EXAFS

Dr. Darshana Mehta

School of Studies in Chemistry and Biochemistry, Vikram University, Ujjain – 456 010, Madhya Pradesh, India

EXAFS

| Acronym	Technique	Application and description of technique
AES	Auger electron spectroscopy	Study of surface composition
EXAFS	Extended X-ray absorption fine structure	Estimation of internuclear distances around a central atom
FTIR	Fourier transform infrared spectroscopy	Study of adsorbed species
HREELS	High-resolution electron energy loss spectroscopy	Study of adsorbed species
LEED	Low-energy electron diffraction	Study of structural features of the surface and of adsorbed species
SIMS	Secondary ion mass spectrometry	Study of surface composition
XPS (ESCA)	X-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis)	Study of surface composition and oxidation states of surface atoms
	XRD X-ray diffraction	Investigation of phases and particle sizes
XANES	X-ray absorption near edge spectroscopy	Study of oxidation states of surface atoms

EXAFS

❖ X-ray absorption spectra can be used to determine the oxidation state of an element in a compound and to investigate its local environment.

❖ The intense X-ray radiation from synchrotron sources may be used to eject electrons from the cores of elements present in a compound.

❖ X-ray absorption spectra (XAS) are obtained by varying the photon energy across a range of energies at which electrons in the various atoms present in a compound can be excited and ionized (typically between 0.1 and 100 keV).

❖ The characteristic absorption energies correspond to the binding energies of different inner-shell electrons of the various elements present. Thus the frequency of an X-ray beam may be swept across an absorption edge of a selected element and information on the oxidation state and neighbourhood of this chosen chemical element obtained.

EXAFS

Absorption edge is the energy at which there is a sharp rise (discontinuity) in the (linear) absorption coefficient of X-rays by an element, which occurs when the energy of the photon corresponds to the energy of a shell of the atom (K, L_I , L_{II}, L_{III}, etc. corresponding to the creation of electron holes in the 1s, 2s, $2p^{1/2}$, $2p^{3/2}$ etc. atomic subshells). The absorption threshold is associated with this transition and is characterized by the corresponding energy (E_o).
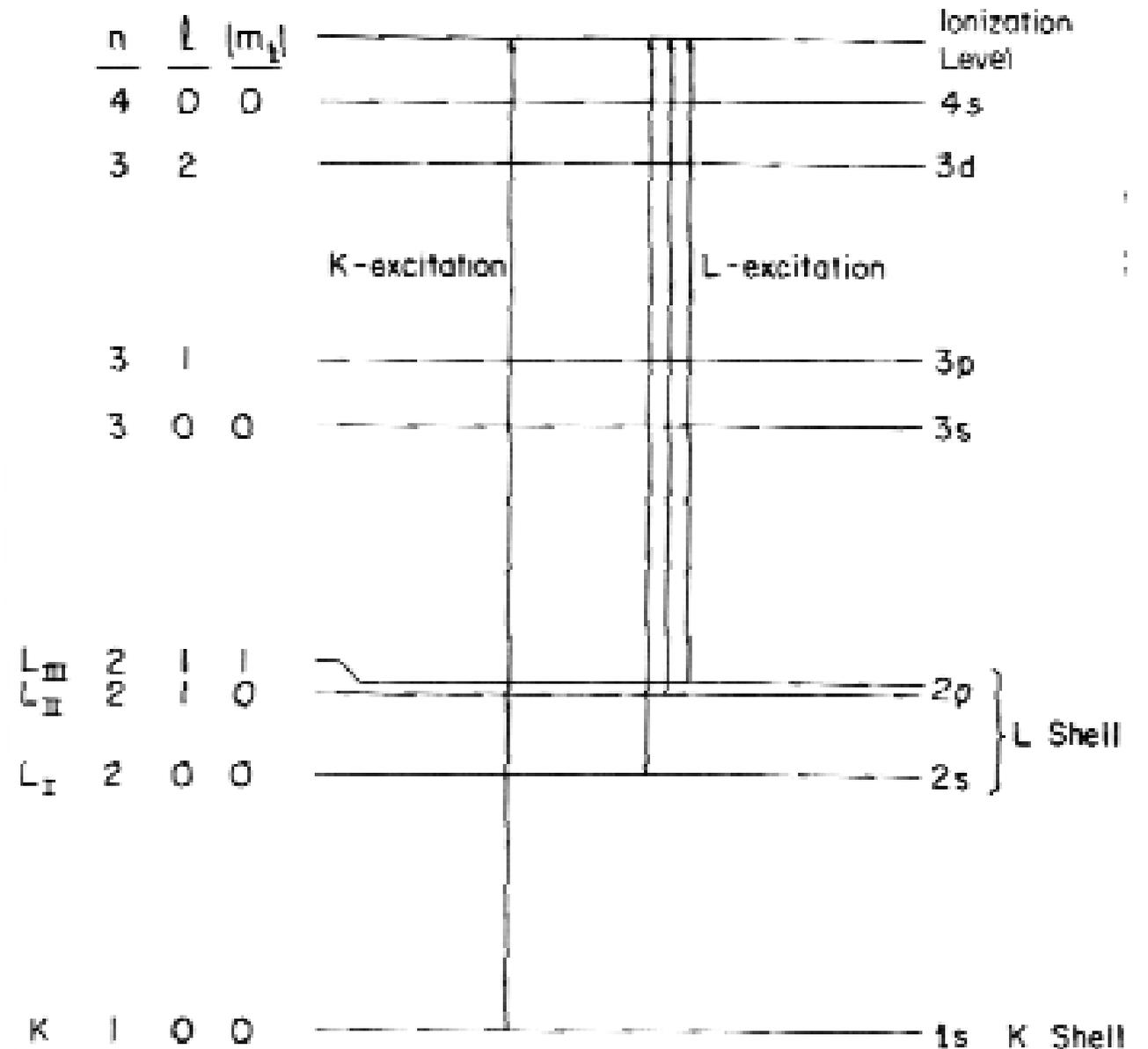
EXAFS

