

NEXAFS (Near-Edge X-ray Absorption Fine Structure)

Near Edge X-Ray Absorption Fine Structure, NEXAFS, spectroscopy refers to the absorption fine structure close to an absorption edge, about the first 30 eV above the actual edge.

This region usually shows the largest variations in the x-ray absorption coefficient and is often dominated by intense, narrow resonances.

NEXAFS is also called X-ray Absorption Near Edge Structure, XANES. Today, the term NEXAFS is typically used for soft x-ray absorption spectra and XANES for hard x-ray spectra.

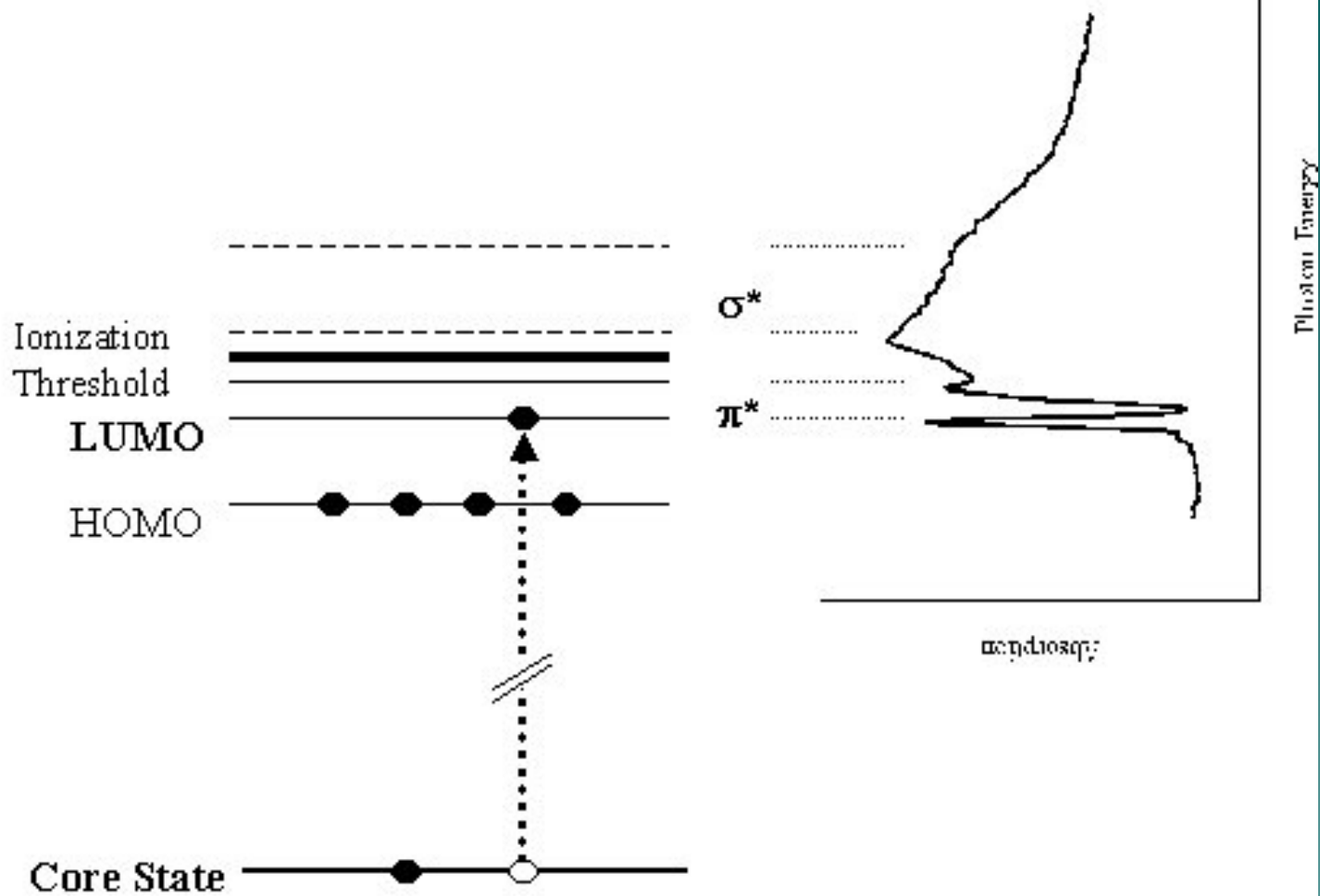
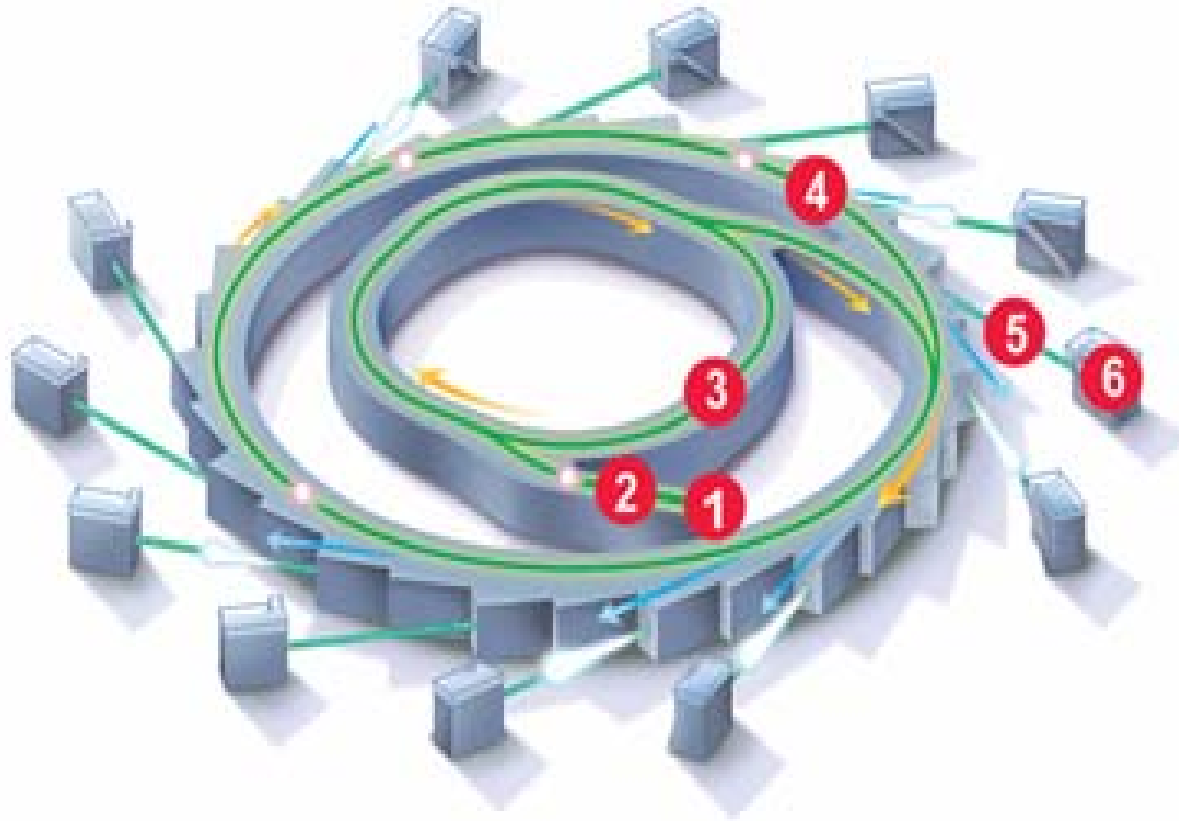


