X-ray absorption spectroscopy (XAS – XANES/EXAFS)

Laura Simonelli
CLÆSS (Core Level Absorption & Emission Spectroscopies)
beamline responsible

OUTLINE

- The absorption process
- The multiple scattering region (XANES)
- The single scattering region (EXAFS)
- Detection methods
- Research field
- Summary

X-rays

Grup de Tècniques de Separació en Química UAB

X-ray Absorption Spectroscopy (XAS)

probe

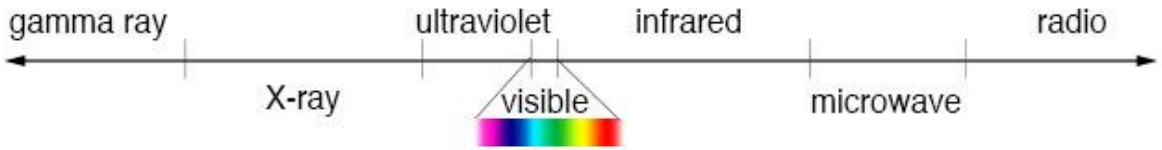
electromagnetic radiation

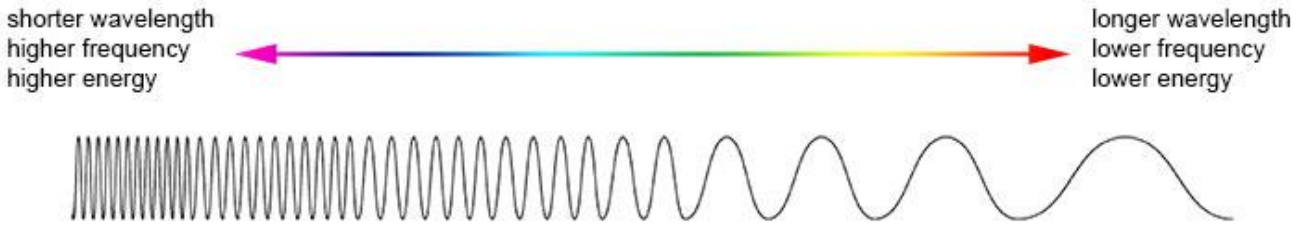
E from 120 eV (soft) to 120 keV (hard);

λ from 100 Å to 0.1 Å

$$E\ (keV) = \frac{12.4\ (keV)}{\lambda\ (Å)}$$

measure the energy of an interaction





Photon absorption

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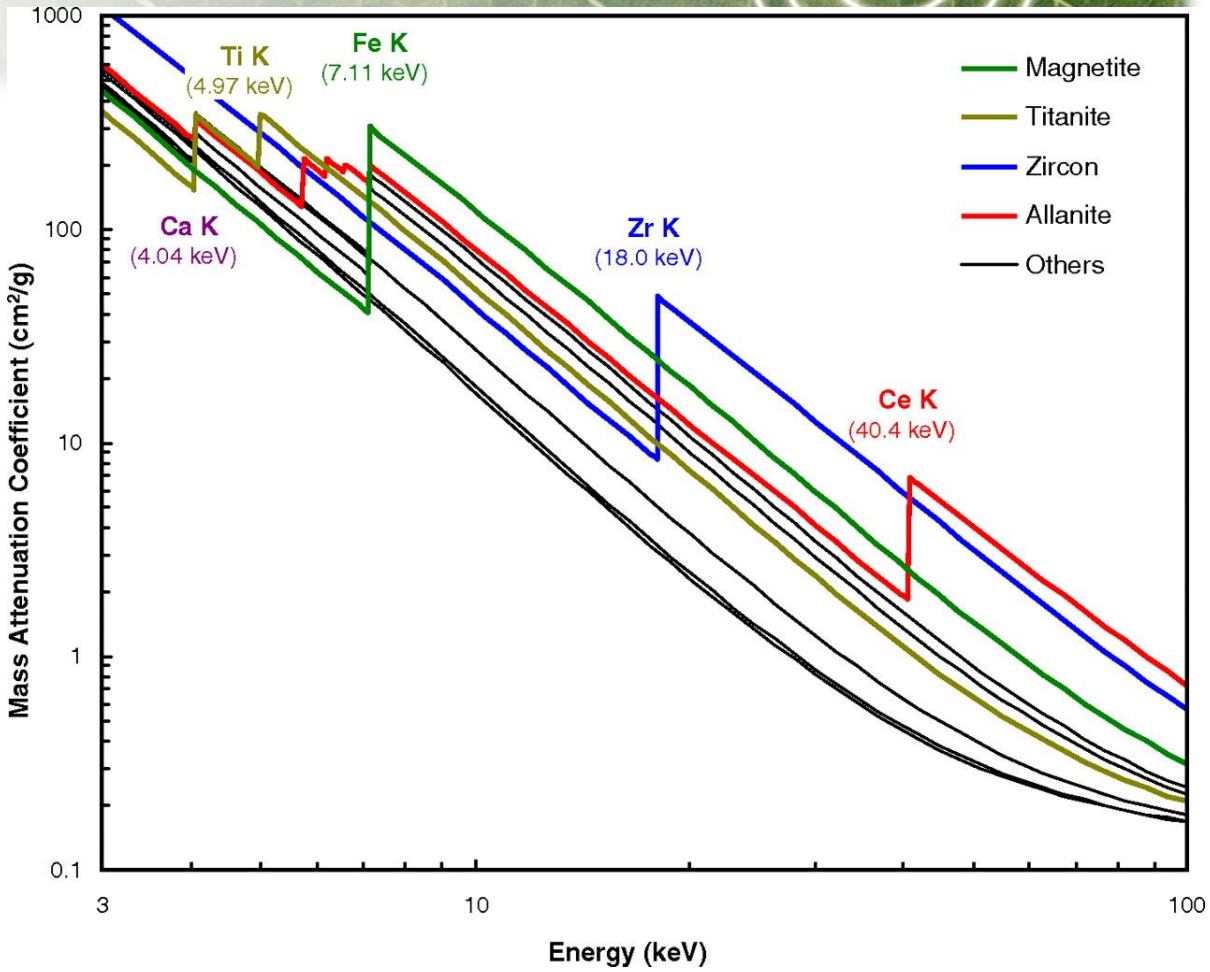
The oscillating electric field of the electromagnetic radiation interacts with the electrons bound in an atom.

Scattered radiation

Absorbed radiation



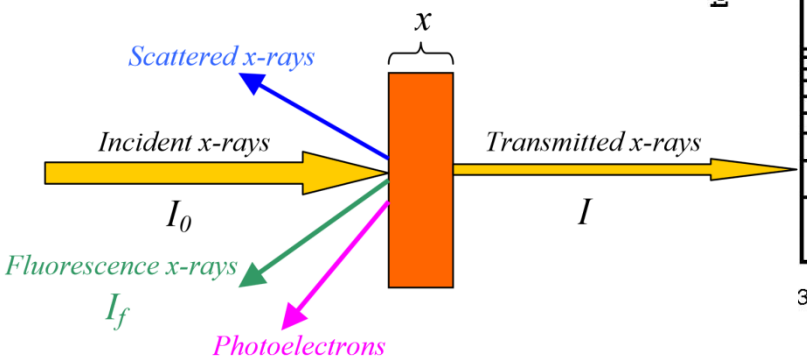
Photon absorption

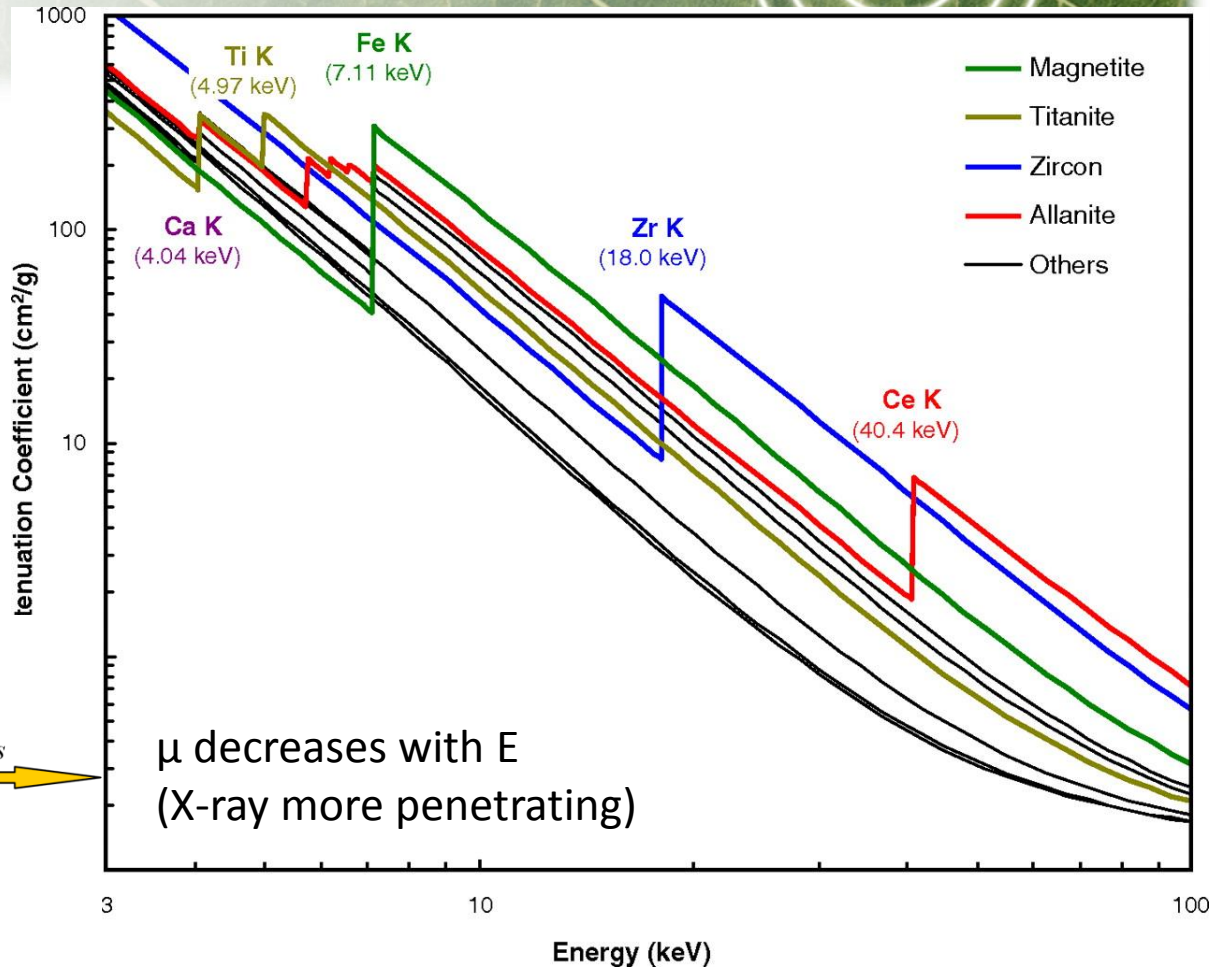
Grup de Tècniques de Separació en Química UAB

A monochromatic x-ray beam of intensity I_0 passing through a sample of thickness *x* will get a reduced intensity *I* according to:

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

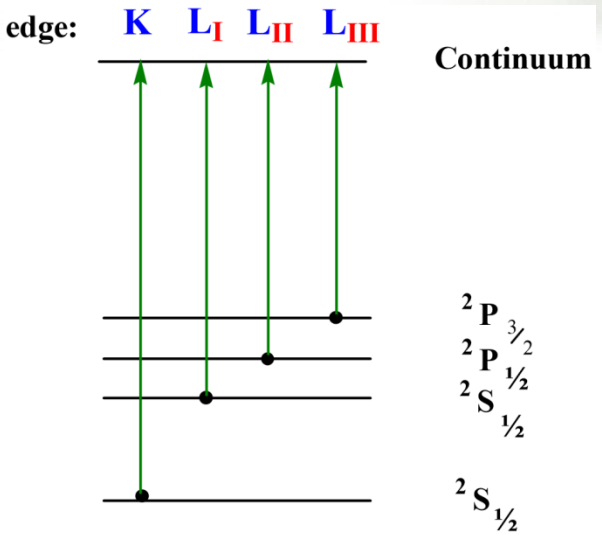
μ = *linear absorption coefficient*





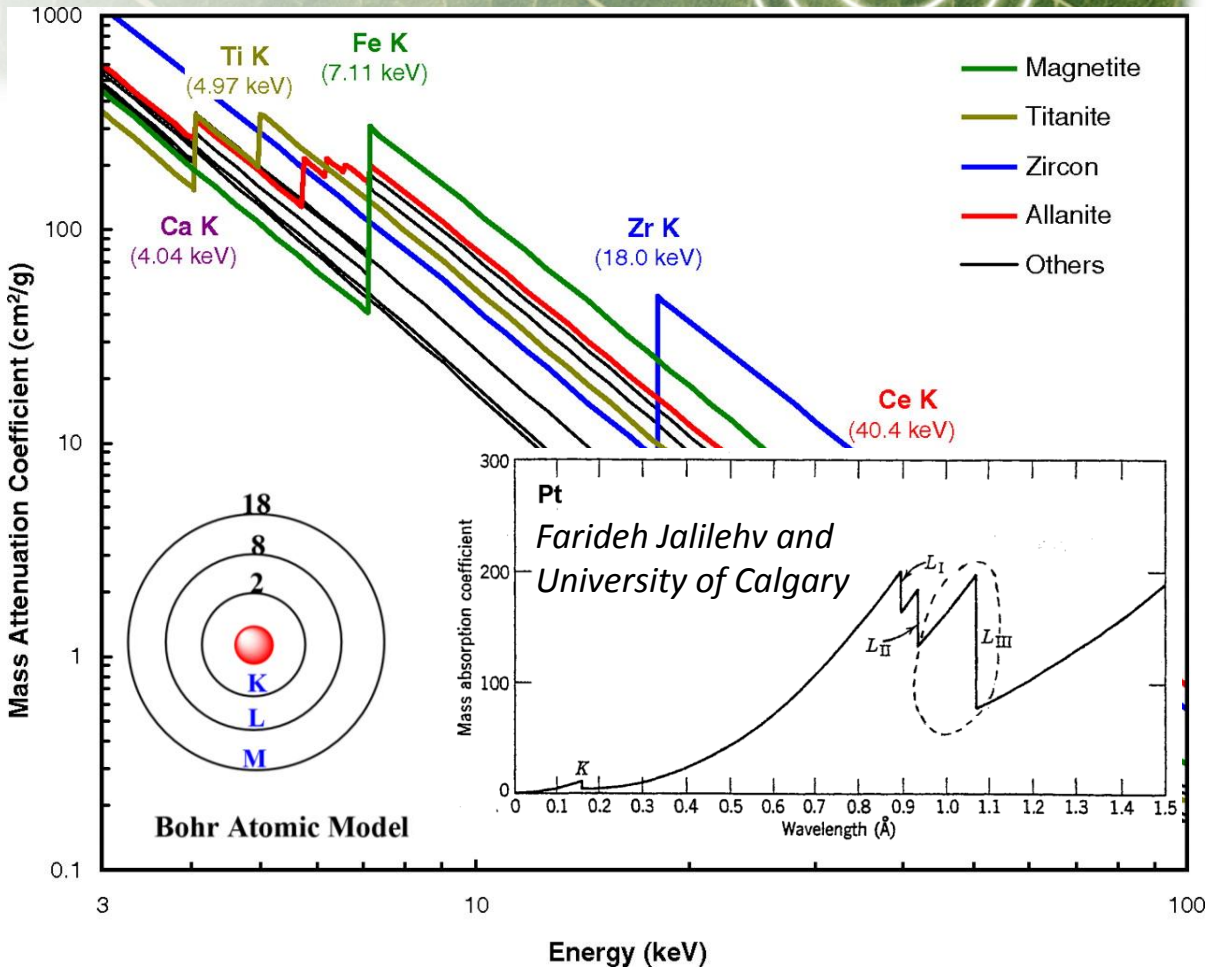
Photon absorption

Grup de Tècniques de Separació en Química UAB



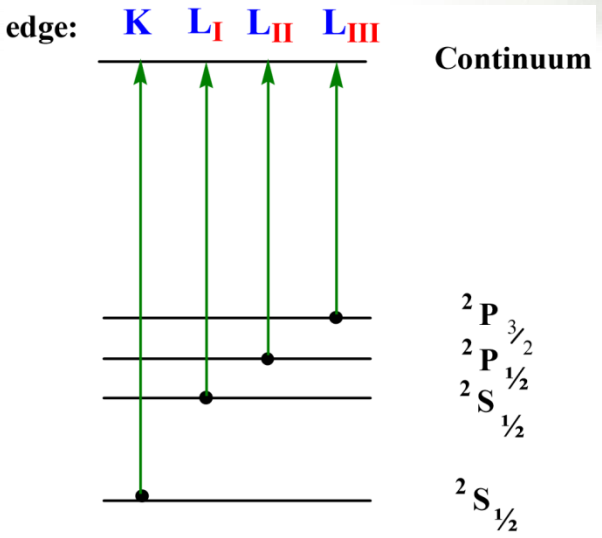
Absorption edges occur for each shell of core electrons when E = binding energy of core electron

K: $1s_{1/2}$ **L_1**: $2s_{1/2}$ **L_2**: $2p_{1/2}$ **L_3**: $2p_{3/2}$ (nl_j notation)



Photon absorption

Grup de Tècniques de Separació en Química UAB



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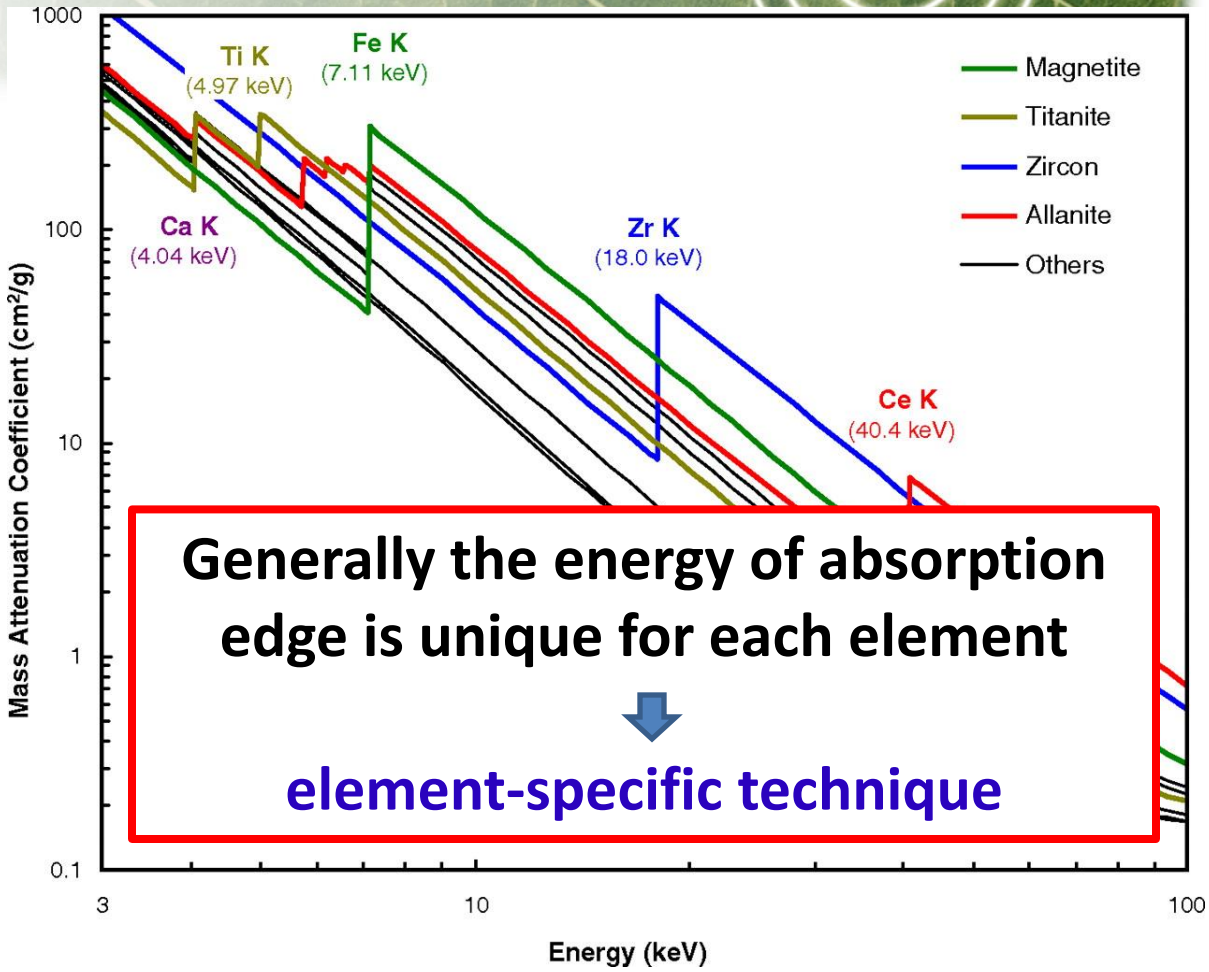
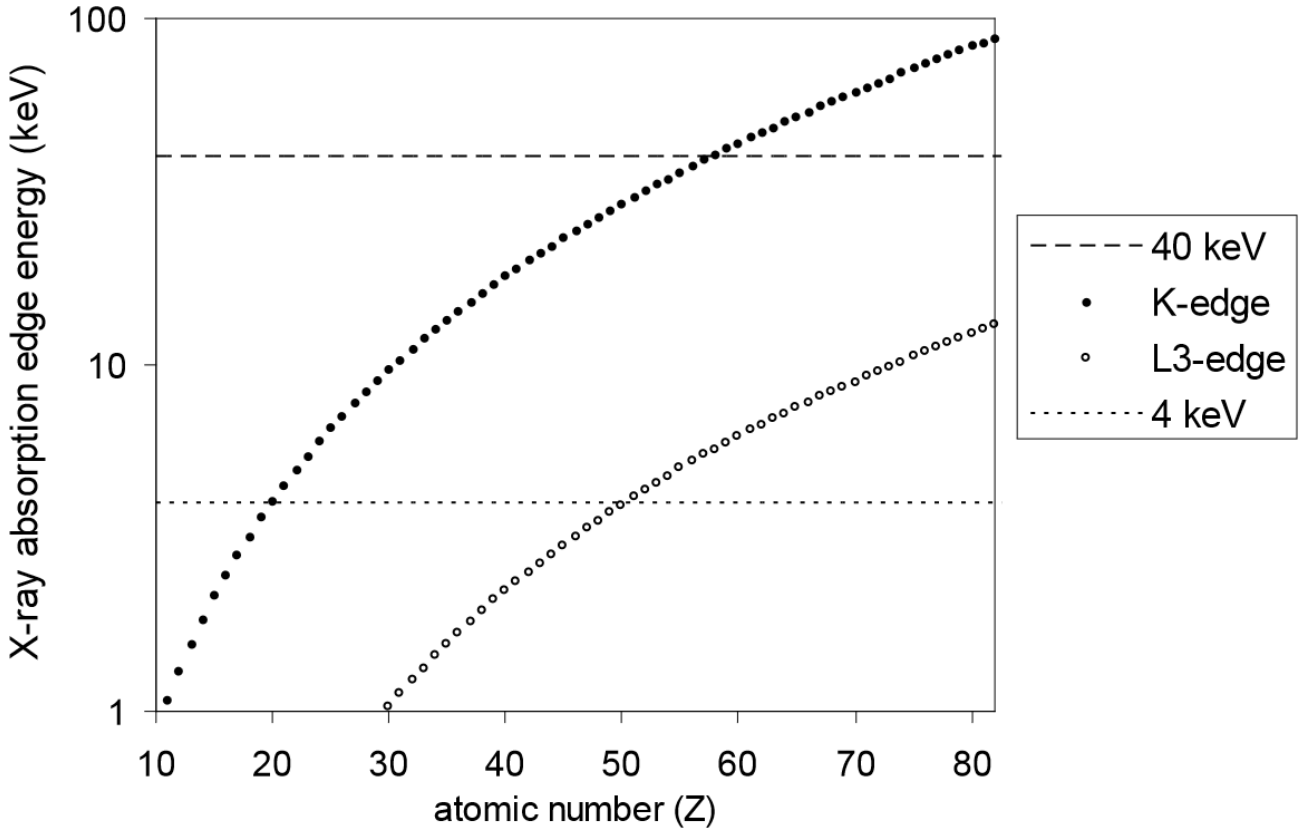


Generally the energy of absorption edge is unique for each element

element-specific technique

Photon absorption:

difficult for light elements, e.g. Z<22 (Ti)
for heavy elements use L3 edge, e.g. Z>57 (La)

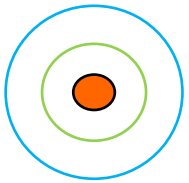


Photon absorption:

Photoelectron like a wave

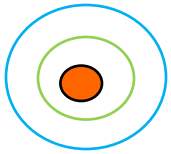
photo-electron excited to state significantly above binding energy – becomes "quasi" free-electron

Atomic absorption



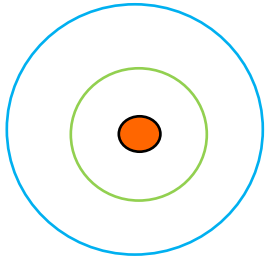
The photo-electron leaves the excited atom with circular wavefunction – wavelength $\lambda = \frac{12.2}{\sqrt{KE(eV)}}$