Each region of the spectrum can provide different useful information on the chemical environment of the element under investigation:

1. **Just prior to the absorption edge is the 'pre-edge' where core electrons are excited to higher empty orbitals but not ejected. This 'pre-edge structure' can provide information on the energies of excited electronic states and also on the local symmetry of the atom.**

2. In the edge region, where the photon energy, E is between Ei and Ei + 10 eV, where Ei is the ionization energy, the 'X-ray absorption near-edge structure' (XANES) is observed. Information that can be extracted from the XANES region includes oxidation state and the coordination environment, including any subtle geometrical distortions. The near-edge structure can also be used as a 'fingerprint', as it is characteristic of a specific environment and valence state. The presence and quantity of a compound in a mixture may be determined from analysis of this region of the spectrum.

EXAFS

3. The 'extended X-ray absorption fine structure' (EXAFS) region lies at energies greater than $E_i + 50$ eV. The photoelectrons ejected from a particular atom by absorption of X-ray photons with energies in this region may be backscattered by any adjacent atoms.

This effect can result in an interference pattern that is detected as periodic variations in intensity at energies just above the absorption edge.

In EXAFS these variations are analysed to reveal the nature (in terms of their electron density) and number of nearby atoms and the distance between the absorbing atom and the scattering atom.

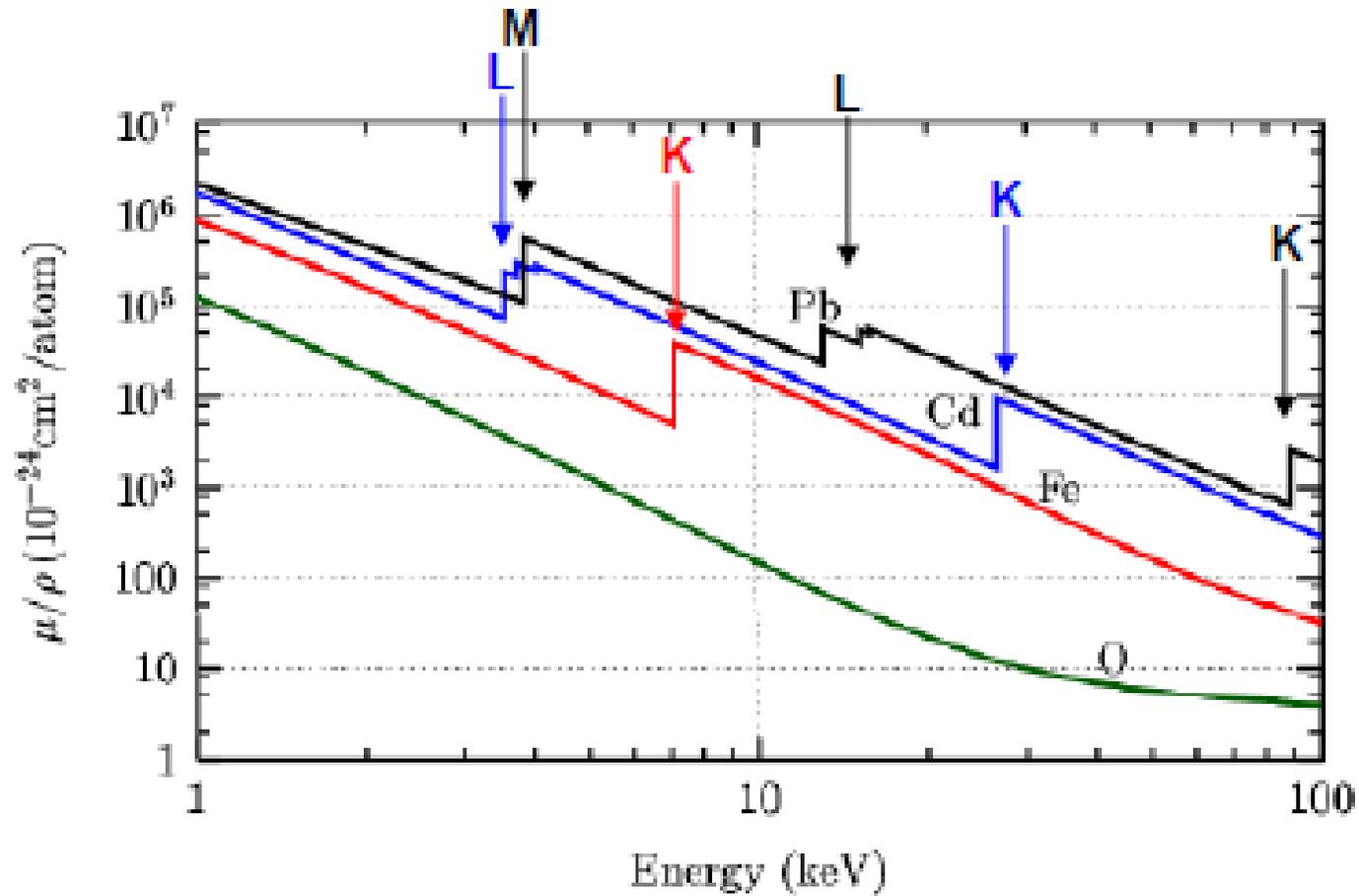An advantage of this method is that it can provide bond lengths in amorphous samples and for species in solutions.