Fig. 2 The near edge x-ray absorption fine structure (NEXAFS) arises from electronic transitions of an inner shell electron to energy levels (orbitals in molecules, bands in solids) which are normally unoccupied in the ground state. The lowest unoccupied molecular orbital (LUMO) is the π^* orbital in essentially all unsaturated compounds.

Opposite to the related x-ray photoemission spectroscopy (XPS or ESCA) technique, where the photon energy is fixed and the electron intensity is measured as a function of electron kinetic energy, in NEXAFS the x-ray energy is scanned and the absorbed x-ray intensity is measured.



1. electron gun
2. linac
3. booster ring
4. storage ring
5. beamline
6. end station

Synchrotron light has a number of unique properties. These include:

High brightness: synchrotron light is extremely intense (hundreds of thousands of times more intense than that from conventional x-ray tubes) and highly collimated.

Wide energy spectrum: synchrotron light is emitted with energies ranging from infrared light to hard, energetic (short wavelength) x-rays.

Tunable: through sophisticated monochromators and insertion devices (see below) it is possible to obtain an intense beam of any selected wavelength.

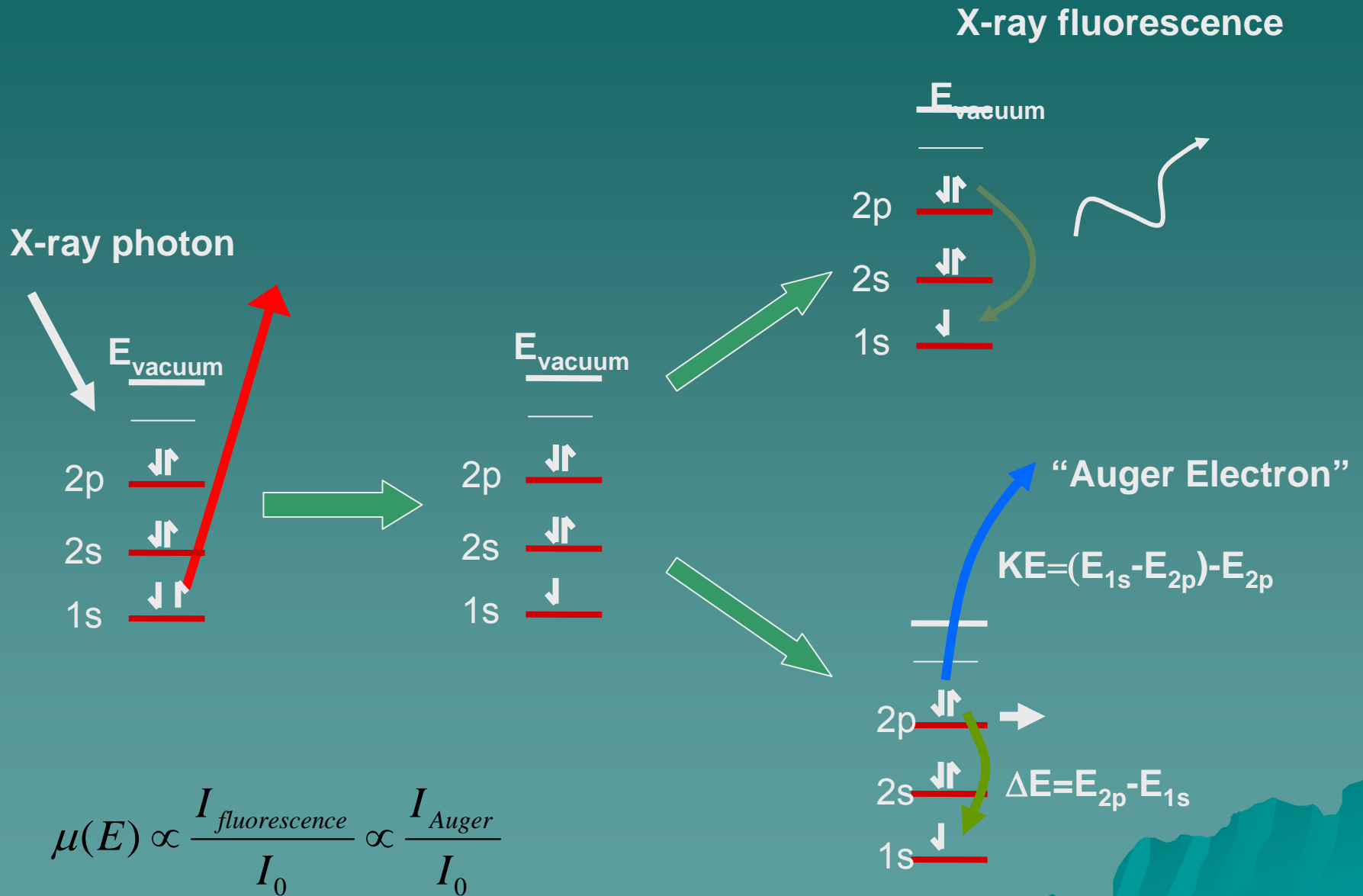
Highly polarised: the synchrotron emits highly polarised radiation, which can be linear, circular or elliptical.

Emitted in very short pulses: pulses emitted are typically less than a nano-second (a billionth of a second).

NEXAFS spectra can be recorded in different ways. The most common methods are transmission and electron yield measurements.

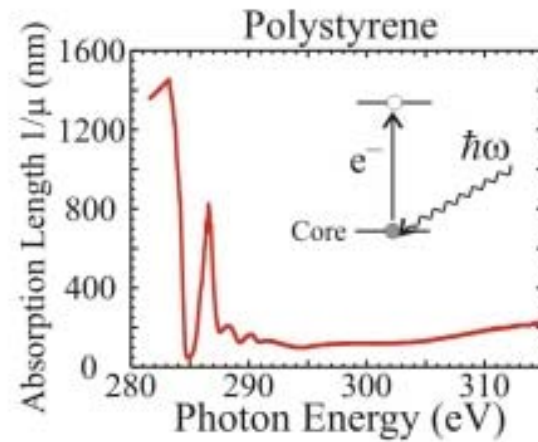
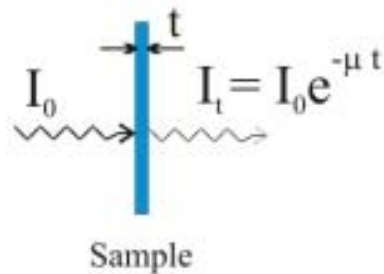
Note that the absorption coefficient μ is obtained either as the logarithm or the direct ratio of the detected intensities I_t and I_e and incident intensity I_0

Detection of x-ray absorption signals

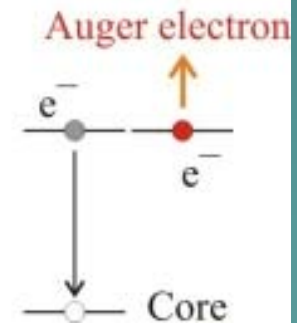
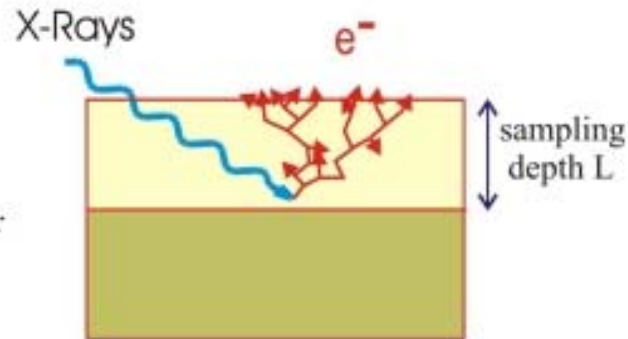
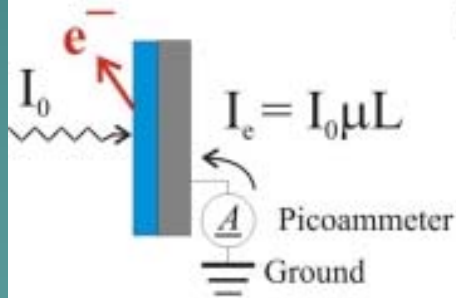