(kinetic energy KE = E - binding energy)



higher E,
larger KE,
Smaller λ

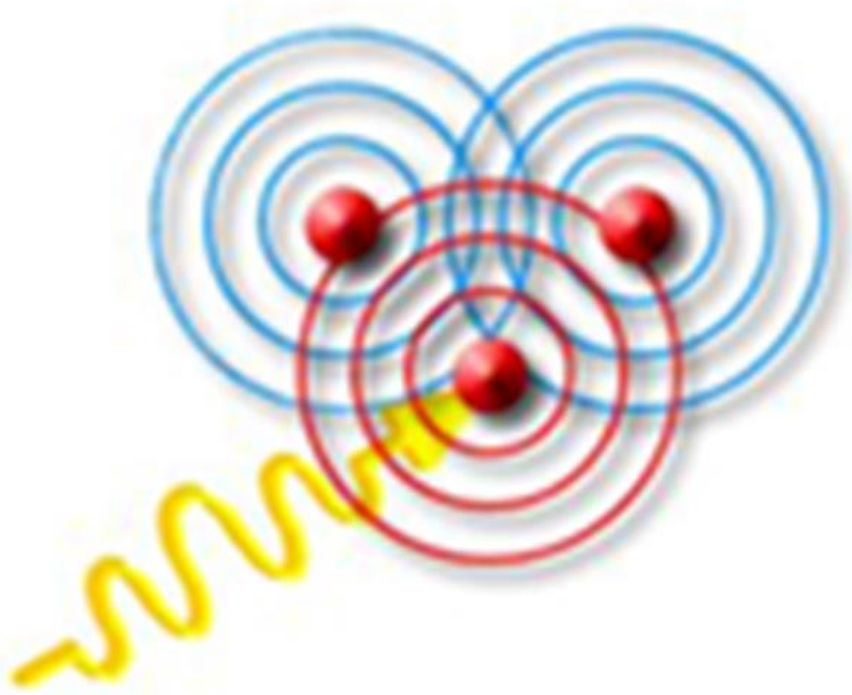
lower E,
smaller KE,
larger λ



Photon absorption:

Photoelectron like a wave

When the photoelectron leaves the absorbing atom, its wave is backscattered by the neighboring atoms.



Photon absorption:

Interference of scattered waves

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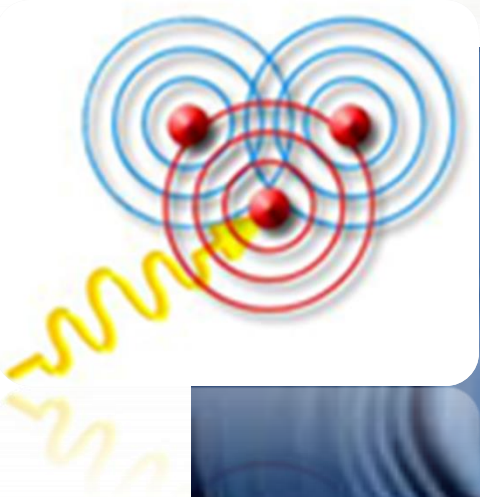
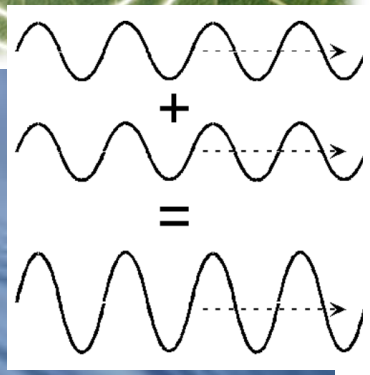
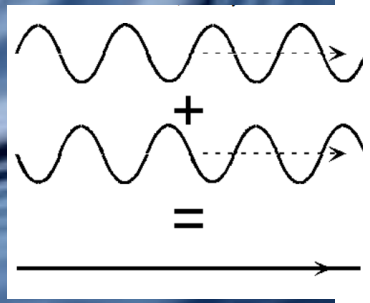


Interference is essentially an energy redistribution process: the energy which is lost at the destructive is regained at the constructive interference.



Constructive



destructive

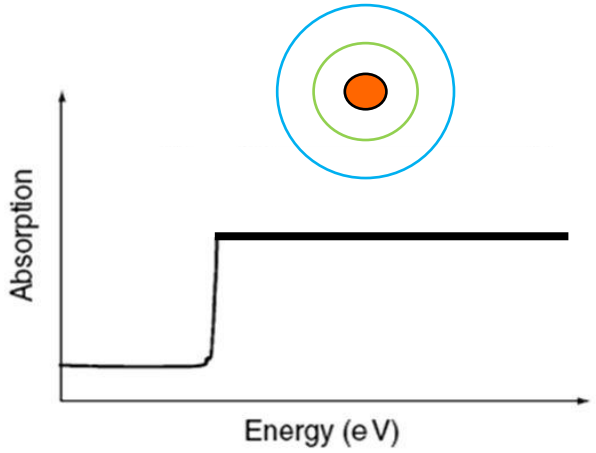
Constructive and destructive interference between the outgoing photoelectron wave and backscattered wave

Photon absorption:

Absorber isolated or embedded in the matter

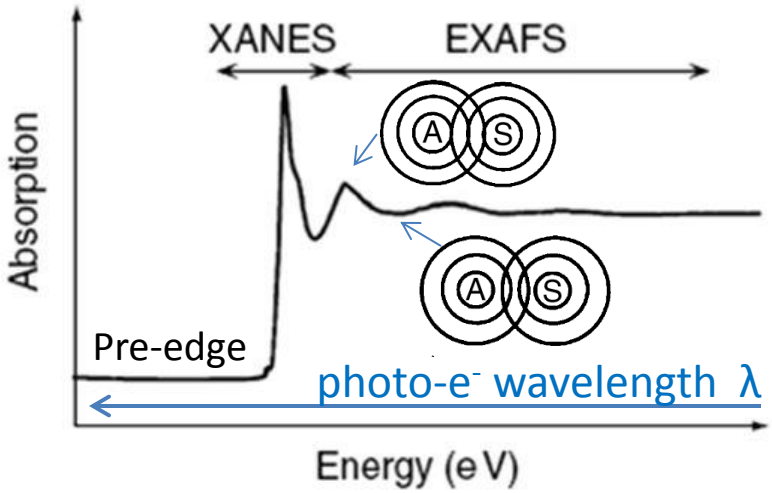
Grup de Tècniques de Separació en Química UAB

Atomic absorption



The absorption of an isolated atom show a step like behavior.

When the absorber is embedded in the matter the photoexcitation cross-section is modulated by the interference between the outgoing and the back-scattered photoelectron waves.



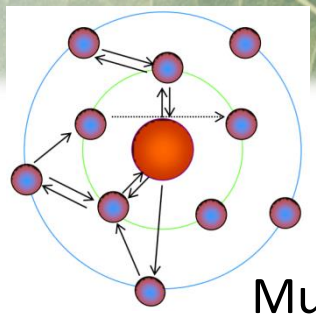
Photon absorption:
XANES & EXAFS

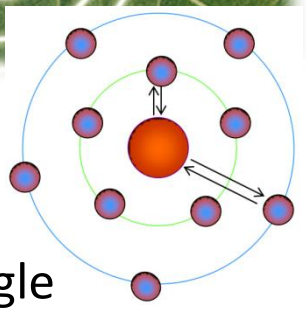
Grup de Tècniques de Separació en Química UAB

XANES (or **NEXAFS)**
(*X-ray Absorption Near Edge Structure*):

≈ -10 eV < $E-E_0$ < 50 eV

Lower energy ➡ *Higher λ* ➡ *multiple scattering*





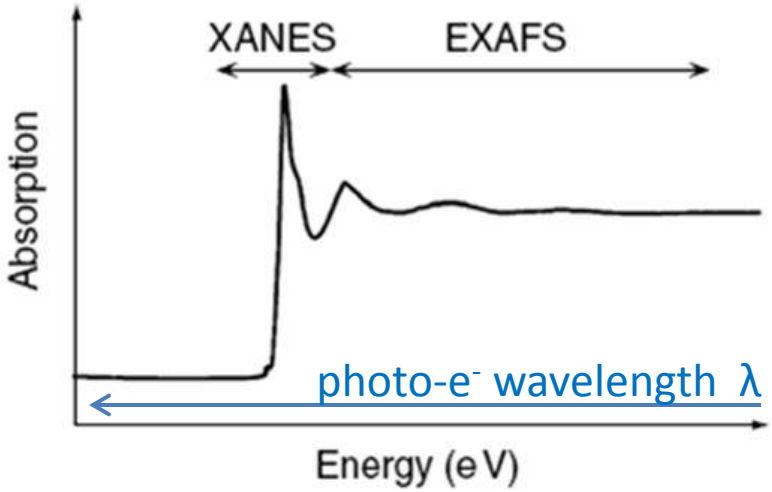
Multiple scattering region

Single scattering region

EXAFS
(*Extended X-ray Absorption Fine Structure*):

≈ 50 eV < $E-E_0$ < 1000 eV

Higher energy ➡ *Lower λ* ➡ *single scattering*



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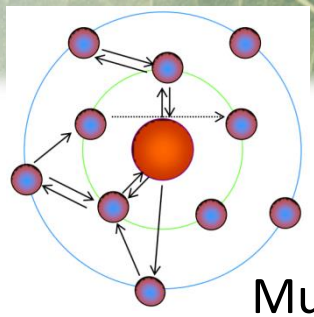

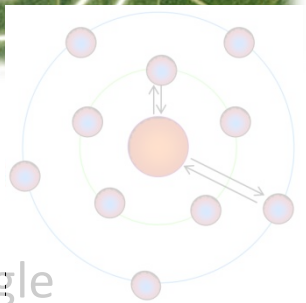

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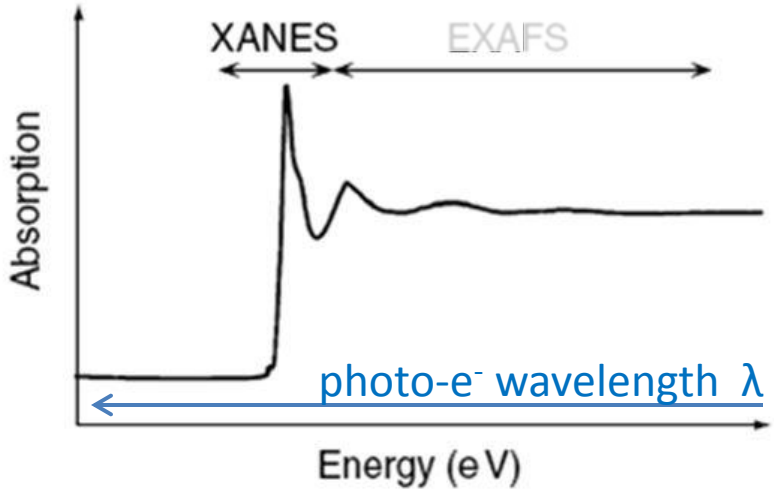


XANES:

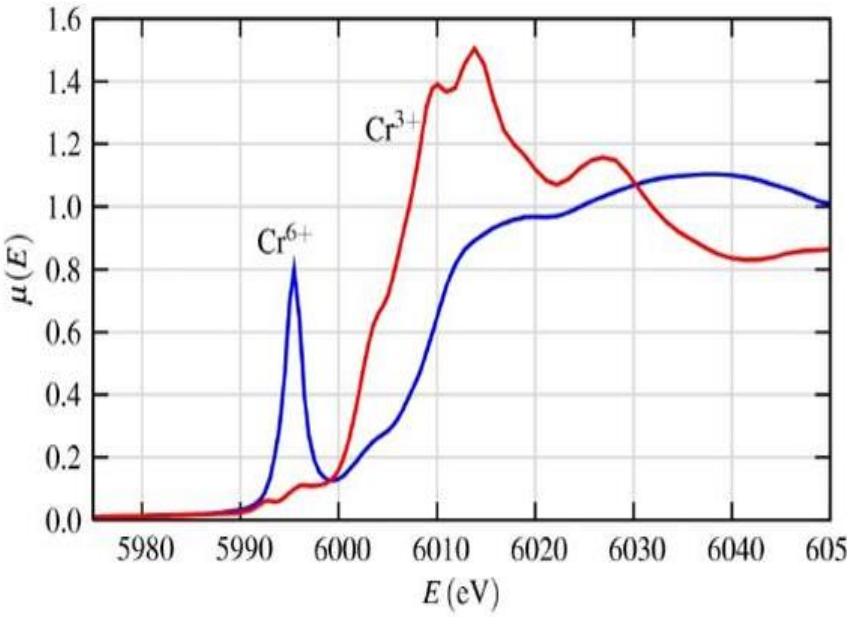
structural and electronic properties

ELECTRONIC AND STRUCTURAL PROPERTIES

Energy, width, and intensity

⇩

- **Oxidation state**
- **Unoccupied electronic states**
- **Spin state**
- **Local structure**



