1 X-ray Photoelectron Spectroscopy (XPS)

In the photoemission process the energy is conserved:

$$E_{\text{kin}} = h\nu - E_{\text{bin}} - \Phi$$
$$E_{textupbin} = h\nu - E_{\text{kin}} - \Phi$$

E_{kin} is the kinetic energy of the electron. $h\nu$ the energy of the ingoing electron, E_{bin} the binding energy of the electron and Φ is the work function of the surface. In XPS photons go in and electrons come out hence photo-electron. The exact binding energy depends heavily on the chemical environment, and this can make a chemical shift of 1 eV–8 eV the with and intensity

$$I(E_{\text{kin}} \approx \text{DOS}(E_{\text{bin}} = h\nu - E_{\text{kin}} - \Phi)$$

The surface core level shift (SCLS) is due to the surface having a different chemical environment (having lost some (3) neighbours) There can even be multiple shifts for each layer, due to reconstruction and relaxation having effects longer into the material.

1.1 Koopman's theorem

This states that the measured binding energies are calculated one electron eigenvalues of the system. This changes the formula:

$$E_{\text{kin}} = h\nu - (E_{\text{bin}} - E_{\text{r}} - \Phi$$

Where $(E_{\text{bin}} - E_{\text{r}})$ is the new "apparent" binding energy.

1.2 Cross section

The XPS peak intensity is, for the element x:

$$I_x = \sigma_x(E)N_x\lambda(E)AD(E)T(E)$$

σ_x is the element specific cross–section, N_x the concentration of the element, λ is the inelastic electron mean free path, A is the sample area, D the detector efficiency and T the analyzer transmission efficiency.

$$\frac{I_A}{I_B} = \frac{\sigma_A(E)N_A\lambda(E)AD(E)T(E)}{\sigma_B(E)N_B\lambda(E)AD(E)T(E)}$$
$$\frac{N_A}{N_B} \approx \frac{I_A}{I_B} \times \frac{\sigma_B\lambda_B}{\sigma_A\lambda_A}$$

The cross section of the system, using the dipole approximation, is:

$$\frac{d\sigma}{d\Omega} \propto |\mathbf{A}_0 \int \psi_f(R)p\psi_i(r)\,dr|^2\partial(E_f - E_i - h\nu).$$

This cross section can be split into an angular part that gives the selection rules $l' = l \pm 1$ and $m' = m, m \pm 1$, and a radial part giving the cross section. The selection rules means that an s state electron must come out with p symmetry, also the polarization matters $\mathbf{A}_0$ is the polarization.

1.3 Spin orbit coupling

Spin orbit coupling means that the J quantum number is $J = L + S$, and it can be either parralel ($j = l + \frac{1}{2}$, $2j + 1$ fold) or anti-parallel ($j = l - \frac{1}{2}$, $2j + 1$ fold). Thus it only occurs for $l = 1, 2, 3$

2 Auger Electron Spectroscopy (AES)

Auger electrons are generated by shooting an electron at the surface, and knocking out a core electron. After this has happened another electron from an outer shell can then take it's place, in doing so releasing energy. The released energy can either be send out a photon, or be used to emit an electron from the original state of the electron.

Say the core electron has energy E_A, the electron jumping into the core has energy E_B and the electron being shot out is in the energy state E_C. This all assumes that the element is in state Z for all events.

$$E_{\text{kin}} = E_A^Z - E_B^Z - E_C^Z - \Phi$$

But there is a core hole after electron A has left:

$$E_{\text{kin}} = E_A^Z - E_B^{Z+1} - E_C^{Z+1} - \Phi$$

But the atom is not $Z + 1$:

$$E_{\text{kin}} = E_A^Z - \frac{1}{2}\left(E_B^{Z+1} + E_B^Z\right) - \frac{1}{2}\left(E_C^{Z+1} + E_C^Z\right) - \Phi$$

is a good compromise, it's known as the $Z + 1$ approximation

The core hole can be generated by x-rays and as such auger electrons will appear in XPS spectrum's, $E_{\text{kin}}^{\text{XPS}}$ depends on the input energy, $E_{\text{kin}}^{\text{AES}}$ does not, so this can be used to differntiate them.

2.1 Auger nomeclature

The nomeclature is (example) KLL, where the first letter is the initial hole, second letter is the shell of the falling electron, and the third letter is the shell of the emitted electron

3 Extended X-ray Absorption Fine Structure (EXAFS)

Possible only with synchrotron radiation!

3.1 EXEFAS

There are oscillations in the absorption spectrum. These are due to the transfer from one atom to the next, so the same atom doesn't absorb and emit the electron.

$$\chi(k) = \frac{\sigma(k) - \sigma_0(k)}{\sigma_0(k)}$$
$$\chi(k) = -k^{-1} \sum{}_i A_i(k) \sin[2kR_i + \phi_i(180°, k)]$$

here the sum is over the shells, the $2kR_i$ term is the actual modulation and the ϕ_i term is the energy dependant phase shift.

$$A_i = \frac{N_i}{R_{i^2}} |f_i(180°, k)| W(T, K) e^{-} \frac{2R_i}{\lambda}$$

where N_i is the number of atoms in sheel i, R_i the radial dependance, making only the first few shells important. f_i the scattering function (atom dependant), W the Debye–Waller factor and the exponential tirm arises form it being inelastic scattering.

3.2 Surface EXAFS (SEXAFS)

Is the surface version of EXAFS, it gives the bond length but not absorption site. However, by polarizing the different neighbours can be seen one by one. There are however problems: Auger electrons will be generated and EXAFS only raises 3 %

3.3 Near-edge EXAFS (NEXAFS)

These are for the oscillations very close to the K-edge of the system. Strong peaks will be seen when enough energy is given to raise the $s1$ electron to the LUMO, LUMO+1, ...

4 Photoelectron diffraction (PhD)

PhD is a lot like XPS, but stems from the fact that the photoelectrons can come from deeper levels, and then create diffraction patterns with teach other. PhD makes 30 %–50 % of the modulations.

$$I(\mathbf{R}) \propto |\psi_0(\mathbf{R} + \sum{}_j \psi_{sj} \mathbf{R}|^2$$
$$I(k) \propto \Big| \cos\Theta_k + \sum_j \frac{\cos\Theta_k}{r_j} |f(\Theta_j, k)| e^{ikr_j(1-\cos\Theta_j) + \phi(\Theta_j, k)} \Big|^2$$

Where the first term is the direct wave and the second is the sum over all scatters. The ϕ term is the phase.

4.1 Angle scan

4.2 Energy scan

5 Generating X-rays