X-Ray Absorption Spectroscopy

Transmission



Electron Yield

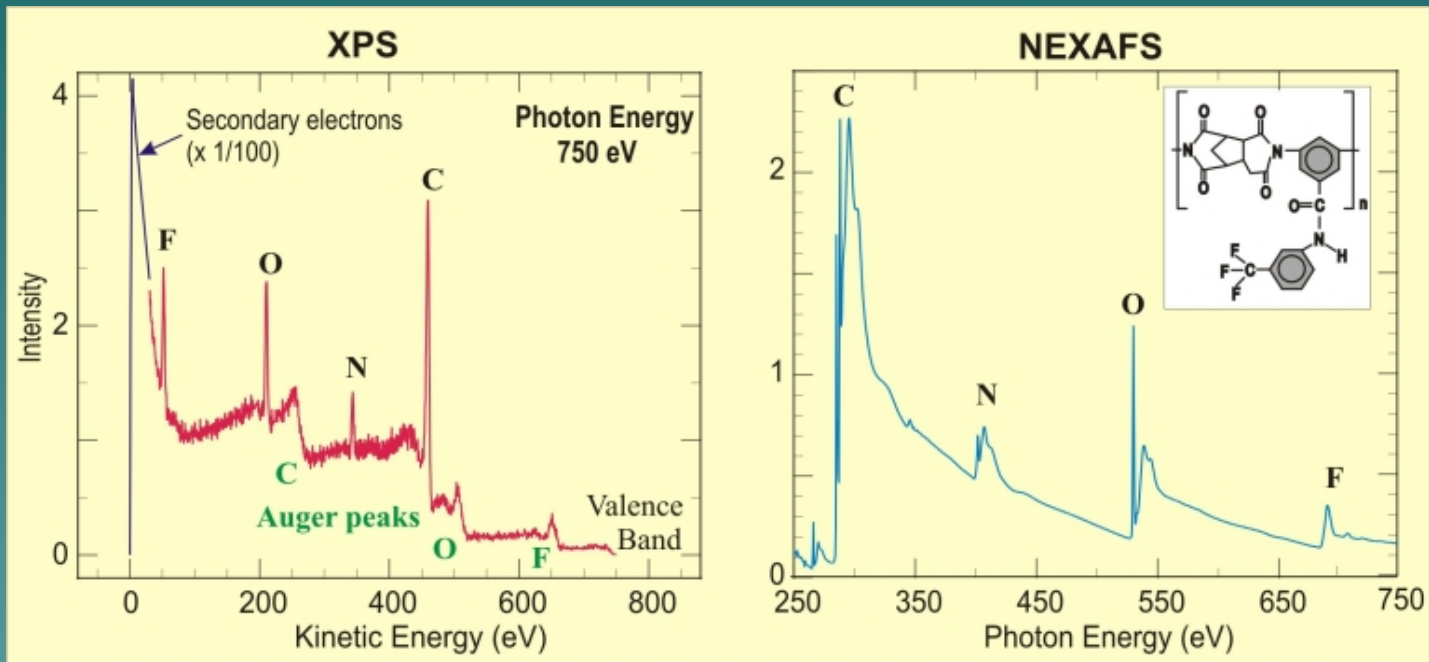


The transmission technique requires thin foils while the electron yield technique, often called total electron yield (TEY) detection, can be used for conventional samples. The absorbed x-ray intensity is not measured directly in TEY measurements, but rather the photoelectrons that are created by the absorbed x-rays. X-rays are absorbed through excitations of core electrons to empty states above the vacuum or Fermi level. The created holes are then filled by Auger decay (dominant in the soft x-ray region over x-ray fluorescence). The intensity of the emitted primary Auger electrons is a direct measure of the x-ray absorption process and is used in so called Auger electron yield (AEY) measurements, which are highly surface sensitive, similar to XPS.

As they leave the sample, the primary Auger electrons create scattered secondary electrons which dominate the total electron yield (TEY) intensity. The TEY cascade involves several scattering events and originates from an average depth, the electron sampling depth L . Electrons created deeper in the sample lose too much energy to overcome the work function of the sample and therefore do not contribute to the TEY. The sampling depth L in TEY measurements is typically a few nanometers, while it is often less than 1 nm for AEY measurements.

NEXAFS is *element specific* because the x-ray absorption edges of different elements have different energies. This is illustrated in the next figure where XPS and NEXAFS spectra of the same polymer are compared. The XPS spectrum was recorded at a photon energy of 750 eV. Both spectra exhibit pronounced peaks corresponding to C, N, O, and F atoms in the sample. For example, the C K-edge threshold peak in the NEXAFS spectrum lies at a photon energy of about 285 eV.