STRUCTURAL PROPERTIES

Angle dependence of multiple scattering

⇩

- **direct information about bond angles.**

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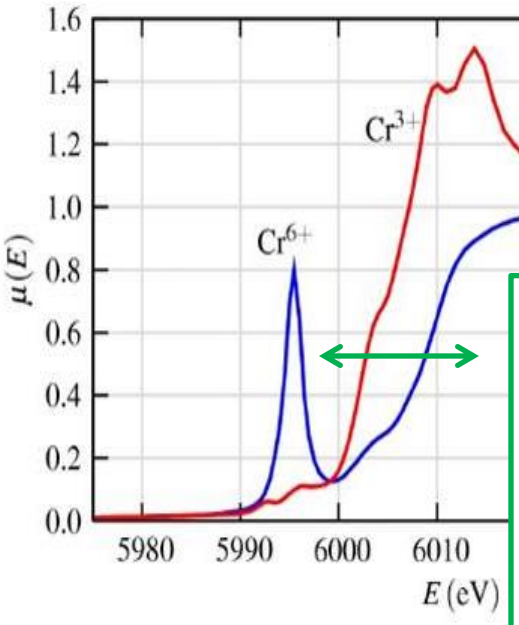

STRUCTURAL PROPERTIES

Angle dependence of multiple scattering

⇩

- **direct information about bond angles.**

The energy of an absorption edge is not well defined. It can be taken as the energy at half-height or as the maximum in the first derivative with respect to energy. It shifts as a function of the oxidation state

XANES:
structural and electronic properties

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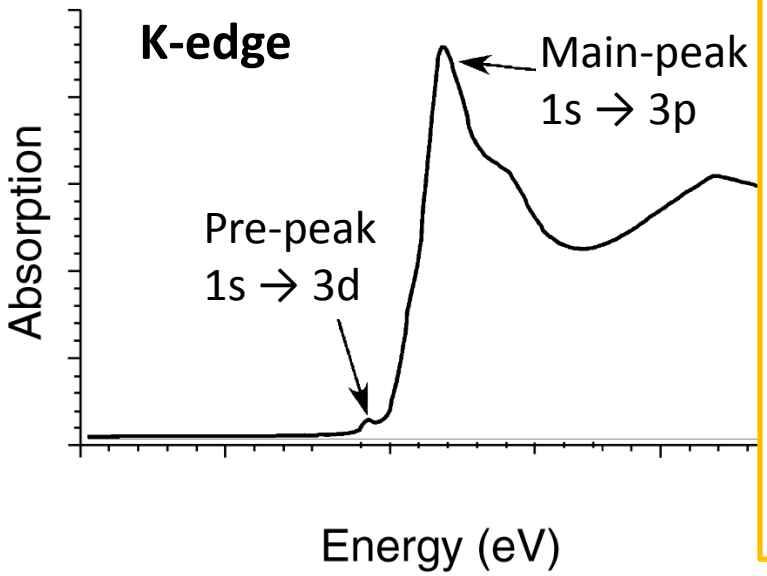

STRUCTURAL PROPERTIES

The most intense features are due to electric-dipole allowed transitions (i.e. $\Delta\ell = \pm 1$) to unoccupied final states. The most intense features of a K-edge are due to transitions from 1s → p-like final states, while the most intense features of the L_3-edge are due to 2p → d-like final states.

XANES:

structural and electronic properties

ELECTRONIC AND STRUCTURAL PROPERTIES

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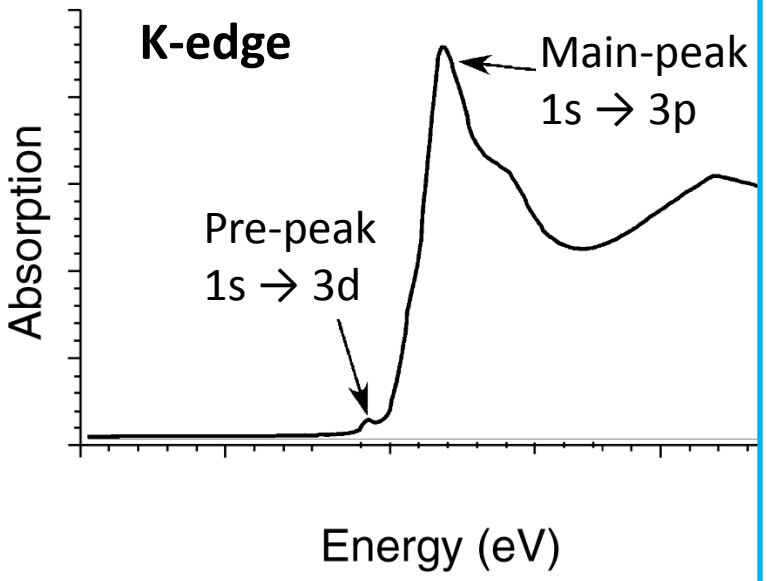
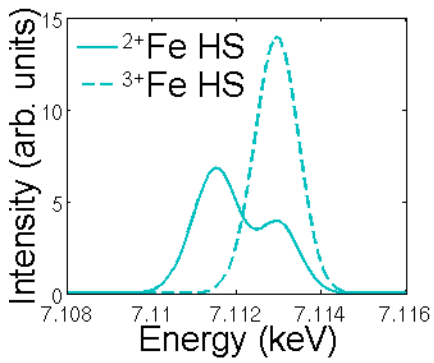


STRUCTURAL PROPERTIES

Theoretical simulation of the pre-edge region for tetrahedral high-spin $^{2+}$Fe (solid line) and $^{3+}$Fe (dashed line) complexes



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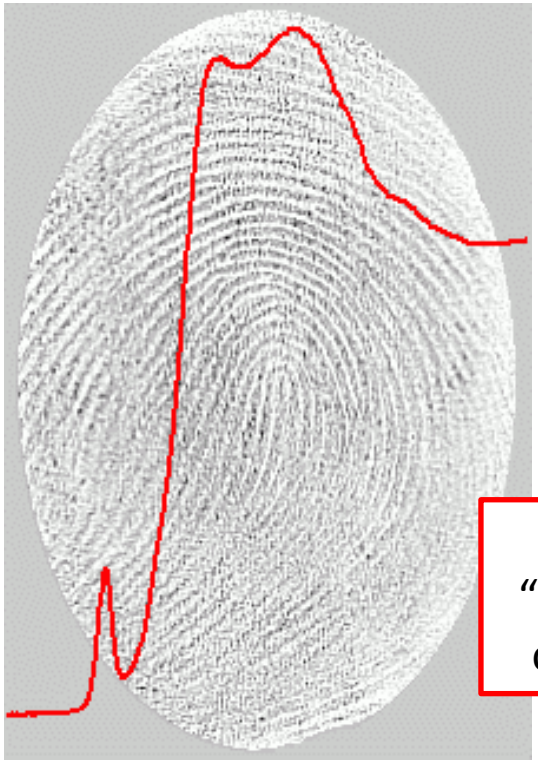


STRUCTURAL PROPERTIES

Angle dependence of multiple scattering

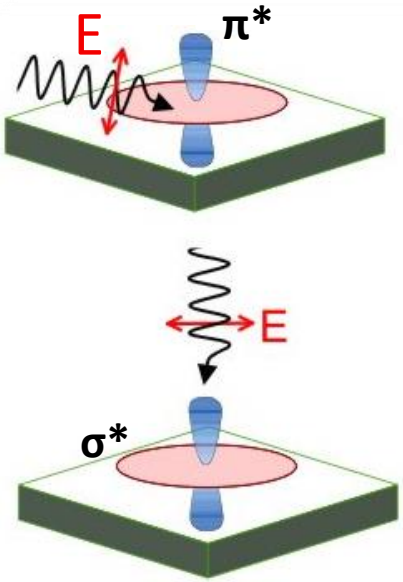
⇩

- **direct information about bond angles.**

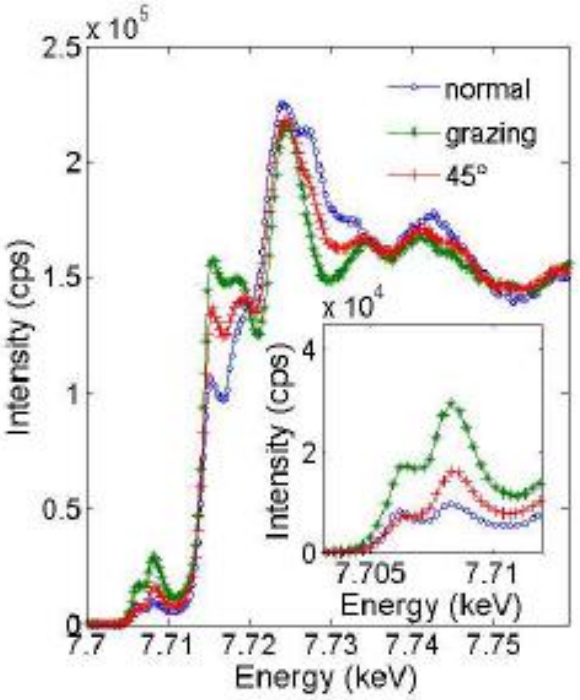
XANES often used as simple "fingerprint" to identify presence of a particular chemical species.

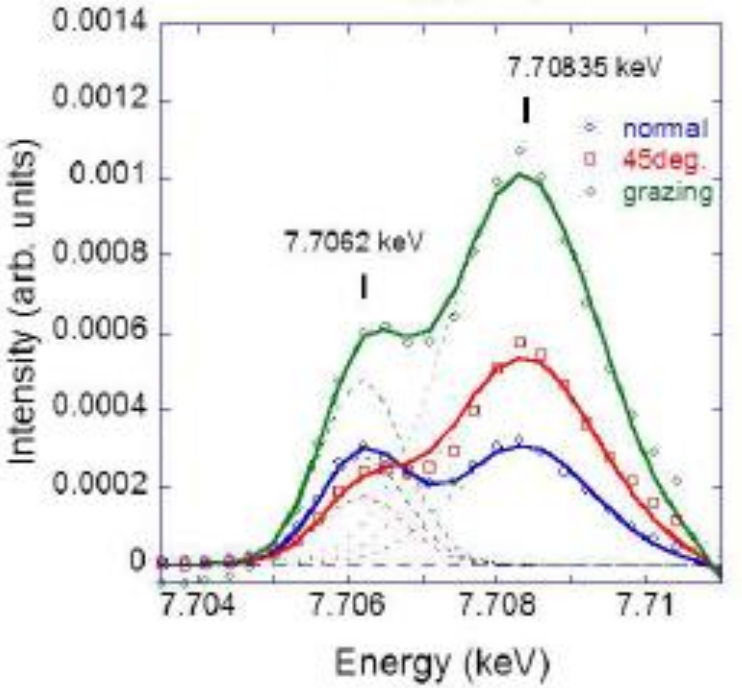
XANES:

Polarization analysis



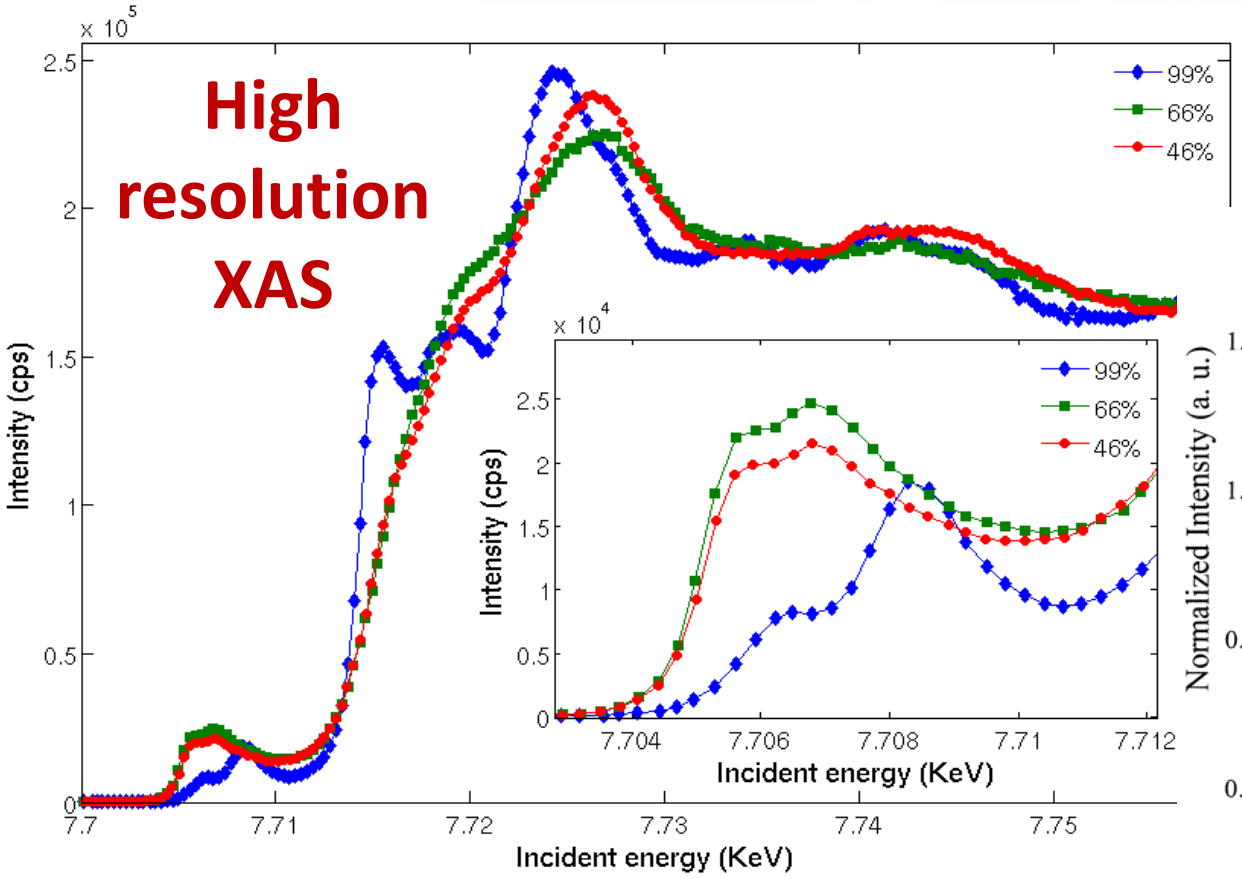
The chosen angle of incidence favors either excitations into the π (top) or the σ* (bottom) orbitals.*



