X-Ray Photoelectron Spectroscopy (XPS)

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Electron Spectroscopy for Chemical Analysis (ESCA)
**Photoelectric effect**

Einstein: \( E = h \nu - \phi \)

**The 3-step model:**
1. Optical excitation
2. Transport of electron to the surface (diffusion energy loss)
3. Escape into the vacuum
The optical excitation probability is given by the photoionization cross-section $\sigma(E)$.

In quantum mechanics $\sigma(E)$ in a subshell $nl$ is given by

$$\sigma_{n,l}(E) = \frac{4}{3} \pi^2 a_0^2 \alpha [N_{n,l} \left( E - E_{n,l} \right) \frac{1}{2l + 1}] \left( lR_{E,l-1}^2 + (l + 1)R_{E,l+1}^2 \right)$$

$n,l$: quantum numbers, $\alpha$: fine structure constant, $a_0$ Bohr radius (0.5 nm), $N_{n,l}$: number of e in the subshell, $E_{n,l}$ the energy of the $nl$ electrons, $E$: KE of the ejected electrons.

The radial dipole matrix elements are

$$R_{E,l\pm 1} = \int_0^\infty P_{n,l}(r) r P_{E,l\pm 1}(r) dr$$

$P_{nl}(r)1/r$ and $P_{E,l\pm 1}(r)1/r$ are the radial parts of the single-particle wave functions of the initial (discrete) and final (continuum) states, respectively.

Photoemission intensity

$$I(\theta) \propto \frac{\sigma_{\text{total}}}{4} \left[ 1 - \frac{\beta}{4\pi} (3 \cos \theta - 1) \right]$$

($\beta$: asymmetry parameter, $\theta$: take off angle and $\sigma_{\text{total}}$ the total cross-section)
Cooper Minimum: $R_{E,l-1} \ll R_{E,l+1}$, thus $R_{E,l+1}$ will give the basic features and the energy dependence of the cross-sections. For a radial wavefunction with nodes, $R_{E,l+1}$ will go through 0 at a particular energy, giving rise to a minimum in the cross-section $\sigma$.

Near photoionization threshold: $R_{E,l+1}$ goes through 0 because

1. Final state (emitted) electron wavefunction is largely excluded from the core region
2. Initial state electron wavefunction has most strength, after it goes through a node.

As the photon energy increases the final state electron wavefunction begins to “penetrate” the core and the overlap goes to 0 due to the node in the initial state wavefunction.

Reference: Cooper Minima in the Photoemission Spectra of Solids, S.L. Molodtsov et al.

Example: Copper (Cu+) versus Silver (Ag+)
→ Increase or decrease of the PE signal of certain states
A Typical XPS spectrum

1. Sharp peaks due to photoelectrons created within the first few atomic layers (elastically scattered).

2. Multiplet splitting (occurs when unfilled shells contain unpaired electrons).

3. A broad structure due to electrons from deeper in the solid which are inelastically scattered (reduced KE) forms the background.

4. Satellites (shake-off and shake-up) are due to a sudden change in Coulombic potential as the photoejected electron passes through the valence band.
5. Plasmons which are created by collective excitations of the valence band

- Extrinsic Plasmon: excited as the energetic PE propagates through the solid after the photoelectric process.

- Intrinsic Plasmon: screening response of the solid to the sudden creation of the core hole in one of its atom

_The two kinds of Plasmon are indistinguishable._

6. Auger peaks produced by X-rays (transitions from L to K shell: O KLL or C KLL).
Survey spectrum

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>Area</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>F 1s</td>
<td>686.80</td>
<td>1.946</td>
<td>20272.3</td>
<td>66.037</td>
</tr>
<tr>
<td>C 1s</td>
<td>289.60</td>
<td>1.669</td>
<td>3315.5</td>
<td>33.963</td>
</tr>
</tbody>
</table>

Loss peaks

C KLL

F KLL

F 1s

C 1s

F 2s
Sharp Peak (core level)

F 1s peak

O 1s peak

<table>
<thead>
<tr>
<th>Variable</th>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L.Sh.</th>
<th>Area</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>O 1s</td>
<td>529.81</td>
<td>1.154</td>
<td>32191.5</td>
<td>82.748</td>
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<tr>
<td>0</td>
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<td>531.03</td>
<td>1.883</td>
<td>6711.5</td>
<td>17.252</td>
<td></td>
</tr>
</tbody>
</table>
Multiplet splitting occurs when there are unfilled shells containing unpaired electrons. For instance, transition metals with unfilled \textit{d} orbitals and rare earths with unfilled \textit{f} orbitals all show multiplet splitting.
**Multiplet splitting**

When an additional vacancy is made by photoionization, coupling occurs between the unpaired electron left behind (after ionization) and the unpaired electron in the originally incompletely filled shell.