This corresponds to a peak in the XPS spectrum at a kinetic energy of $750 \text{ eV} - 285 \text{ eV} = 465 \text{ eV}$.

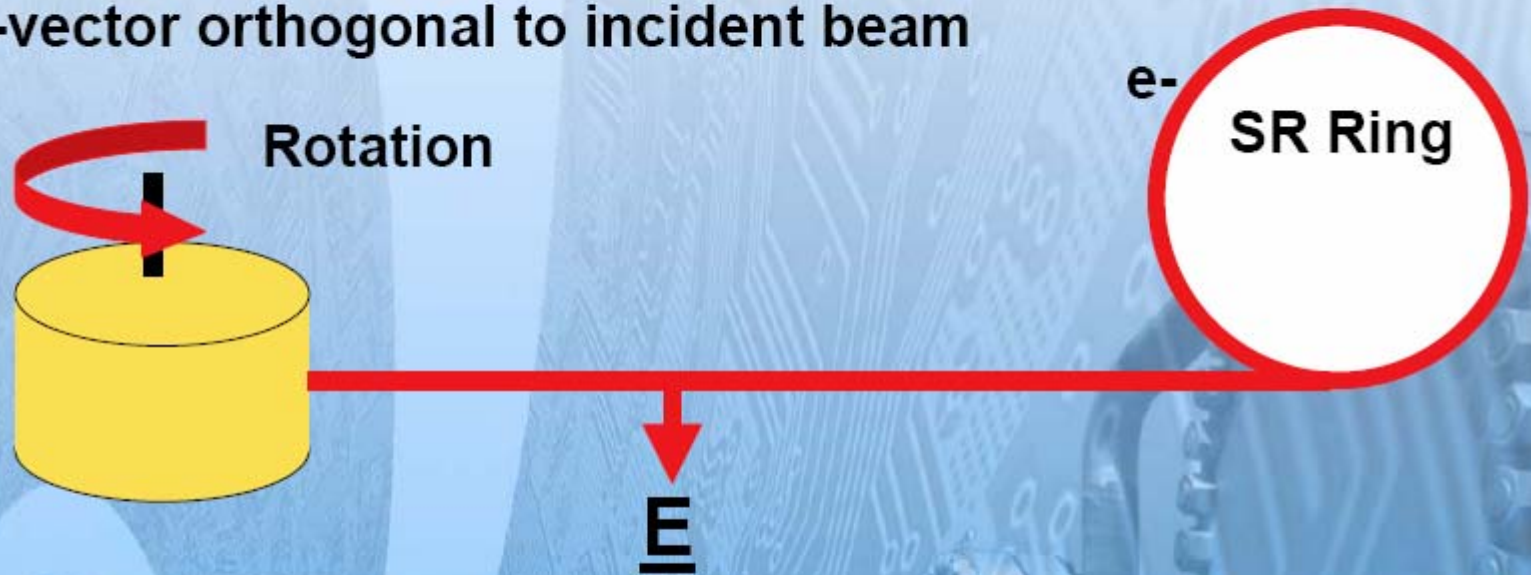


Another great asset of NEXAFS spectroscopy is its *polarization dependence*.

Linearly polarized x-rays are best suited for covalent systems like low-Z molecules, macromolecules and polymers, which possess directional bonds. In this case the directional electric field vector of the x-rays can be viewed as a "search light" that can look for the direction of chemical bonds of the atom selected by its absorption edge.

Polarised XAFS (NEXAFS) Spectroscopy

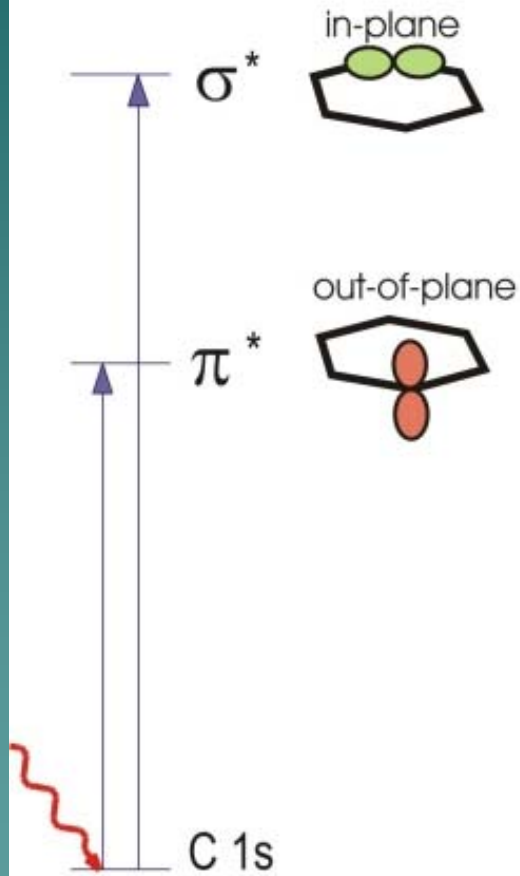
- SR light: linearly polarised (approx) in storage ring plane: E-vector orthogonal to incident beam