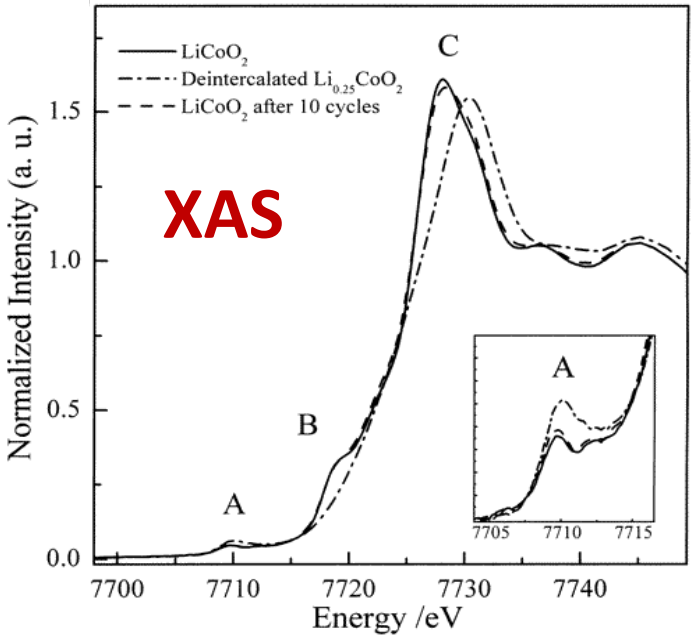


XANES:

High resolution x-ray absorption or Partial Fluorescence Yield (PFY)



By collecting an emission intensity line and scanning the incident energy across the edge.



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EXAFS

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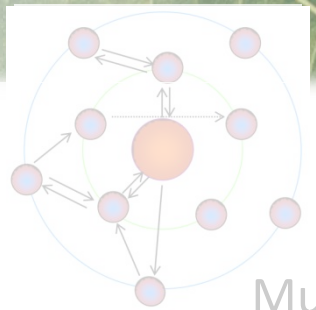

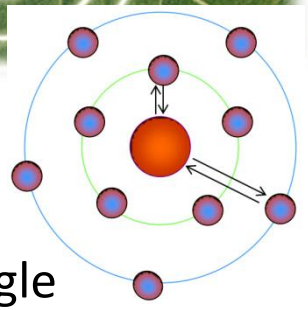

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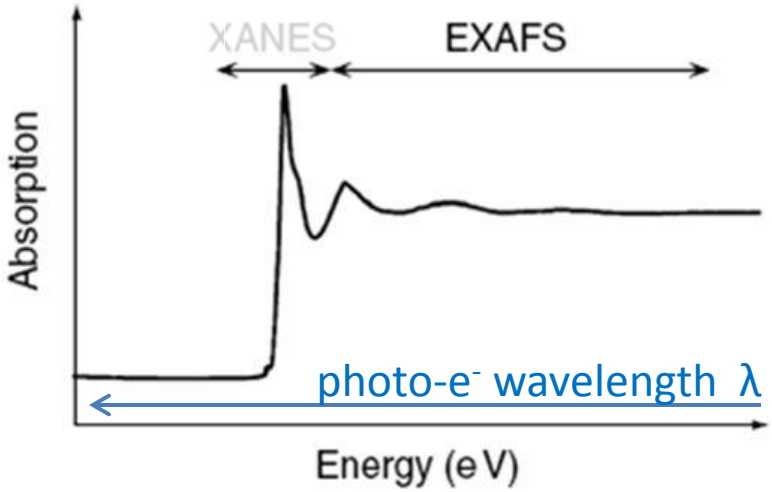
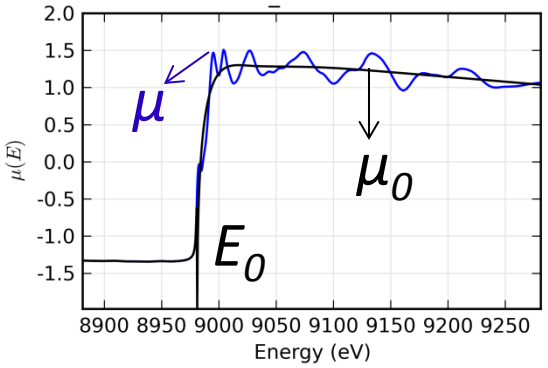
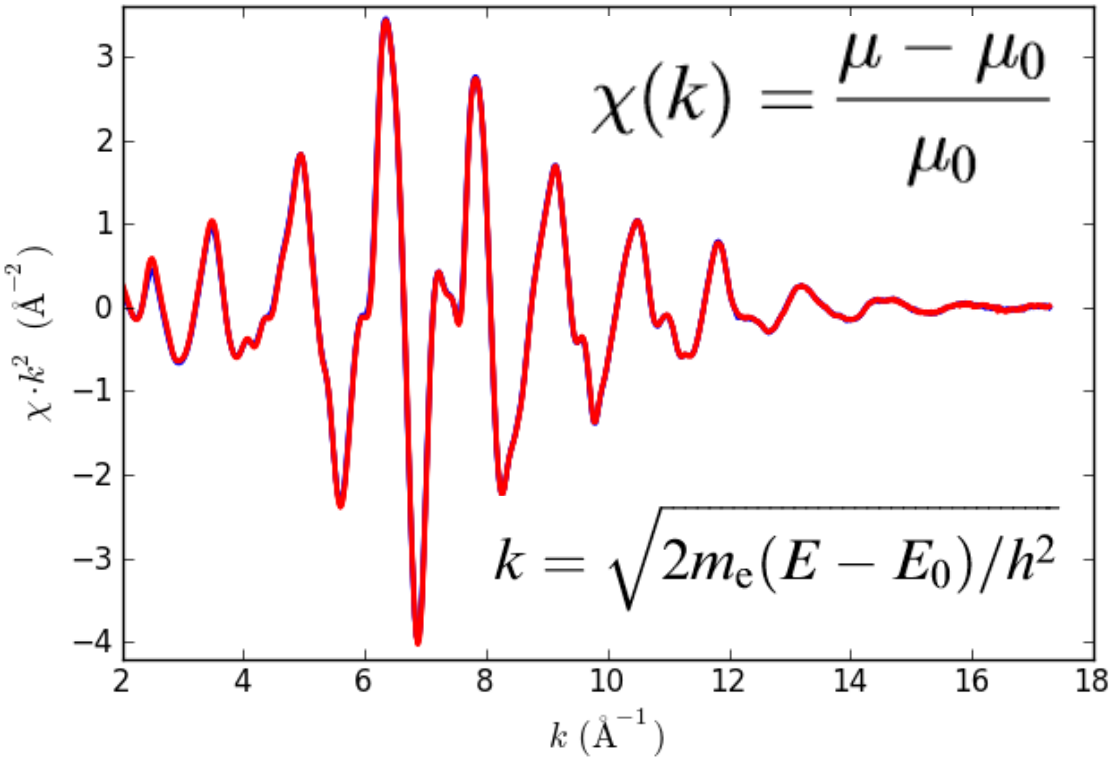


EXAFS:

The $\chi(k)$ function

The structural information are encoded in the amplitude, shape, phase, and frequency of the oscillations represented by χ.

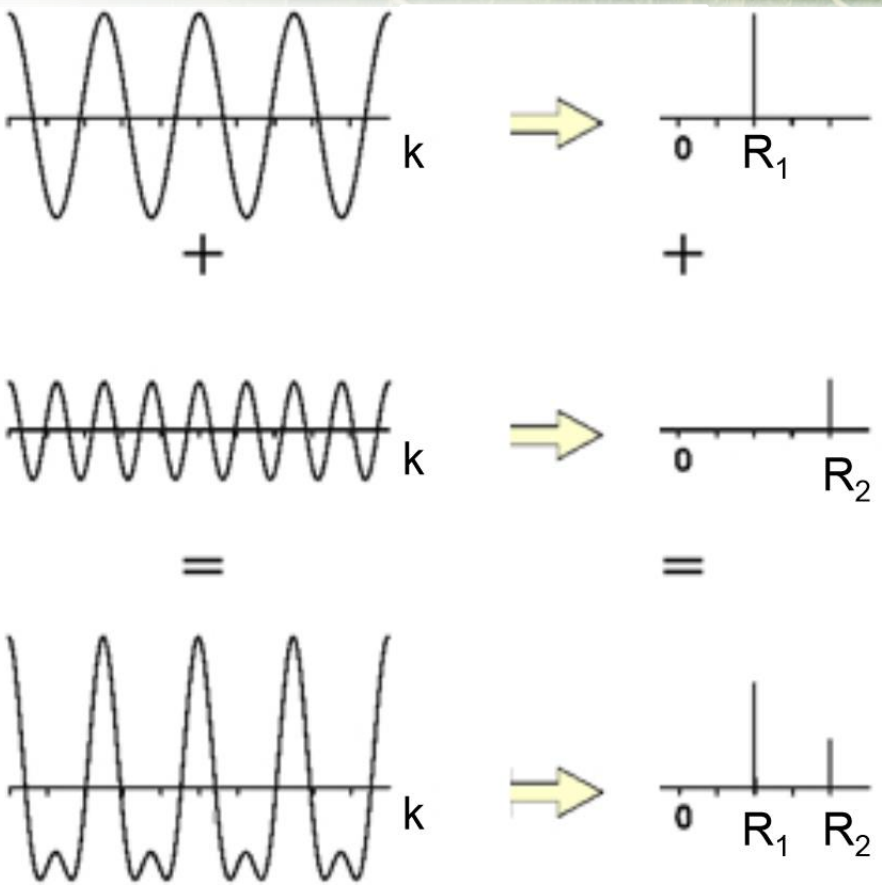




For a single absorber–scatterer pair the interferences will give rise to sinusoidal oscillations in μ if the energy is given in units proportional to the photoelectron wavevector, k, and the threshold energy, E_0, is the binding energy of the photoelectron.