*Example: Fe$_2$O$_3$ has 5 unpaired electrons in the 3d shell as shown below.*

*Following photoionization in the 3s shell, there are 2 possible final states.*

**Schematic of Multiplet Splitting following photoionization in Fe$^{3+}$ and XPS spectrum**
Satellites

Arise when a core electron is removed by a photoionization. There is a sudden change in the effective charge due to the loss of shielding electrons. (This perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionization. Two types of satellite are detected.

**Shake-up:** The outgoing electron interacts with a valence electron and excites it (shakes it up) to a higher energy level. As a consequence the energy core electron is reduced and a satellite structure appears a few eV below (KE scale) the core level position.

**Shake-off:** The valence electron is ejected from the ion completely (to the continuum). Appears as a broadening of the core level peak or contribute to the inelastic background.
Shake-up satellites distinct peaks a few eV below the main line
Shake-off satellites broad feature at lower energy w.r.t. to main line
This feature is specific to clean surfaces. The photoelectron excites collective oscillations in the conduction band (free-electron gas), so called Plasmons. (discrete energy loss).

The plasmon (bulk) energy is

$$\hbar \omega_p = \hbar \left( \frac{4\pi ne^2}{m} \right)^{1/2}$$

$n$: e density, $e$: charge of e, $m$: mass of e electron.

Surface plasmon: bulk plasmon / 1.414.

For Al, Mg, Na etc… the energies are 15.3 eV, 10.6 eV and 5.7 eV, respectively.
Auger electron emission occurs also when x-rays impinge a sample. Auger electron is initiated by the creation of an ion with an inner shell vacancy. Auger electrons are emitted in the relaxation of the excited ion. An electron from a higher lying energy level fills the inner shell vacancy with the simultaneous emission of an Auger electron.

It is a three-electron process.

3 Distinct Auger Peaks are seen in the data for Copper.
Chemical shift

Chemical shift arises in the initial state from the displacement of the electronic charge from the atom towards its ligands, reducing the electrostatic potential at the atom. There is a final state shift due to the polarization of the ligand by the core on the central atom.

Core electron BE in molecular systems exhibits chemical shifts which are simply related to various quantitative measures of covalency. Greater the electronegativity of the ligands, the greater the BE of the core electron of the ligated atom.

Basic concept: The core electrons feel an alteration in the chemical environment when a change in the potential (charge distribution) of the valence shell occurs. 

For example assume that the core electrons are inside a hollow spherical charged shell. Each core electron then sees a potential. A change in Q by ΔQ gives a change in V.

\[ \Delta V = \frac{1}{4\pi \varepsilon_0} \frac{\Delta Q}{R} \]

where \( \Delta V \) is the chemical shift.
Oxidized and clean Cr 2p spectra (left). Oxidized and clean Cu 2p spectra (right). The oxide layer resulted in extra peaks (shoulder at higher BE—left of the main line). Satellites are also seen on the Cu 2p spectra.
Angular Distributions

The mean free paths (IMFP) are in the range of 5 - 100Å falling within 5 – 40 Å for inorganic materials. To enhance the surface signal we can vary the photon energy—closer to the attenuation length minimum or decrease the angle of electron emission relative to a solid surface.

For example: for Au 4f the IMFP (d) is about 22Å at angle of 90° using AlKα. The depth (d) probed by XPS becomes about 4-5 Å at angle = 10°.
The curve fitting of the main hydrocarbon line \((C_xH_y)\) reveals chemical shifts corresponding to

- Ether and alcohol groups (C-O at 1.55 eV higher BE),
- Carbonyl groups (C=O at 2.8 eV higher),
- Ester and acid functional at 4.2 eV
- Carbonate groups at 5.2 eV higher BE.

Finally, the \(\pi - \pi^*\) satellite at 291.5 eV appears at the extreme left.
Spin-orbit and lines intensity

Multiplet splitting occurs when the system has unpaired electrons in the Valence levels.

Example: Mn\(^{2+}\) 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 3d\(^5\) 4s\(^2\) (3d\(^5\) all unpaired and with // spins)

Also the total electronic angular momentum (j) is a combination of the orbital angular (l) and spin (s) momenta. The j-j coupling is equal to \(|L \pm S|\) where L and S are the total orbital angular and spin momenta, respectively.

For angular quantum number \(l \neq 0\) the line is a doublet. \((p_{1/2}, p_{3/2})\).

Splitting: Final states are given by: \(j_+ = l + s\) and \(j_- = l - s\)

Examples: For p orbitals the doublet will be \(p_{1/2}\) and \(p_{3/2}\) because \(l = 1\) and \(s = \pm 1/2\) therefore \(j_- = 1/2\) and \(j_+ = 3/2\).

