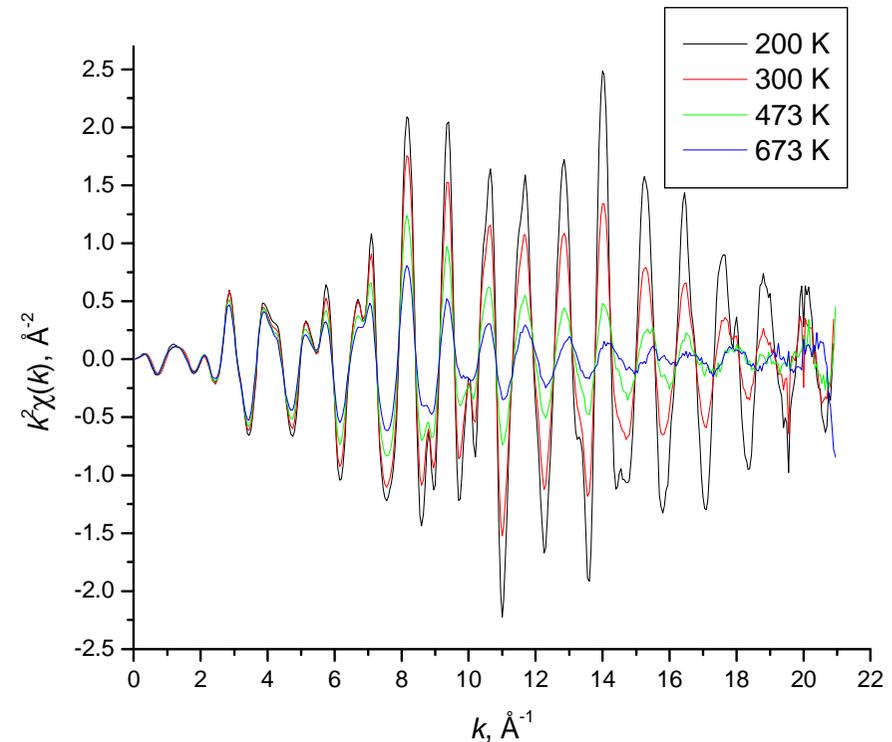
Nucl. Instrum. Methods of Phys. Res.  
207, 437 (1983)

# Amplitude factors and their effects on EXAFS

T=200 K; Size is varied



Bulk Pt; Temperature is varied



$$\chi(k) \sim N e^{-2\sigma^2 k^2}$$

As a function of size, EXAFS amplitude is scaled **uniformly** throughout the  $k$ -range

As a function of temperature, EXAFS amplitude is scaled **nonuniformly**

# Vibrational bond dynamics by EXAFS

$$\Delta F^{vib} = -k_B T \ln Z^{vib}$$

$$\Delta F^{vib} = \frac{1}{N_{Pt}} \left( k_B T \sum_j \ln \left[ 2 \sinh \left( \frac{h\nu_j}{2k_B T} \right) \right] \right)$$

$$S = -\frac{\partial F}{\partial T}$$

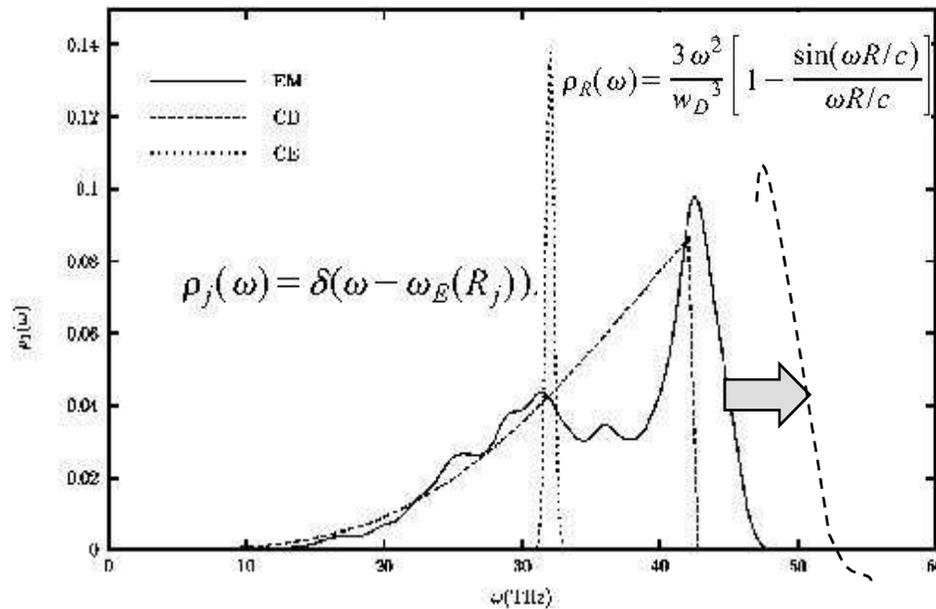
$$E = F + TS$$

$$C = -\frac{\partial E}{\partial (k_B T)}$$

Grigoryan,  
Sprinberg  
*Phys. Rev. B* 83,  
155413 (2011).