EXAFS:

The Fourier transform of sin(2kR)

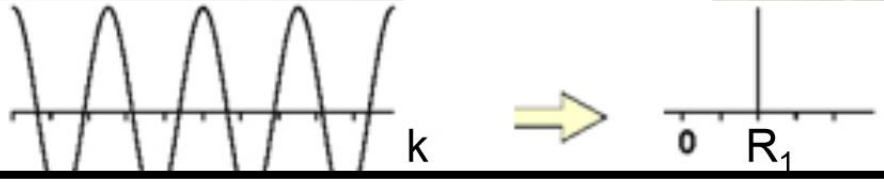


Interference gives an oscillating function of wavevector k

Fourier Transform Gives a peaked function of distance R

EXAFS:

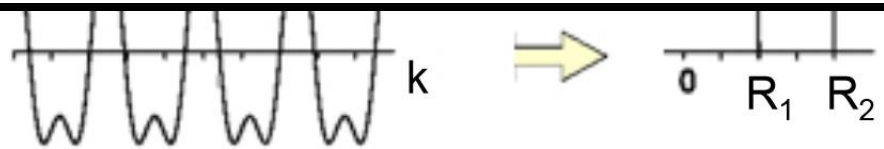
The Fourier transform



Interfere ... Transform
an os ... peaked
fun ... ion of
of wav ... nce R

A good Fourier Transform requires large value of k, hence large range of E

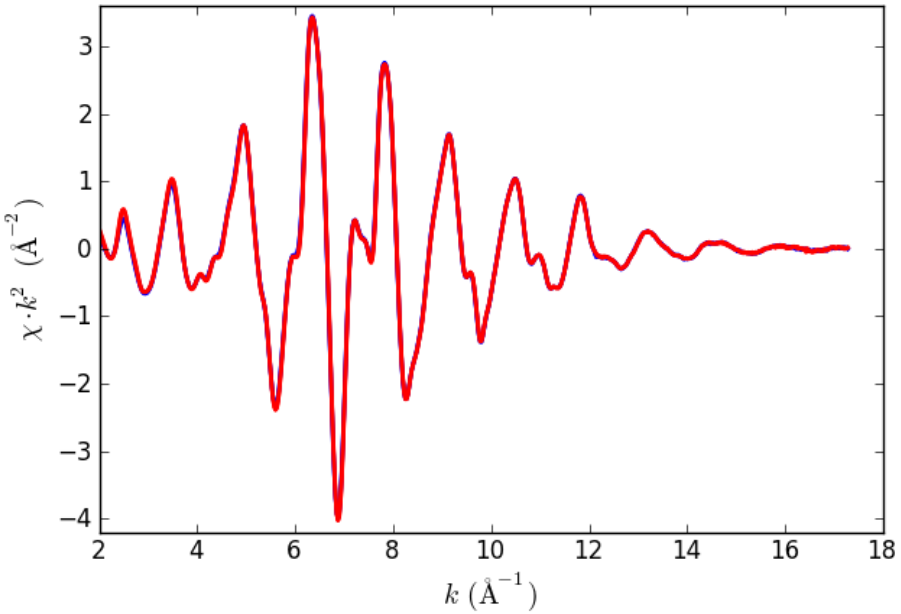
scan X-ray energy up to E_0+1000 eV
photo-electron k up to 16 Å^{-1}

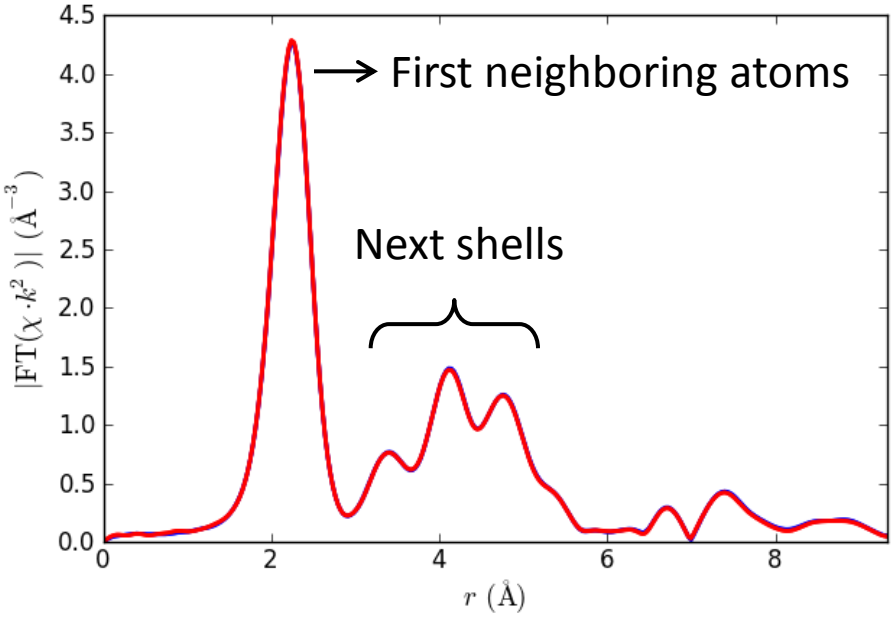


EXAFS:

The Fourier transform

Fourier transformation can be used to decompose a k-space signal into its different constituent frequencies. The Fourier transform (FT) of an EXAFS spectrum gives a pseudo-radial distribution function.

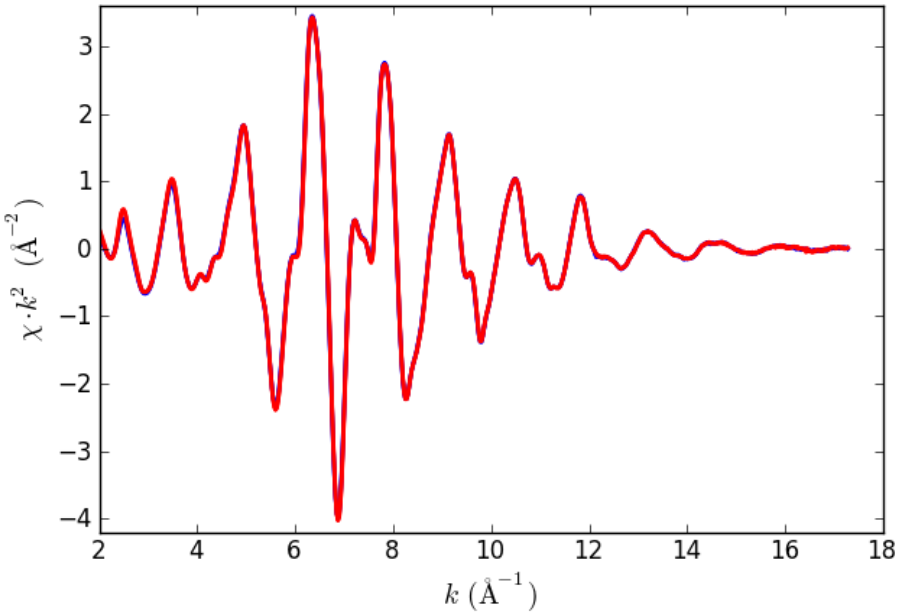


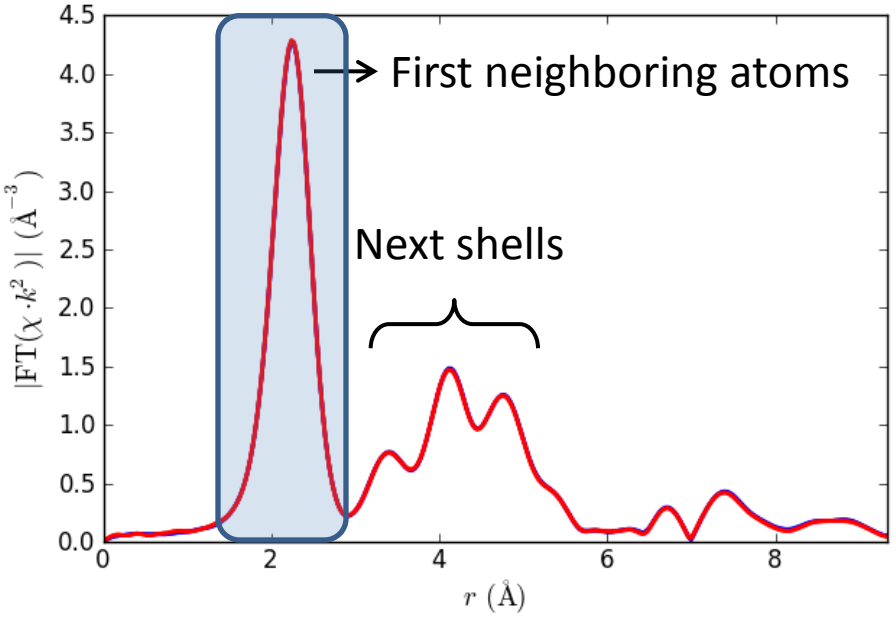


EXAFS:

Filtered back Fourier analysis

First shell parameters can be obtained by fitting directly the filtered back Fourier transform.





EXAFS:

Filtered back Fourier analysis

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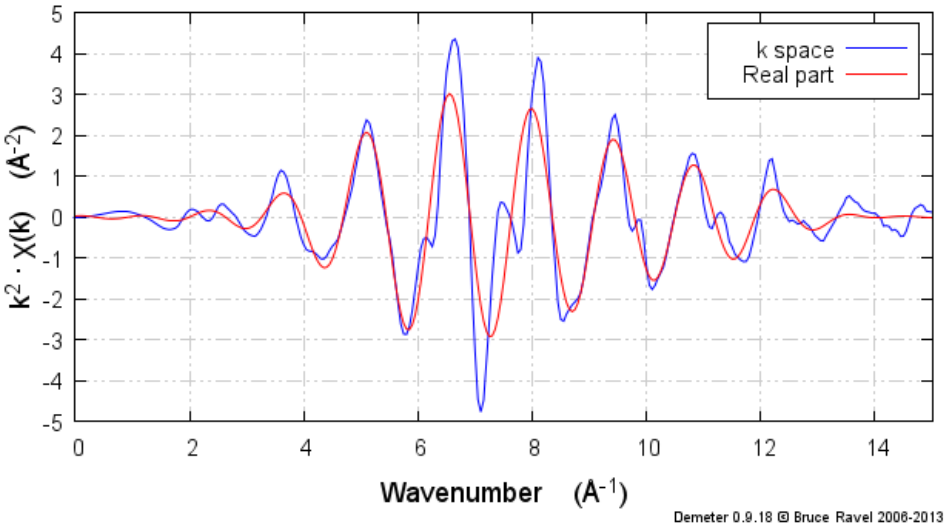
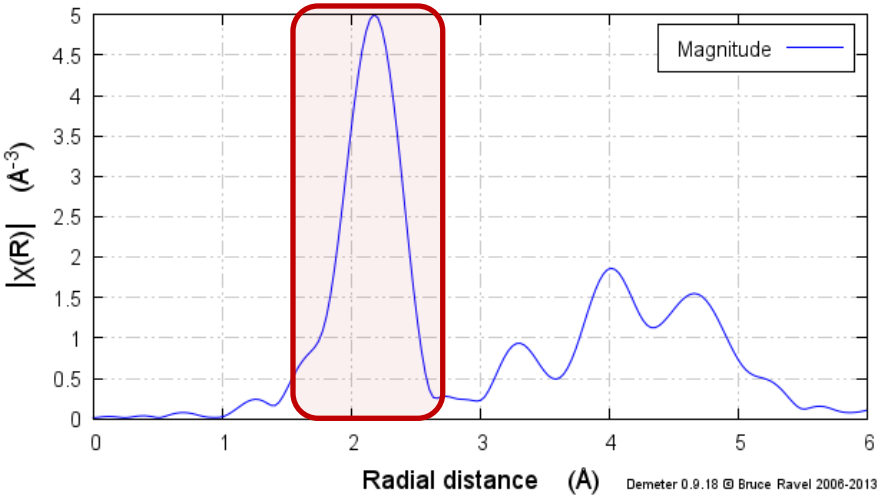


First neighboring atoms



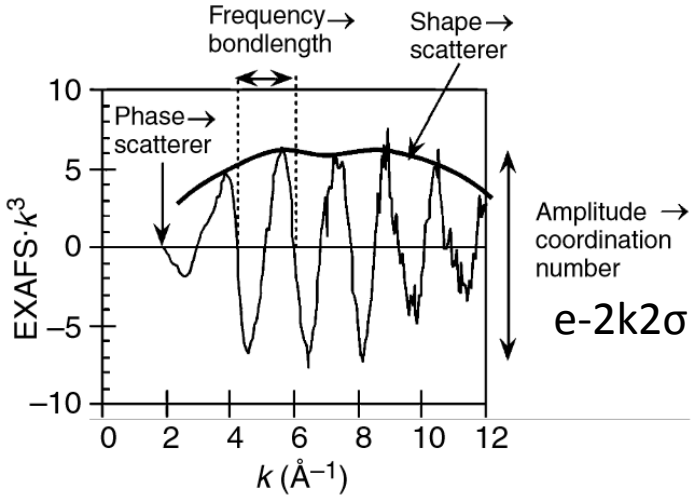
EXAFS:

The $\chi(k)$ function modeling

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} \qquad k = \sqrt{2m_e(E - E_0)/h^2}$$

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

The amplitude of the oscillations is proportional to the number of scattering atoms N_i, the frequency of the oscillations is inversely proportional to the absorber–scatterer distance R_i, and the shape of the oscillations is determined by the energy dependence of the photoelectron scattering, which depends on the identity of the scattering atom.



EXAFS:

The $\chi(k)$ function modeling

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} \qquad k = \sqrt{2m_e(E - E_0)/\hbar^2}$$

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

$N_i = 3\cos^2\vartheta_i$ ⟹ number of neighboring atoms at a distance R_i at an angle ϑ_i with respect to the x-ray beam polarization.