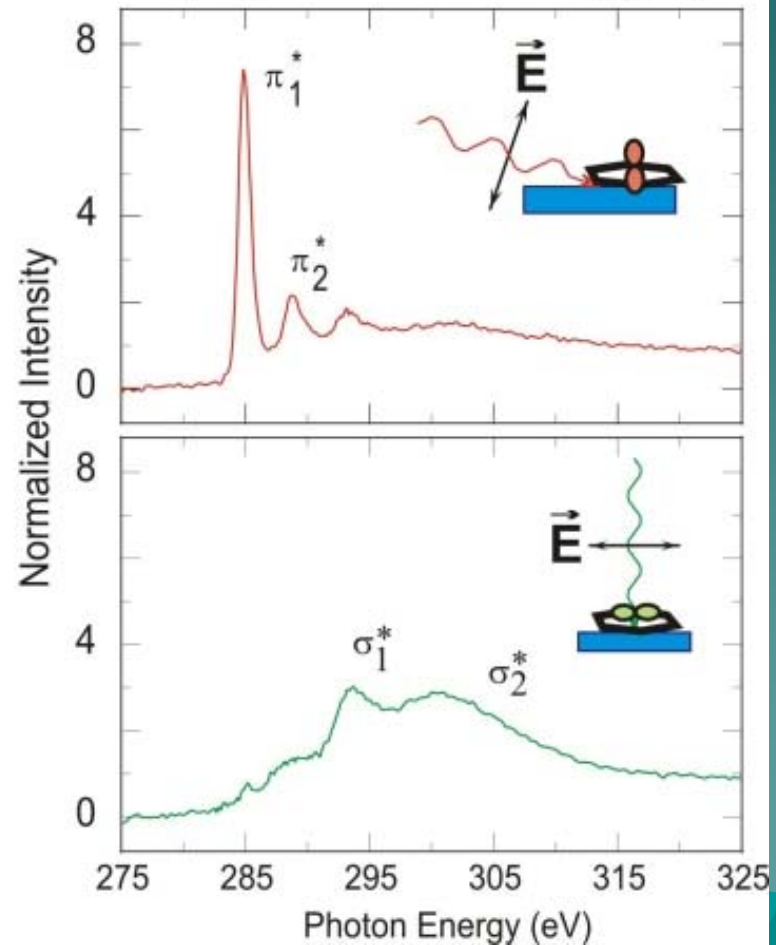
- NEXAFS spectra recorded as function of sample rotation about vertical axis - reveals evidence for molecular order within sample
- Soft X-rays: low penetration into sample – thus structure in surface regions analysed

The Search Light Effect

Benzene Molecular Orbitals



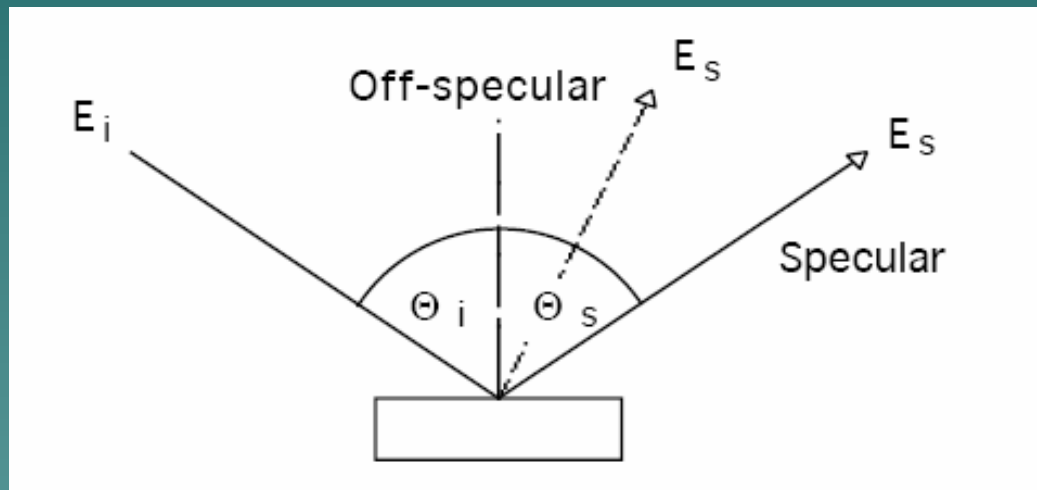
Lying-down benzene on Ag (110)



An example is shown for the benzene molecule. Benzene, C_6H_6 , has unoccupied orbitals of σ and π symmetry which are oriented in and perpendicular to the ring plane, respectively, as shown on the left side. Polarization dependent NEXAFS spectra for benzene chemisorbed on Ag(110) are shown on the right. When the electric field vector E is aligned along the surface normal, peaks due to the out-of-plane π orbitals are seen and when E is parallel to the surface resonances due to the in-plane σ orbitals are dominant. This shows that benzene lies down on the Ag surface. In fact, benzene is only relatively weakly chemisorbed on Ag. For stronger chemisorption bonds (e.g. C_6H_6 on Mo or Pt) the π resonances broaden significantly, because the π orbitals are involved in the bond to the surface.