Einstein and Debye temperatures, relevant for measuring

- Dynamic disorder,
- Force constants,
- Static disorder,
- Elastic strain energy



High frequency modes → force constant stiffening

# Applications of XAFS

## Chemistry

- catalysis, intermediates states, active sites

## Physics

- phase transformations, alloys, amorphous/disordered solids

## Materials Science and Engineering

- synthesis and characterization of novel materials, mechanisms of work

## Structural biology

- enzymatic catalysis, speciation

## Pharmaceutical industry

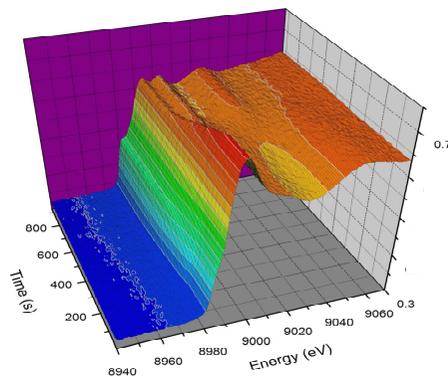
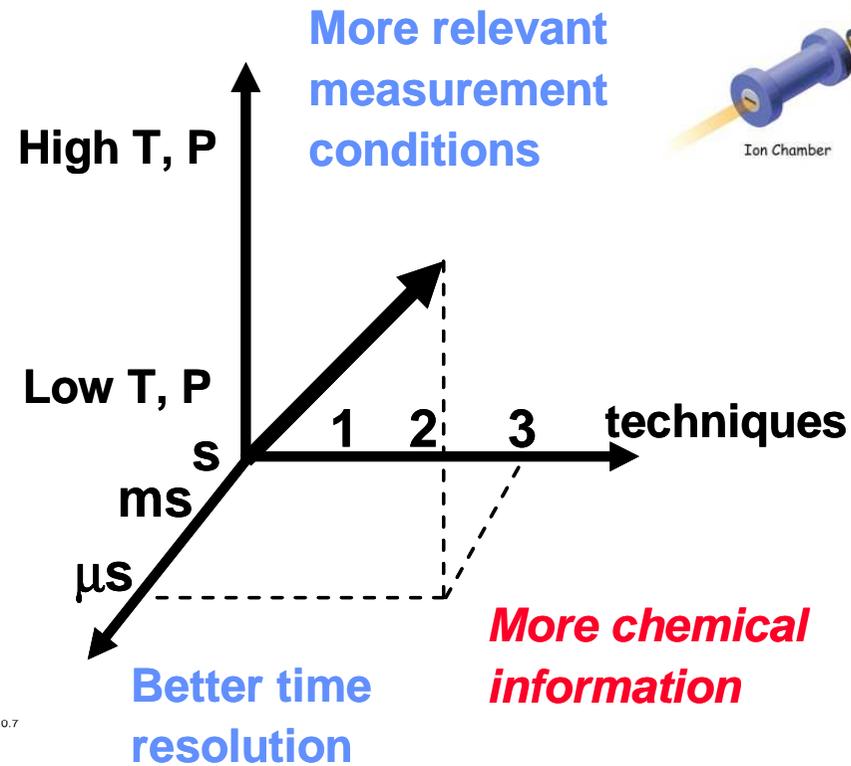
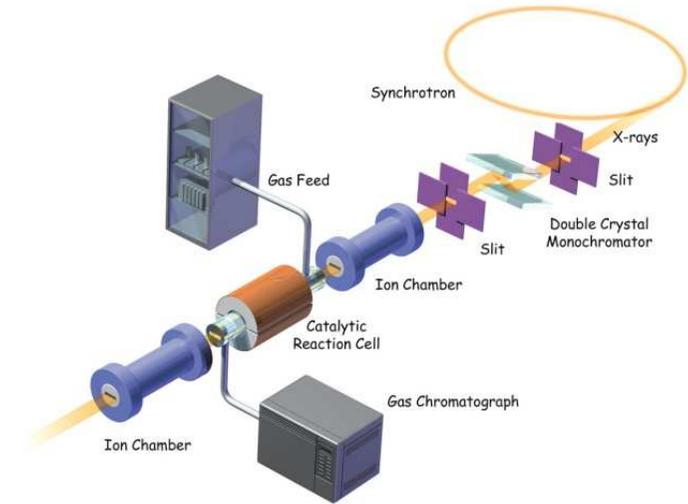
- drug design

## Environmental science

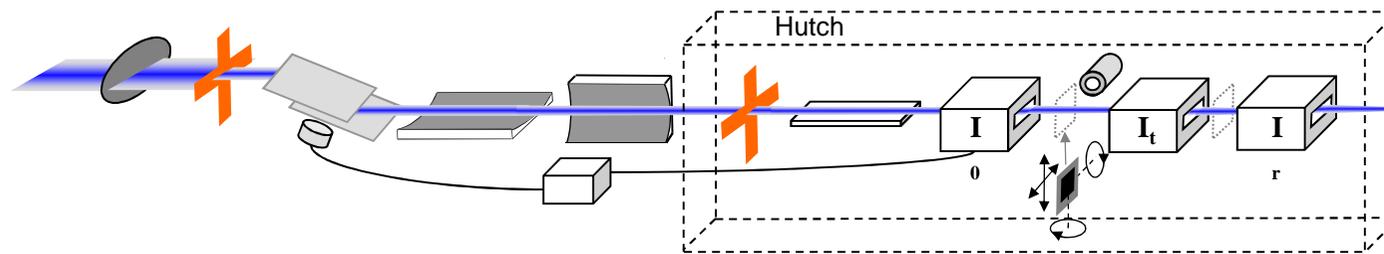
- speciation of soils, wastes, remediation