S_0^2 ⟹ passive electrons reduction factor (to allow for inelastic loss processes)

$f_i(k, R_i)$ ⟹ backscattering amplitude (energy dependence of the photoelectron scattering)

λ ⟹ photoelectron mean free path

δ_i ⟹ phase shift (that the photoelectron wave undergoes when passing through the potential of the absorbing and scattering atoms)

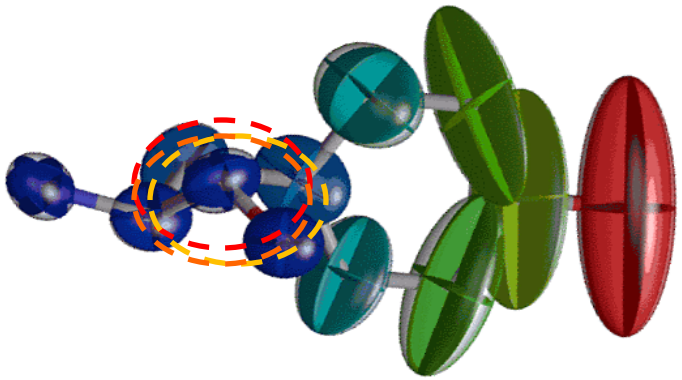
σ_i^2 ⟹ correlated Debye–Waller factor (root-mean-square deviation in absorber–scatterer distance)

EXAFS:

Static and dynamic disorder

Temperature dependence of the DW

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



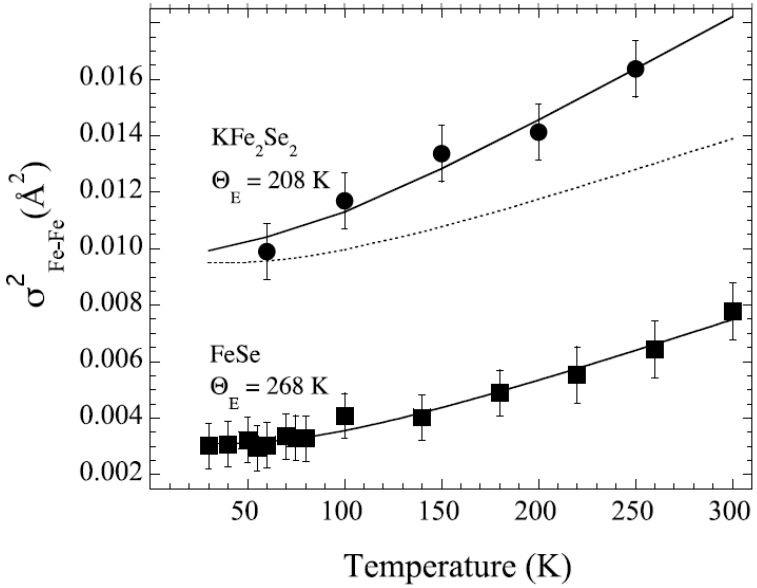
$$\sigma^2 = \sigma_0^2 + \sigma^2(T)$$

$$\sigma^2(T) = \frac{\hbar^2}{2\mu k_B \theta_E} \coth \frac{\theta_E}{2T}$$

EXAFS:

Static and dynamic disorder
Temperature dependence of the DW

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



$$\sigma^2 = \sigma_0^2 + \sigma^2(T)$$

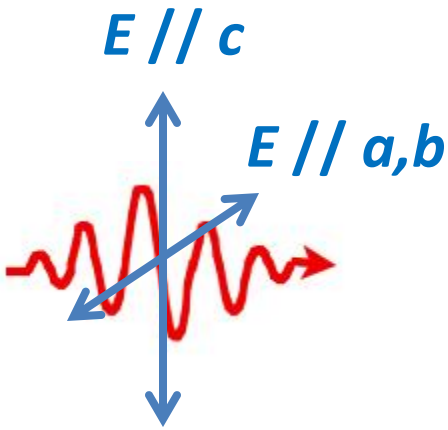
Einstein's formula:

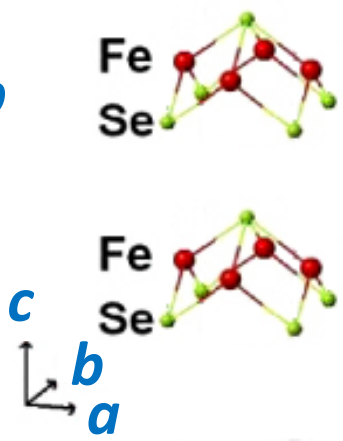
$$\sigma^2(T) = \frac{\hbar^2}{2\mu k_B \theta_E} \coth \frac{\theta_E}{2T}$$

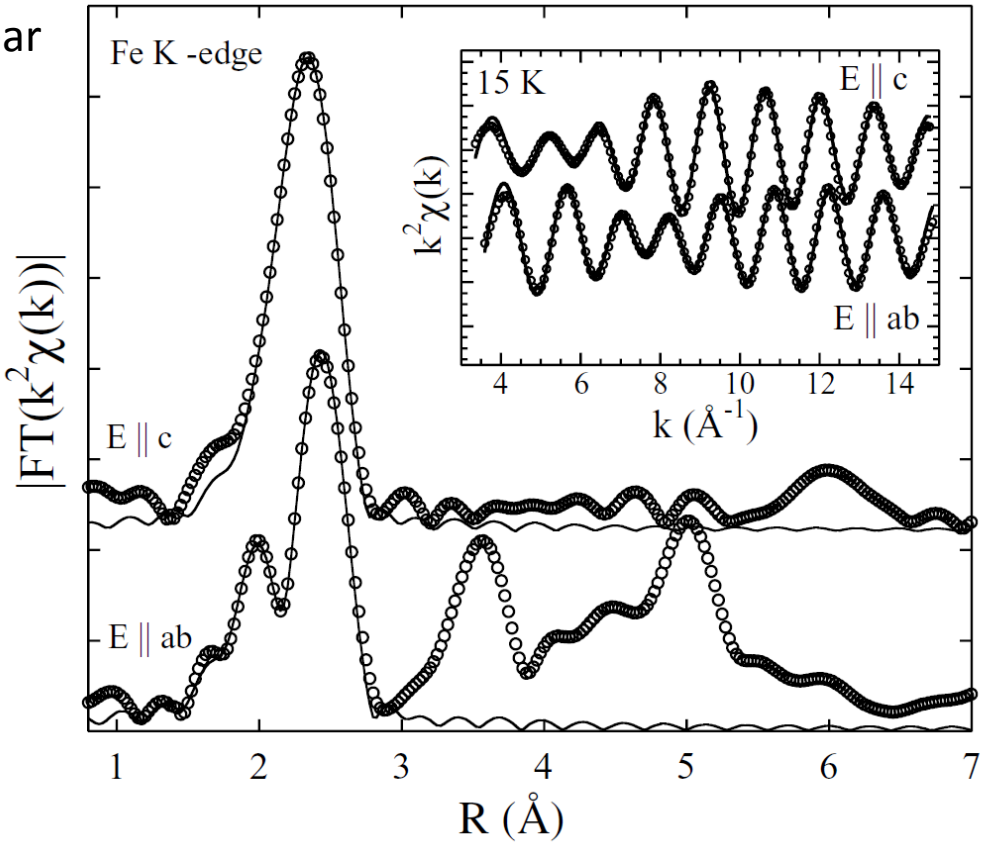
EXAFS:

Polarization analysis

The contributions of Fe-Se and Fe-Fe appear mixed in the E_{ab} polarization,
While only the Fe-Se contribute to the E_c main peak in the Fourier transform.







EXAFS & XANES:

Complementary information

Grup de Tècniques de Separació en Química UAB

XANES

- Oxidation state
- Unoccupied electronic states
- Spin state
- Local structure
- direct information about bond angles.

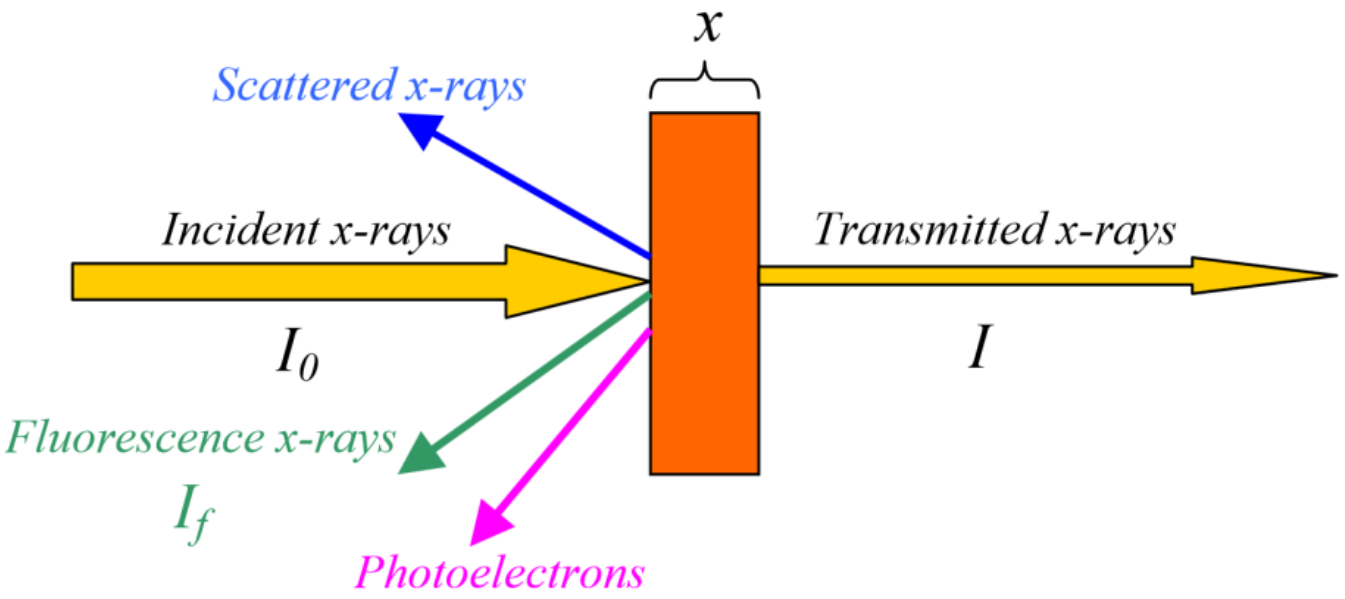
EXAFS

- Bond distances
- Coordination number
- Static and dynamic disorder

XANES & EXAFS:

Detection methods:
Transmission & fluorescence modes

Absorption of an ionizing X-ray results in photoelectron ejection, leaving behind a highly excited core-hole state. This can relax by a variety of mechanisms, with the two most important being emission of an Auger electron and X-ray fluorescence.



XANES & EXAFS:

Detection methods:
Transmission & fluorescence modes

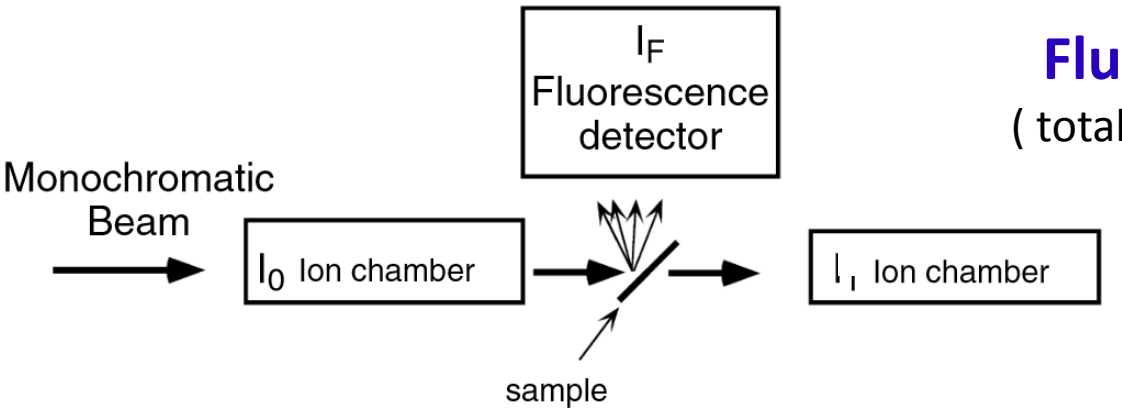
Providing the sample is dilute or thin (total absorbance <<1), the intensity of the fluorescence X-rays is proportional to the X-ray absorption cross-section.

In order to have good sensitivity, the fluorescence detector needs some kind of energy resolution to distinguish between the signal and background X-rays.

Transmission: $\mu x = \ln (I_0 / I_1)$

Fluorescence: $\mu \propto (I_F / I_0)$

(total absorbance << 1 $e^{-\mu x} \rightarrow 1-\mu x$)



XANES & EXAFS:

Fluorescence method and the self absorption effect

FLUORESCENCE MODE:

$\mu \propto (I_F / I_0)$ is only true in the limit of very thin or very dilute samples

What is happening for thick or concentrated samples?