EXAFS

Fine structure

Isolated atom

Atom with neighbors
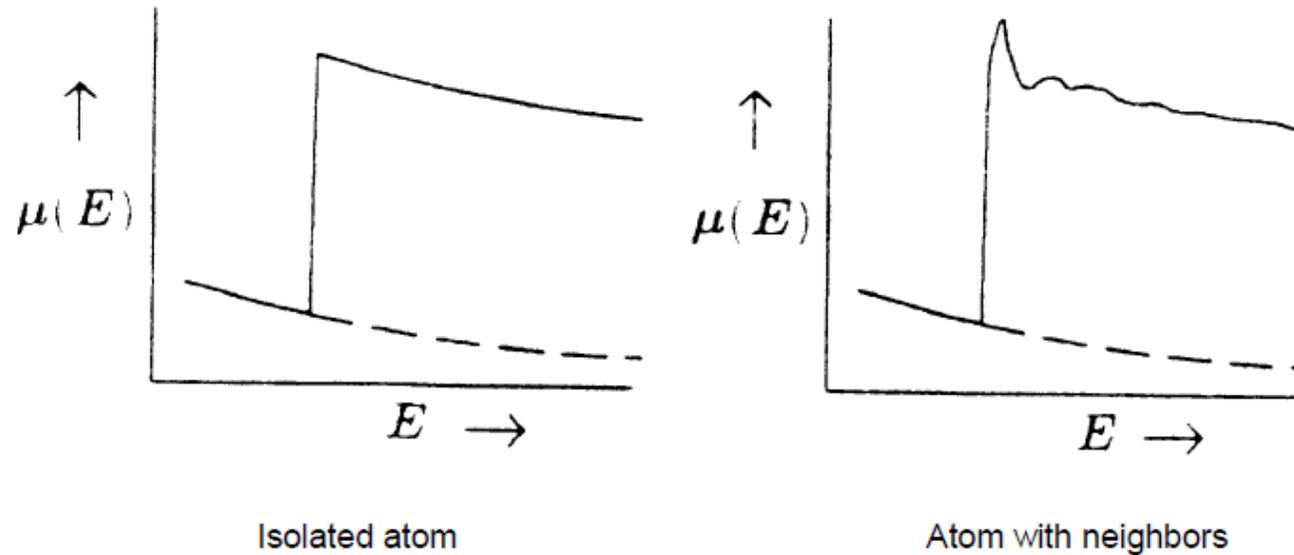
EXAFS contains information about the local environment of the absorber

EXAFS

sharp absorption edges in μ
↓
characteristic core level energies

EXAFS

Elements for EXAFS
(hard X-rays)

EXAFS

❖ X-ray photons from the incoming beam eject core electron beyond the ionization threshold

❖ The atom is in an excited state, i.e. there is a core hole. Electron ejected is called a photo-electron

❖ The x-ray intensity is measured before and after the sample and the X-ray absorption coefficient μ is calculated


$$I = I_0 e^{-\mu t}$$
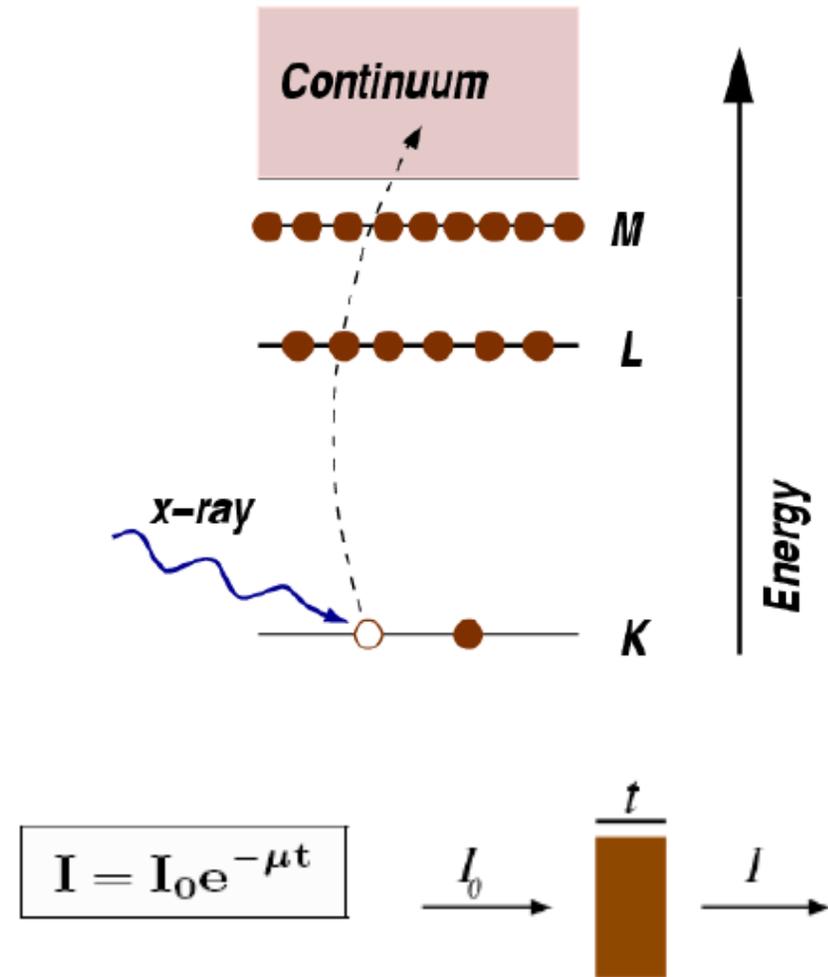
EXAFS

The X-ray absorption coefficient for an atom, indicated as µx, is directly proportional to the probability of absorption of one photon and is a monotone decreasing function of energy. It shows several discontinuities known as absorption edges:

they occur when the energy of the incident photons equals the binding energy of one electron of the atom and are classified with capital letters (K, L, M...) according to the principal quantum number of the electron in the ground state (n = 1, 2, 3...).