High-Resolution Electron Energy Loss Spectroscopy (HREELS)

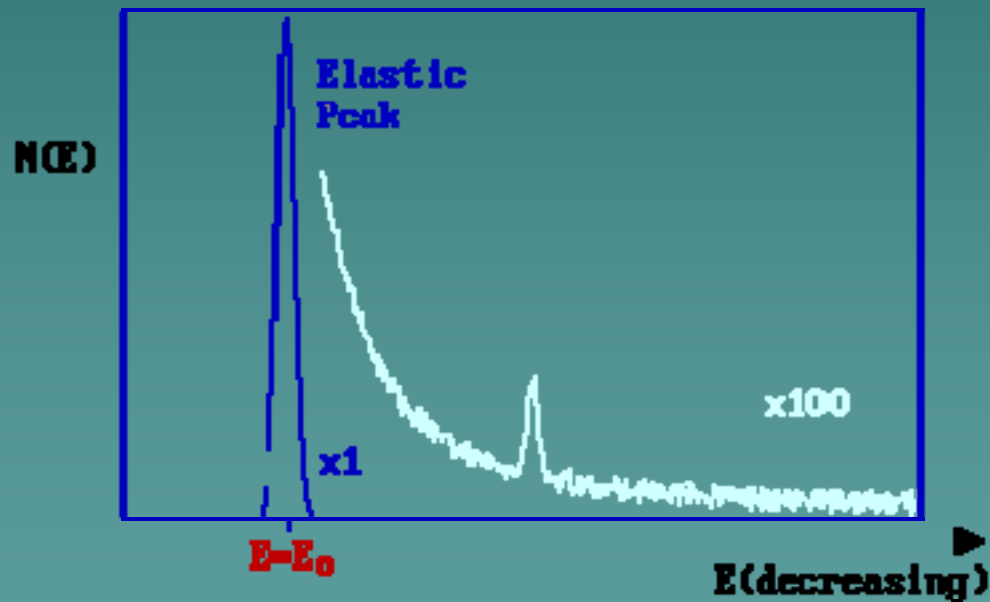
Based on inelastic scattering of monoenergetic beam of low energy electrons ($E_i = 1-10$ eV) from surface



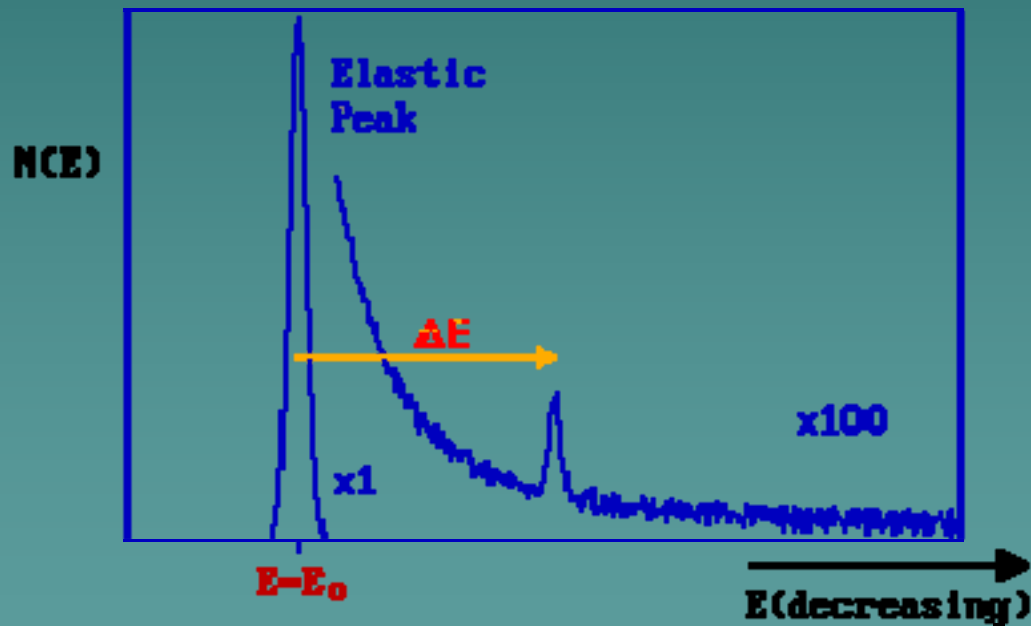
kinetic energy analysis of inelastically-scattered electrons gives information about energy transfer to surface vibrational modes