For d orbitals, the doublet will be \(d_{x^1}\) and \(d_{x^2}\) because \(l = \) and \(s = \pm 1/2\) therefore \(j_- = x1\) and \(j_+ = x2\).
Intensity ratio is given by \((2j - +1) / (2j + +1)\)

For p orbitals the ratio is given by \(2 \times \frac{1}{2} + 1 = 2 (p_{1/2})\) and \(2 \times \frac{3}{2} + 1 = 4 (p_{3/2})\). Therefore the ratios for p orbitals doublet is \(1/2\), for d orbitals doublet is \(4/6 = 2/3\)

Ni 2p spectrum

Ratio = 1/2

Au 4f spectrum

Ratio = ??
**Static Charging**

**XPS:** It arises as a consequence of the build-up of a positive charge at the surface of non-conducting specimens. The rate of photo-electron loss is greater than that of their replacement from within the specimen. It produces a retarding field at the surface that will shift the peaks (reduce the KE of the ejected electrons).

Suggestions:

1) Use of the adventitious Carbon line to correct any shift (most materials exhibit a C 1s line).

2) Deposition of a very thin layer of gold (as use in SEM).

3) Use of a “flood gun” low energy electrons (0-5 eV).
Static Charging (cont.)

**Auger:** Sample charging is a function of the total electron yield, \( f(\Sigma) \). \( \Sigma \) is the sum of secondary electron and backscattering coefficient.

\( \Sigma > 1 \) samples charge positively. Auger (and XPS) peaks shift to lower KE (higher BE).

\( \Sigma < 1 \) samples charge negatively. Auger (and XPS) peaks shift to higher KE (lower BE).

Case 1, the emitted electrons have a reduced KE by a few tens of eV

**Identification remains possible**

Case 2, the KE of the emitted electrons increases due to the repulsive forces between the charged surface and emitted electrons.

**Analysis is often impossible.**
Linewidths ($\Gamma$)

The irreducible width $\Gamma$ in XPS is due to the *lifetime* of the core hole state

$$\Gamma = \frac{2\hbar}{\tau}$$  
(Ag 3d core level $\tau = 10^{-14} - 10^{-15}$ s)

The resulting line shape is Lorenzian. *A core level has a number of decay channels that contribute to the width of the line.*

Measurement of the lifetime width of a core hole state is complicated by the existence of:

1. *Resolution of the instrument: dual anode long tail due to the lifetime width of the K-shell hole.*
2. *Phonon broadening (excitation of the lattice vibrations)*
3. *Inhomogeneous broadening (superposition of lines with different chemical shifts).*
Photoelectron lines have a **Lorenzian shape** corresponding to the lifetime of the core hole that is created. Gaussian or Gaussian Lorentzian shape GL(30) curves are often used for curve fitting purposes.
Peak Widths and Intensities

**Peak widths:** it is a convolution of the natural width of the core level, the width of the x-ray line and the analyzer resolution:

\[
\Delta E = \left( \Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2 \right)^{1/2}
\]

**Intensities:** Only the ratio of area of lines has some meaning (relative concentration).

\[
\begin{bmatrix}
A \\
B
\end{bmatrix} = \frac{\sigma_b \varsigma_b \lambda_b \eta_b I_a}{\sigma_a \varsigma_a \lambda_a \eta_a I_b}
\]

\(\sigma:\) cross-section; \(\varsigma:\) fraction of PE events (w/o intrinsic plasmon excitation); \(\lambda:\) mean free path; \(\eta:\) KE dependent spectrometer transmission and \(I:\) area of the line
Quantitative Analysis

1. **Use of standards:**
   - $I_x$ is the amplitude of the element X in your sample,
   - $I_{x,\text{std}}$ is the amplitude of the element X in pure material

   The concentration of X in your sample is THEN given by $C_x = \frac{I_x}{I_{x,\text{std}}}$
   
   **PROBLEM** with this approach is that you need a large No of Standards.

2. **Modify Method:**
   It introduces the relative sensitivity factor, $S_x$ based upon one pure element standard (usually Ag, silver standard). So, if we want to calculate $S_x :$
   sensitivity for element X from a compound $X_a Y_b$ we could do it by using:

   $$S_x = \frac{(A + B)}{A} \frac{I_x}{I_{\text{Ag(pure)}}}$$
Quantitative Analysis (cont.)

\[ S_x = \frac{(A + B)}{A} \frac{I_x}{I_{Ag(pure)}} \]

Where \( I_x \) is the amplitude of the known compound, \((A+B)/A\) is the 1 / fraction of X atoms and \( I_x / I_{Ag} \) the ratio of peak to peak amplitudes.

THEN from an unknown sample: \( C_x = \frac{I_x}{S_x} \). \( S_x \) = concentration

OR to make it self consistent

\[ C_x = \left( \frac{I_x}{S_x} \right) / \sum_a \left( \frac{I_a}{S_a} \right) \]

where \( I_x \) and \( I_a \) are measured and \( S_x \) and \( S_a \) are obtained from standards as mentioned above.
References and Websites


• Practical Surface Analysis by D. Briggs and M. P. Seah.

**Websites:**

http://srdata.nist.gov/xps,
http://www.xpsdata.com,
http://www.lasurface.com,
http://www.eaglabs.com