It is possible to recognize four edges due to K and L (LI, LII and LIII) electrons in the diagram of the absorption coefficient of atomic rhodium. The edge energy is characteristic of each atom. In the case of an isolated atom (monatomic gas), the absorption coefficient decreases monotonously with energy between two subsequent edges. In all other situations, the spectrum also shows oscillations that start at the edge and finish a thousand eV above.

EXAFS
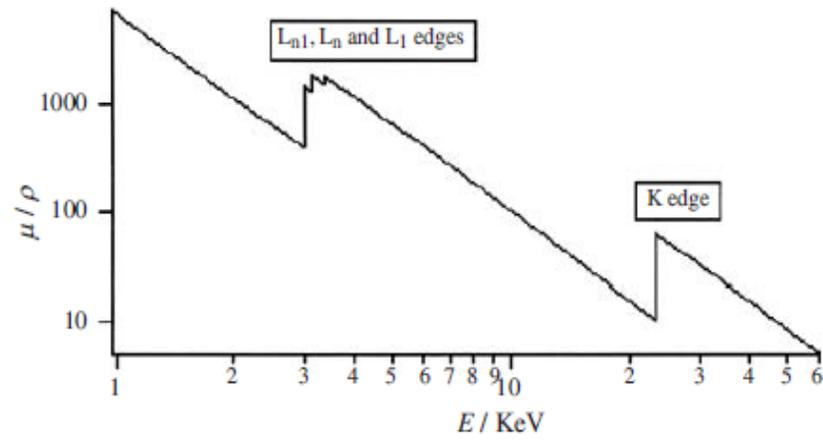
Absorption spectrum for Rh atoms.
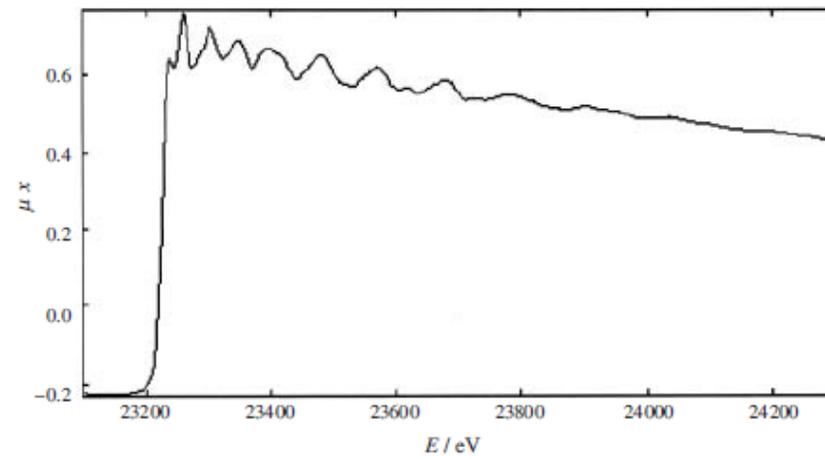
Absorption spectrum for metallic Rh (K edge) showing EXAFS signal.

EXAFS

An incident photon is able to extract a core electron if its energy is equal to or greater than the edge energy. The ejected electron is called photoelectron and it has the characteristics of both a particle and a wave. Its kinetic energy is given by:
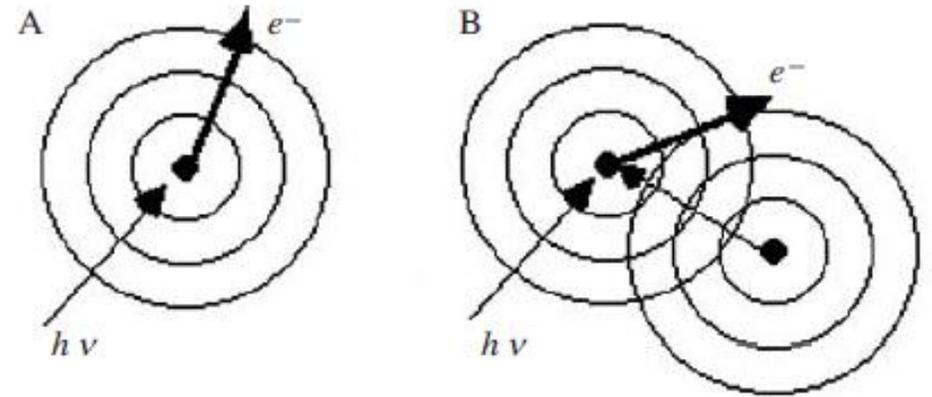
$$E = E_x - E_0$$

where E_x is the energy of the X-ray photon and E_o the energy of the edge. Its wave vector modulus is given by:

$$|k| = \frac{2\pi}{\lambda} = \sqrt{\frac{8\pi^2 m}{h^2}(E_x - E_0)} = \sqrt{0.2624 \cdot E}$$
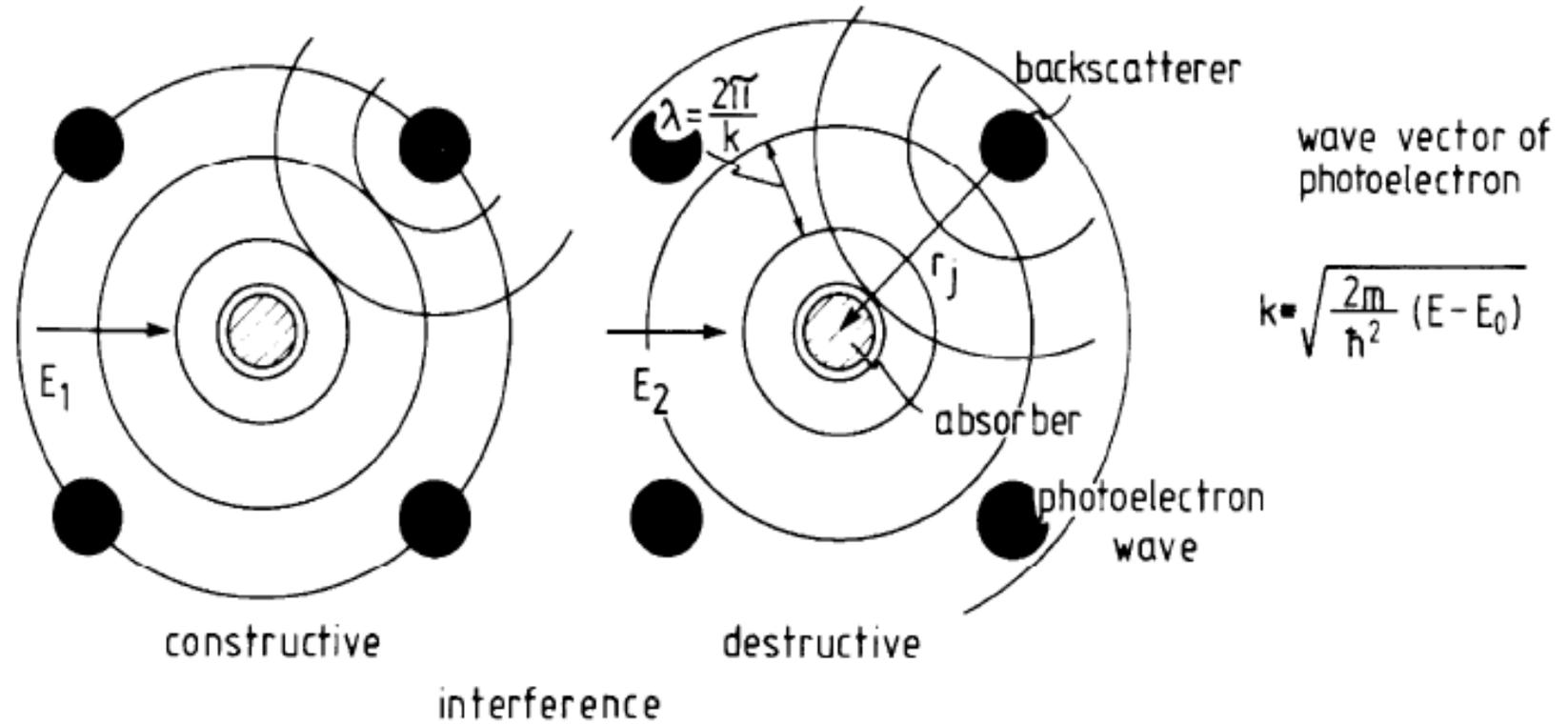
EXAFS

If the absorbing atom is isolated in space, the photoelectron propagates as an unperturbed isotropic wave (Figure A), but in most cases there are many other at oms around the absorber. These become scattering centers of the photoelectron wave (Figure B). The final state of the photoelectron can be described by the sum of the original and scattered waves. This leads to an interference phenomenon that modifies the interaction probability between core electrons and incident photons. Constructive interference increases while destructive interference decreases the absorption coefficient of the atom. This interference phenomenon, for a given energy of the photoelectron, depends on the distance between emitting and scattering atoms, and their atomic numbers.

Scattering processes

EXAFS

$$\lambda = \frac{2\pi}{k}$$

backscatterer

r_j

absorber

photoelectron wave

constructive

destructive

interference

wave vector of photoelectron

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

E_1

E_2

EXAFS

EXAFS analytical expression like the one suggested by
E. A. Stern in 1974:

$$\chi(k) = \frac{1}{k} S_0^2 \sum \frac{N_i}{R_i^2} \cdot \exp(-2\sigma^2 k^2) \cdot \exp\left(\frac{-2R_i}{\lambda(k)}\right) \cdot$$

$$\left|f_i(k)\right| \cdot \sin[2kR + \Phi_i(k)]$$

This Equation is able to describe only single scattering processes. However, it has been demonstrated that considering also multiple scattering processes leads to a very similar analytical expression. Introducing multiple scattering allows one to obtain also stereochemical information about the local structure

where:

– k is the wave vector modulus for the photoelectron;

– N_i is the number of atoms of type i at distance R_i from the absorber;

– the exponential term $\exp(-2\sigma^2 k^2)$ takes account of fluctuations of distances due to a structural and/or thermal disorder, under the assumption of small displacements and Gaussian distributions of distances;

– the exponential term $\exp\left(\frac{-2R_i}{\lambda(k)}\right)$ takes account of finite elastic mean free paths of photoelectrons $\lambda(k)$ (between 5 and 10 Å for photoelectron energies from 30 to 1000 eV);

– S_0^2 is an average amplitude reduction factor; its value is the percent weight of the main excitation channel with respect to all possible excitation channels; its value is usually 0.8–0.9;