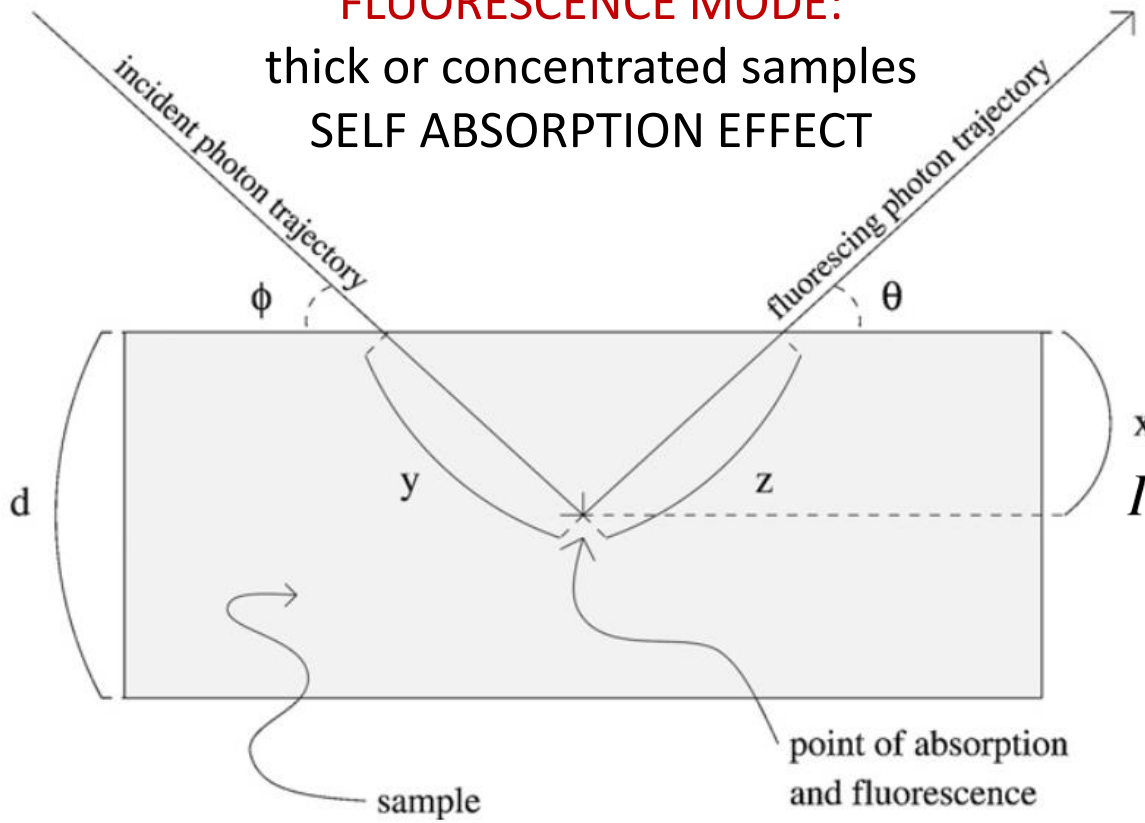
XANES & EXAFS:

Fluorescence method and the self absorption effect

FLUORESCENCE MODE:

thick or concentrated samples

SELF ABSORPTION EFFECT



The depth into which the incident beam can penetrate changes as fine structure of μ(E) changes. As the oscillatory part wiggles up, the penetration depth diminishes. As it wiggles down, the depth increases. This serves to attenuate the oscillatory structure.

$$I_f = I_0 e^{-\mu(E)y} e^{-\mu(E_f)z} \epsilon_a(E) \mu_a(E)$$

E_f = energy of the fluorescing photon

ε_a = fluorescence efficiency per unit solid angle

μ_a = absorption due to the given core excitation of the absorbing atom

XANES & EXAFS:

Fluorescence method: the self absorption effect

FLUORESCENCE MODE:

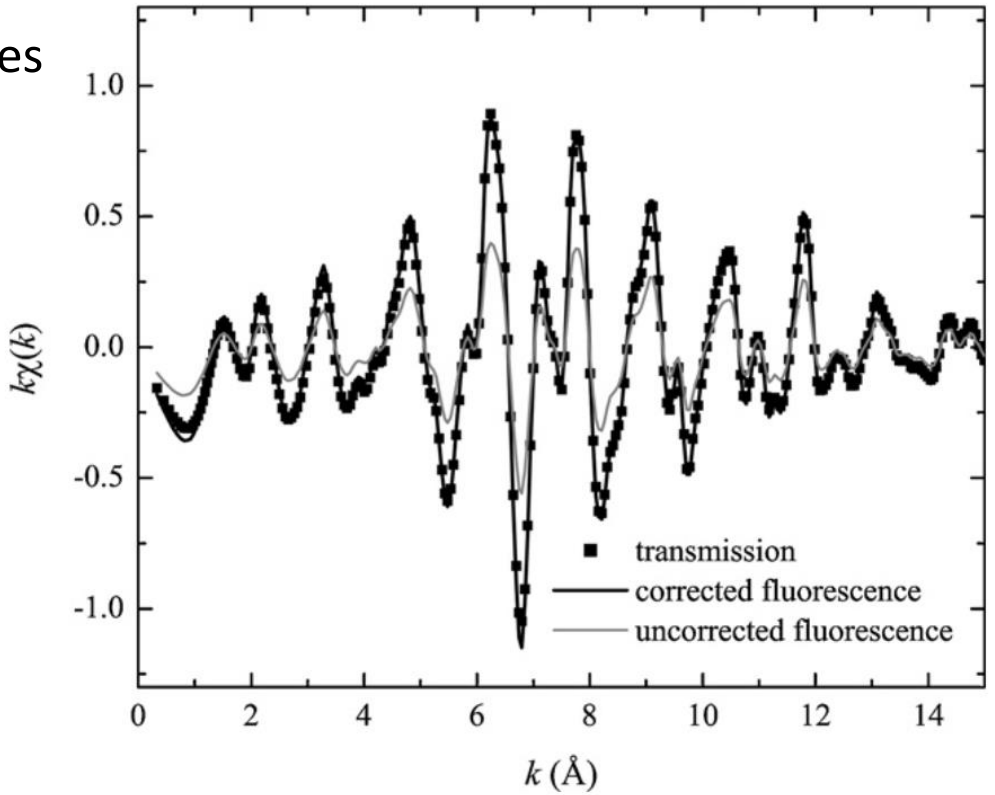
thick or concentrated samples

SELF ABSORPTION EFFECT

$$\chi = \frac{\chi_{exp}}{1 - \frac{\bar{\mu}}{\alpha}\chi_{exp} - \frac{\bar{\mu}_a}{\alpha}}$$

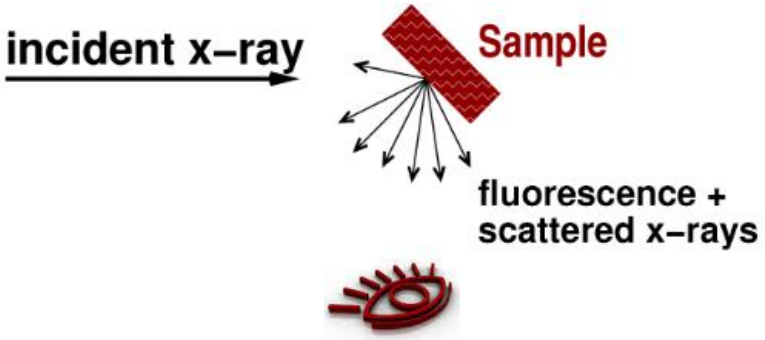
$$\alpha \equiv \bar{\mu}_T + g\mu_f$$

$$g \equiv \sin\phi / \sin\theta$$

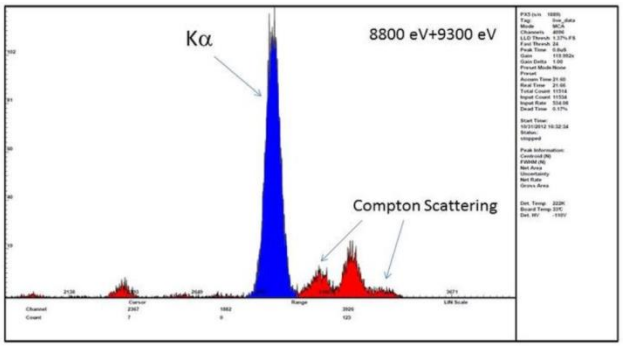


XANES & EXAFS:

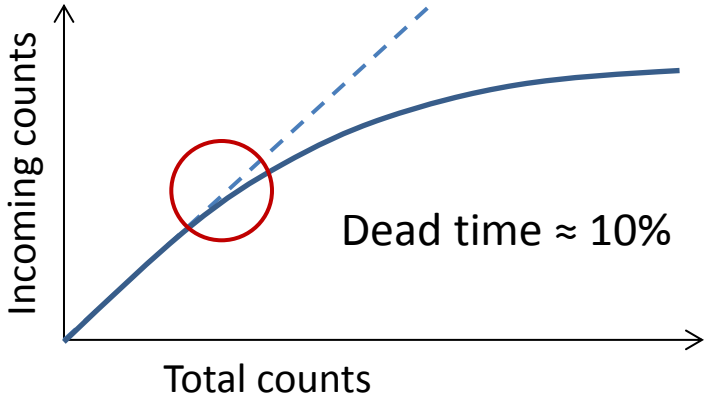
Fluorescence method: detector dead time



Energy dispersive detector

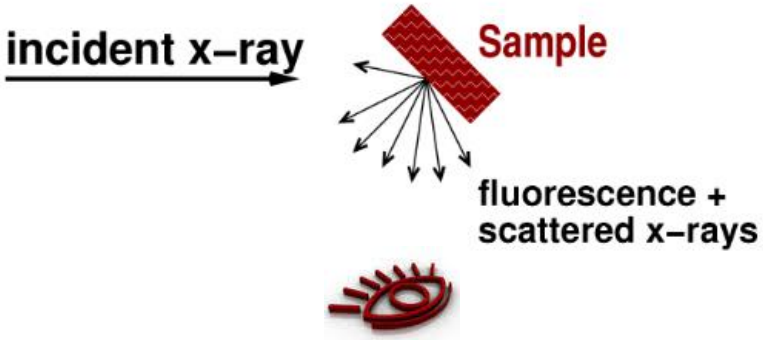


Dead time: the electronic energy discrimination takes a finite amount of time, which limits the total amount of signal that can be processed. When the count rates are exceeded, the detector is effectively unable to count all the fluorescence for some fraction of the time. The limit of total intensity incident on these detectors can limit the quality of the measured XAFS.



XANES & EXAFS:

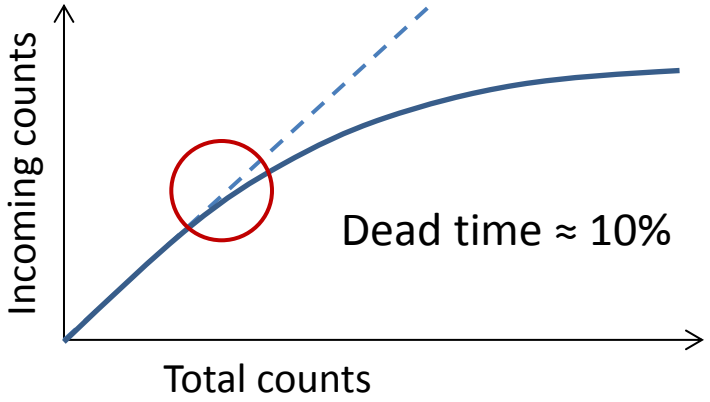
Fluorescence method: detector dead time



Energy dispersive detector

(E discrimination can potentially allow to suppress the scatter peak and other fluorescence lines, collecting only the intensity of the fluorescence lines of interest.)

Dead time: the electronic energy discrimination takes a finite amount of time, which limits the total amount of signal that can be processed. When the count rates are exceeded, the detector is effectively unable to count all the fluorescence for some fraction of the time. The limit of total intensity incident on these detectors can limit the quality of the measured XAFS.

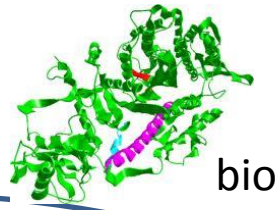


Research fields:

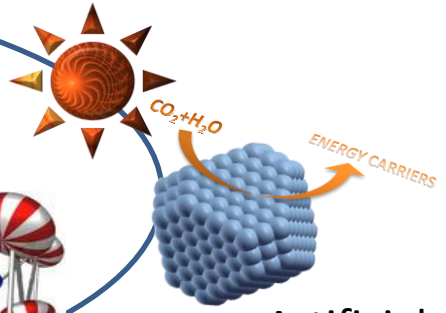
To give an idea…

Cultural Heritages

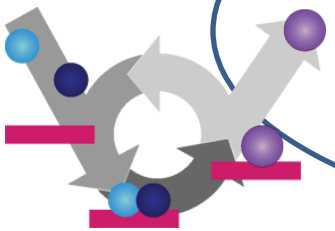
Energy storage materials



biophysics

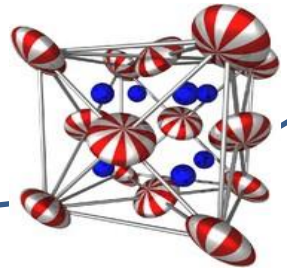


Artificial Photosynthesis



Catalysis

Environmental Science



Solid State Physics

Why so many?

To give an idea…

XAS can be applied to any kind of materials:
Crystals, glass, liquids, etc…

SUMMARY

XAS (XANES/EXAFS)

element sensitive local probe that can be applied to any kind of material

COMPLEMENTARY INFORMATION

XANES

- **Oxidation state**
- **Unoccupied electronic states**
- **Spin state**
- **Local structure**
- **direct information about bond angles.**

EXAFS

- **Bond distances**
- **Coordination number**
- **Static and dynamic disorder**

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