# Roadmap for *in situ* Spectroscopy

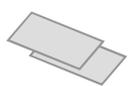
Enhanced spatial, temporal, & energy resolution



# A Typical XAS Beamline



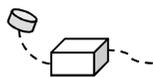
**Window:** Typically a Be foil window designed to protect the storage ring vacuum from beamline gas pressure, or protect one section of the beamline from another. The window may also be used to filter out X-rays of a particular energy range.



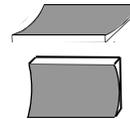
**Double crystal monochromator (mono):** Driven by motors, the mono is a set of parallel single crystals that rotate and allow X-rays of a narrow, Bragg diffracted, band of energy downstream to the experimental hutch. At a low energy beamlines the mono may be gratings-based, rather than crystal-based.



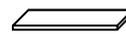
**(Entrance/Exit) beam defining aperture:** Horizontal and vertical slits that determine the spot-size on the mono (entrance) and on the sample (exit). Changing the entrance aperture will change the heat load on and, therefore, the atomic spacing of the mono crystal. Sufficient time must be allowed after changing the entrance aperture to let the mono equilibrate to the new heat load.



**Piezoelectric crystal:** The crystal provides fine mono manipulations in order to locate the position providing the maximum beam intensity (read near the sample). This position of maximum intensity can be locked-in during mono excursions using a lock-in amplifier.



**Focusing mirror(s):** A device with a curved surface and high reflectivity over the energy range of the beamline may be used to focus the beam down to a smaller spot size. The Kirkpatrick-Baez mirror system contains two mirrors that focus in orthogonal planes.



**Harmonic rejection mirror:** This device is used to reflect through total external reflection (at very shallow angles) the primary beam to the sample while absorbing the higher order harmonics.



**Ionization chamber:** A typical detector used at XAS beamlines, an ionization chamber allows a fraction of the beam to transmit downstream, making a train of simultaneous detection possible.



**Fluorescence detector:** These detectors measure fluorescence emissions from the sample. Typically they are ionization chambers (e.g. Lytle), energy dispersive solid-state detectors (e.g. Si drift) or solid-state non-energy-dispersive detector (e.g. PIPS). A filter can be used to reduce the amount of elastically scattered primary beam from entering the detector.



**Sample stage:** The sample stage typically allows for motorized manipulation of the sample in the path of the beam. Rotation and tilting of the sample may be possible on the sample stage as well.

# Synchrotron Catalysis Consortium (SCC)

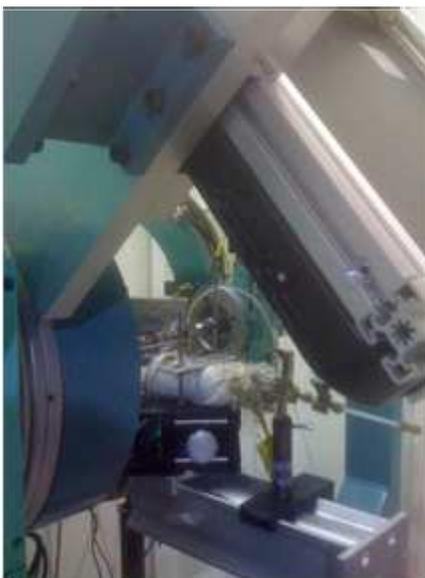
Beamlines X18B, X19A, X18A (NSLS),  
BL2-2 (SSRL), QAS and TES (NSLS-II)



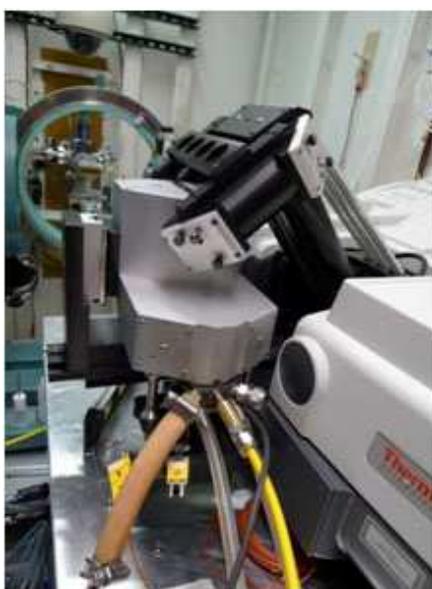
In situ reactors



Controlled environment



Combined XAFS/XRD/DAFS



Combined XAFS/DRIFTS



QEXAFS

<http://yu.edu/scc>