– $|f_i(k)|$ is a scattering amplitude function characteristic of the i-th atom;

– $\Phi_i(k)$ is a phase function that takes account of the varying potential field along which the photoelectron moves; it can be expressed as the sum of two potential terms, $\Phi_i(k) = 2\,\delta(k) + \varphi_i(k)$, the former given by the absorber, the latter given by the scatterer.
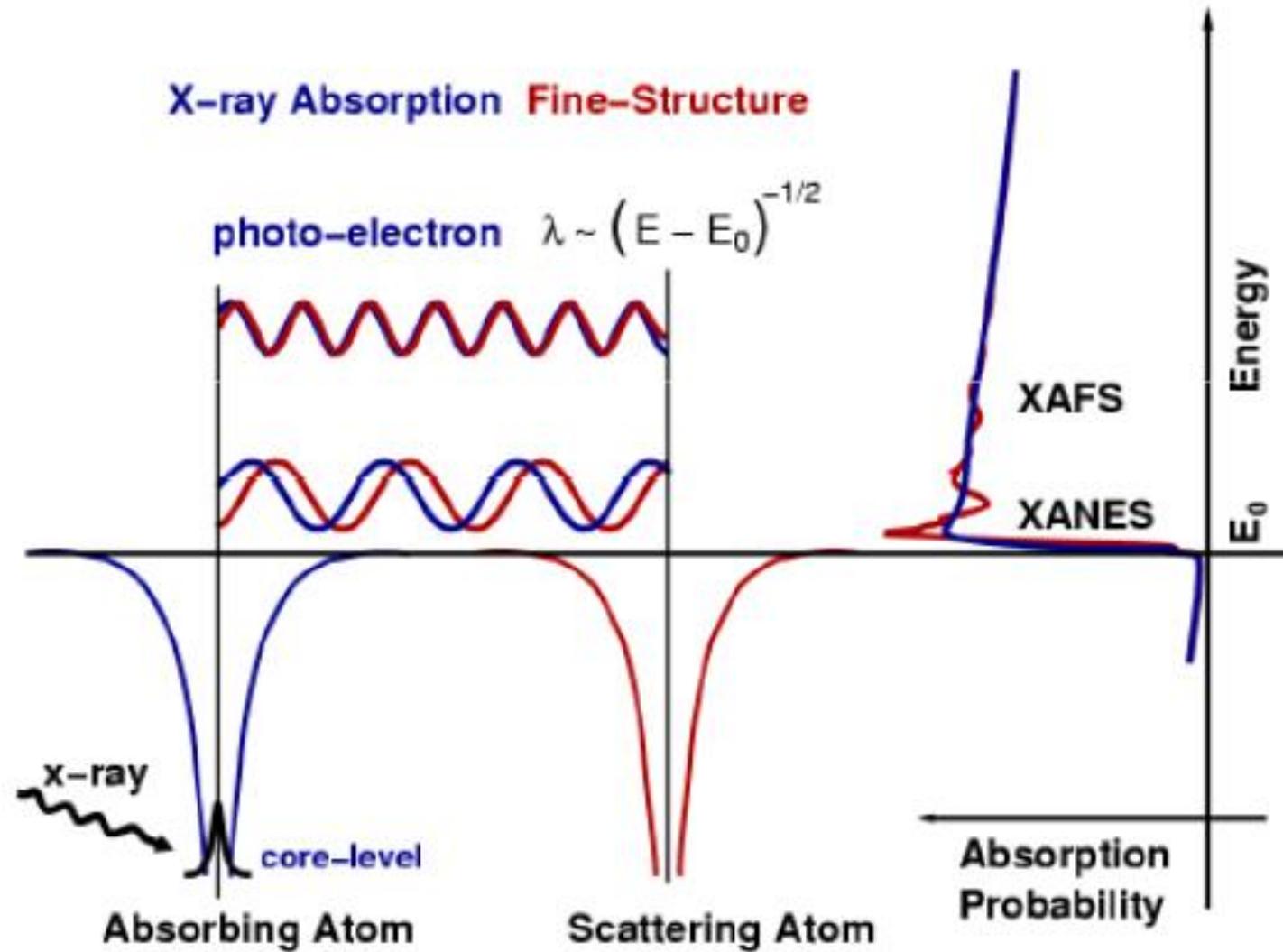
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EXAFS spectroscopy provides structural information about a sample by way of the analysis of its X-ray absorption spectrum. It allows determining the chemical environment of a single element in terms of

❖ The number and type of its neighbor's

❖ Inter-atomic distances

❖ Structural disorders.

This determination is confined to a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5 and 10 Å radius from the element.

EXAFS

EXAFS

EXAFS is

❖ independent of long range order

❖ complementary to diffraction

❖ gases, liquids, amorphous and crystalline solids

❖ highly dispersed phases (catalysis!)

❖ in general a bulk technique, but has a detection limit in the ppm range

❖ Nanoparticles, diluted systems, promoters (catalysis!)

EXAFS

EXAFS is a technique selective for a particular element and sensible only for a short-range order, it is one of the most appropriate spectroscopies to be applied in the following cases:

❖ amorphous solids, e.g., ceramics

❖ liquids, e.g., solutions of ionic compounds or gels which cannot be studied by X-ray diffraction biomolecules, e.g., solutions of metalloproteins

❖ homogeneous and heterogeneous catalysts

EXAFS Summary

❖ EXAFS oscillations $\chi(k)$ are due to interference of the photoelectron wave coming from the absorber atom and backscattered waves from the neighboring atoms, various scattering paths contribute

❖ The shape of $\chi(k)$ is determined by the local environment around a specific element

❖ $\chi(k)$ contains information on the neighboring atom type, the inter-atomic distances and the coordination number

❖ EXAFS works on all kinds of material, most elements and can be applied in-situ

❖ Synchroton radiation is required

Surface-extended X-ray absorption fine structure (SEXAFS)

Surface-extended X-ray absorption fine structure (SEXAFS) is the surface-sensitive equivalent of the EXAFS technique. Joachim Stöhr played a major role in the initial development of this technique.