$$E_s = E_i - h\nu \leftarrow \text{energy loss}$$

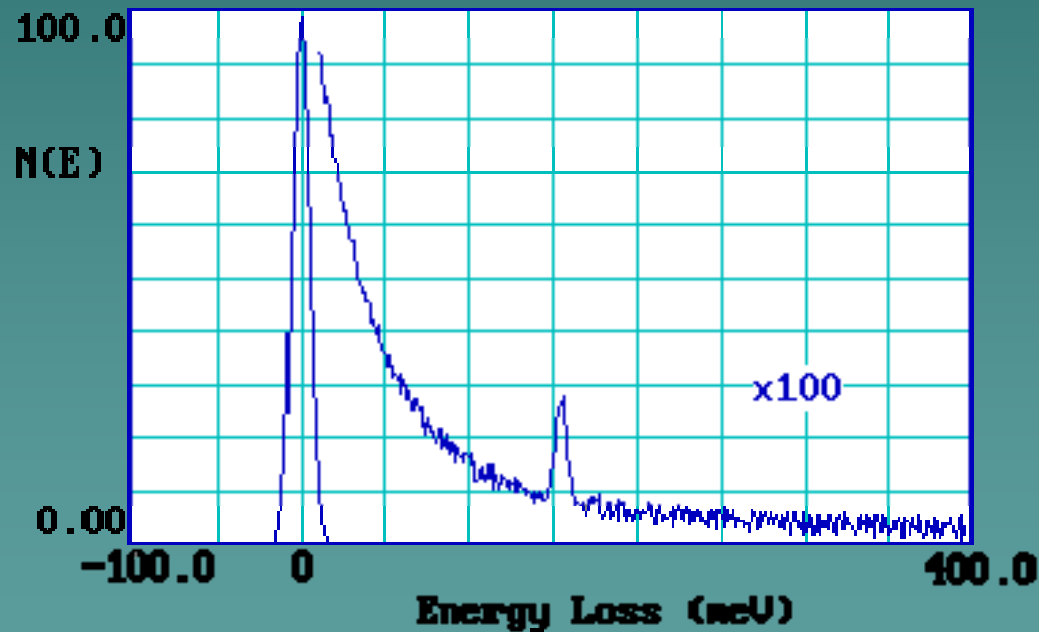
A substantial number of electrons are elastically scattered ($E = E_0$) - this gives rise to a strong *elastic peak* in the spectrum.



On the low kinetic energy side of this main peak ($E < E_0$), additional weak peaks are superimposed on a mildly sloping background. These peaks correspond to electrons which have undergone discrete energy losses during the scattering from the surface



The magnitude of the energy loss, $\Delta E = (E_0 - E)$, is equal to the vibrational quantum (i.e. the energy) of the vibrational mode of the adsorbate excited in the inelastic scattering process. In practice, the incident energy (E_0) is usually in the range 5-10 eV (although occasionally up to 200 eV) and the data is normally plotted against the energy loss (frequently measured in meV).



Electron Scattering Mechanisms in EELS

Three basic scattering modes for electron,
each with own selection rules:

(1) *Dipole* scattering

(2) *Impact* scattering

(3) *Negative ion resonance* scattering

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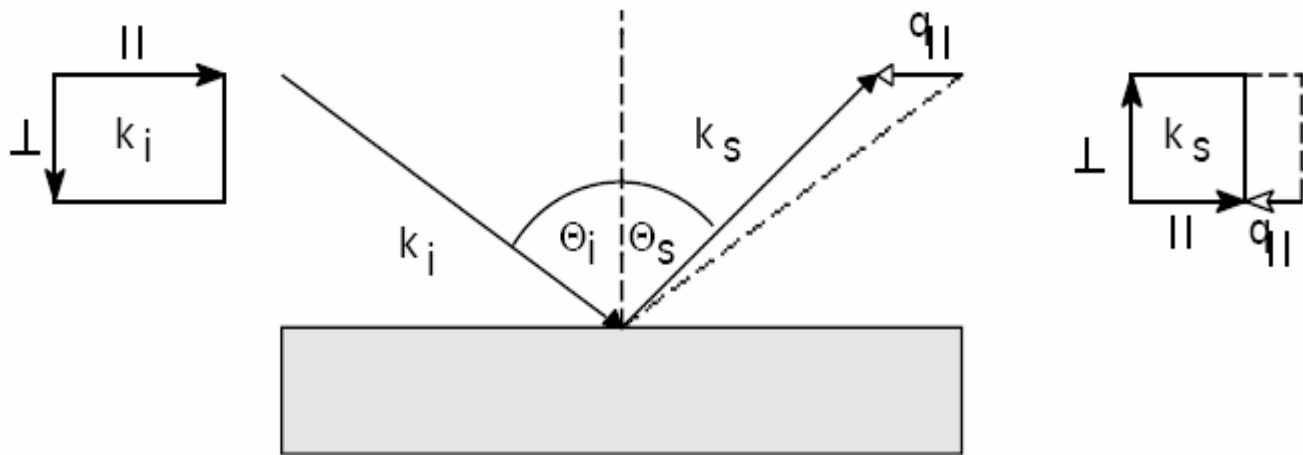
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Only modes with component of vibration perpendicular to surface can be excited (not parallel modes) - *surface selection rule*



small momentum loss $q_{||} = \hbar v$

Total dipole = 2μ

Total dipole = 0

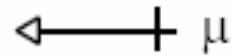


Image
dipoles

Impact scattering

Electron is "kinematically" scattered at short range (few Å) by atomic core potentials of surface - modulated by nuclear motion (vibration)

Electron scattered over wide range of angles (in and out of plane of incidence)

Probability of scattering depends on surface dipole amplitude/direction (symmetry of mode) and electron energy (momentum)

Neither electron momentum \parallel nor \perp
conserved

one can see vibrational modes with dynamic
dipoles both \parallel and \perp to
surface plane (only off-specular)

Much lower cross-section than dipole
scattering (weak loss features)