This technique involves the illumination of the sample by high-intensity X-ray beams from a synchrotron and monitoring their photoabsorption by detecting in the intensity of Auger electrons as a function of the incident photon energy.

Surface sensitivity is achieved by the interpretation of data depending on the intensity of the Auger electrons (which have an escape depth of ~1–2 nm) instead of looking at the relative absorption of the X-rays as in the parent method, EXAFS.

SEXAFS
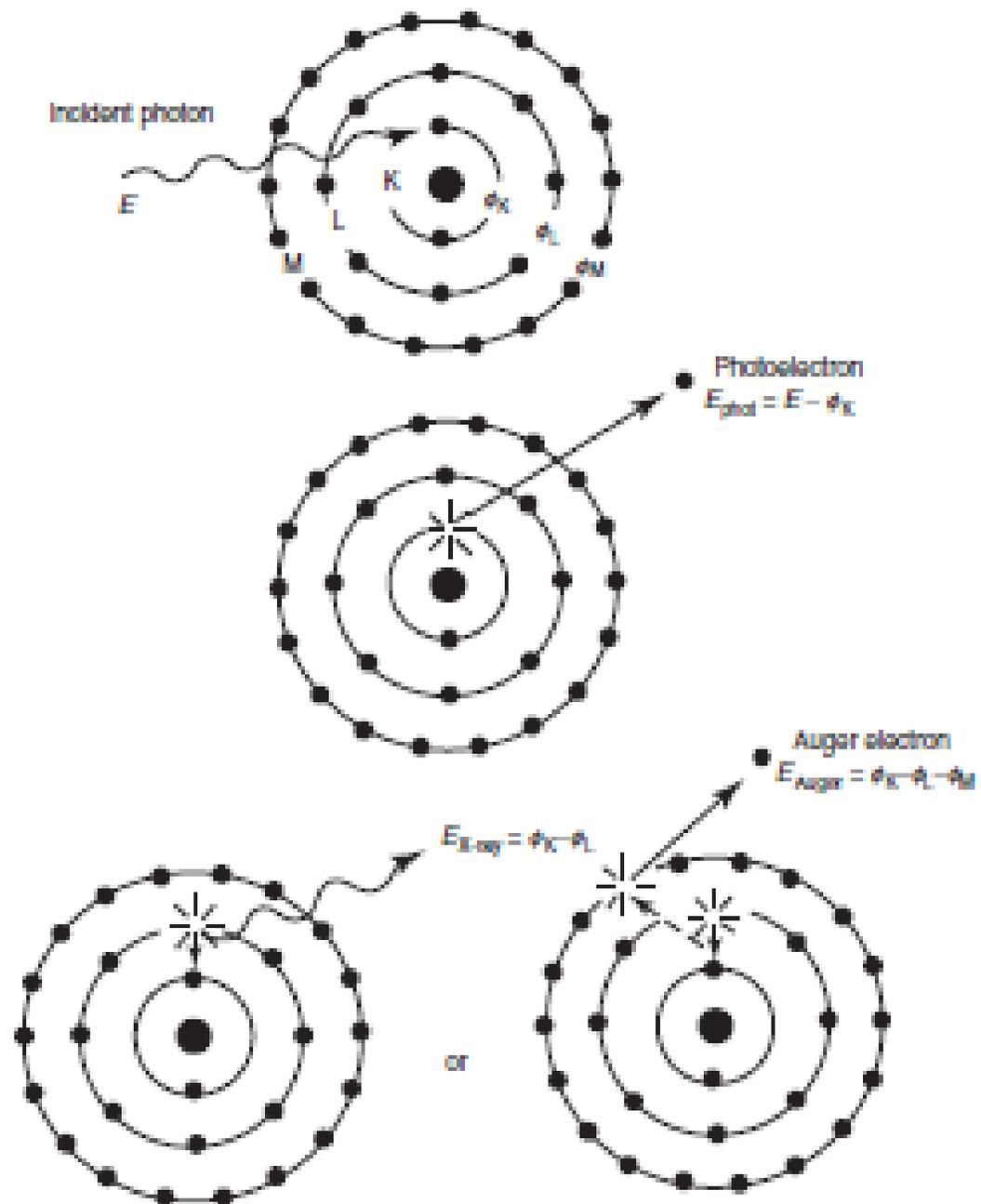
SEXAFS

The photon energies are tuned through the characteristic energy for the onset of core level excitation for surface atoms. The core holes thus created can then be filled by nonradiative decay of a higher-lying electron and communication of energy to yet another electron, which can then escape from the surface (Auger emission).

The photoabsorption can therefore be monitored by direct detection of these Auger electrons to the total photoelectron yield. The absorption coefficient versus incident photon energy contains oscillations which are due to the interference of the backscattered Auger electrons with the outward propagating waves.

SEXAFS

The period of this oscillations depends on the type of the backscattering atom and its distance from the central atom. Thus, this technique enables the investigation of interatomic distances for adsorbates and their coordination chemistry.

This technique benefits from long range order not being required, which sometimes becomes a limitation in the other conventional techniques like LEED (about 10 nm). This method also largely eliminates the background from the signal. It also benefits because it can probe different species in the sample by just tuning the X-ray photon energy to the absorption edge of that species.

SEXAFS

N/Cu(100)

N K Emission

UPS (HeII)

N/Cu

Clean Cu

Binding Energy (eV)
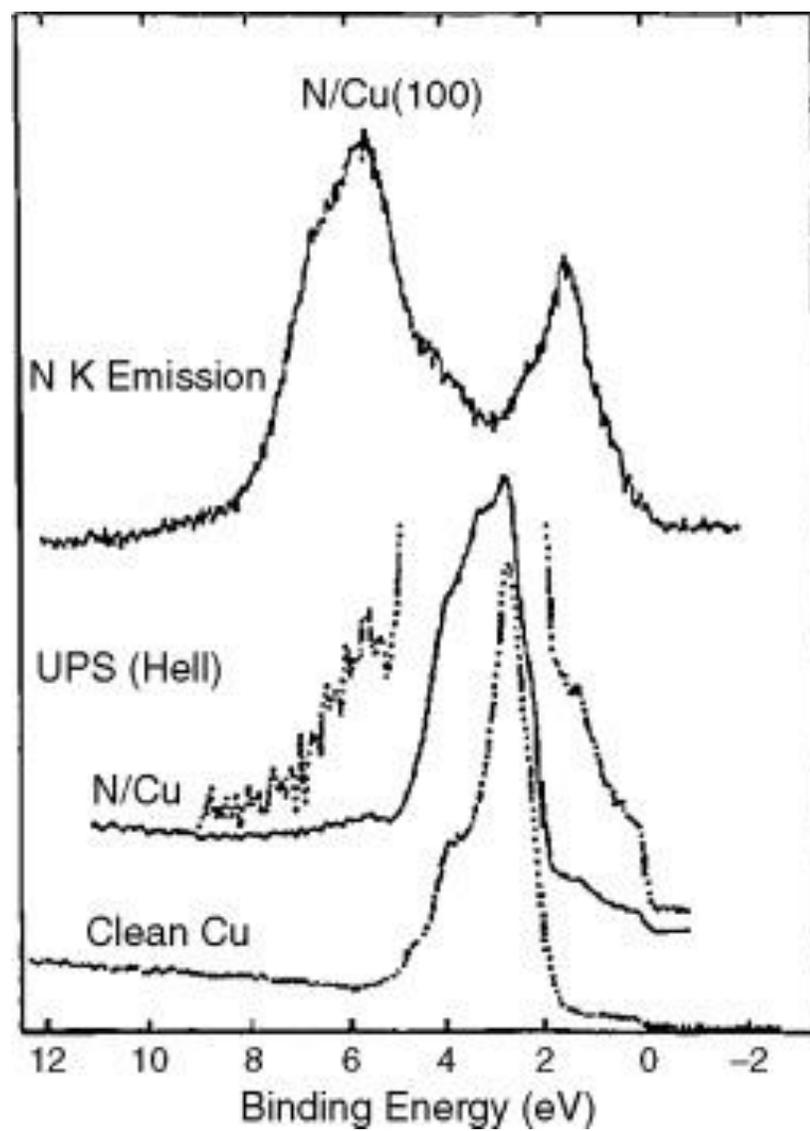
SEXAFS

Normally, the SEXAFS work is done using synchrotron radiation as it has highly collimated, plane-polarized and precisely pulsed X-ray sources, with fluxes of 1012 to 1014 photons/sec/mrad/mA and greatly improves the signal-to-noise ratio over that obtainable from conventional sources. A bright source X-ray source is illuminating the sample and the transmission is being measured as the absorption coefficient as

$$\mu = \ln (I) / \ln (I_o)$$

where I is the transmitted and Io is the incident intensity of the X-rays. Then it is plotted against the energy of the incoming X-ray photon energy.

SEXAFS

❖ **In SEXAFS, an electron detector and a high-vacuum chamber is required to calculate the Auger yields instead of the intensity of the transmitted X-ray waves.**

❖ **The detector can be either an energy analyzer, as in the case of Auger measurements, or an electron multiplier, as in the case of total or partial secondary electron yield.**

❖ **The energy analyzer gives rise to better resolution while the electron multiplier has larger solid angle acceptance.**

SEXAFS

- ❖ SEXAFS probes the local short-range surface structure, rather than the long-range order

- ❖ It provides details of the local coordination environment, i.e., the number of neighbors surrounding a particular atom and their interatomic separation, and precise details of the atomic positions

- ❖ It gives information concerning the surface geometry of chemisorbed species, providing detailed information on the nature of adsorption sites.

SEXAFS

EXAFS finds widespread application in the study of disordered, polycrystalline and amorphous materials, providing details of the local coordination environment, SEXAFS measurements of the surfaces of such materials suffer from considerable random electron scatter, which coupled to the low signal intensity, make SEXAFS measurements on polycrystalline and amorphous materials difficult.

Consequently nearly all SEXAFS studies have been carried out using single crystal surfaces. SEXAFS has been used to determine local coordination environments and coordination sites in many adsorbate systems; nearest-neighbor metal–adsorbate atom distances are obtained, together with next nearest neighbor distances if the data quality is sufficiently good.

SEXAFS

❖ Surface-extended X-ray absorption fine structure (SEXAFS) uses Auger or photoelectrons to detect the EXAFS signal.

❖ This ensures that this technique has a much **higher surface sensitivity** than EXAFS acquired using the TEY method.

❖ SEXAFS requires UHV and the detection instrumentation normally associated with the AES or XPS techniques.