Surface Analysis of Nanomaterials

(나노소재표면분석)

Surface and Thin Film Analysis (표면 및 박막 분석)

장소: E6, Room 116

시간: 월7A-8A, 수7A-8A

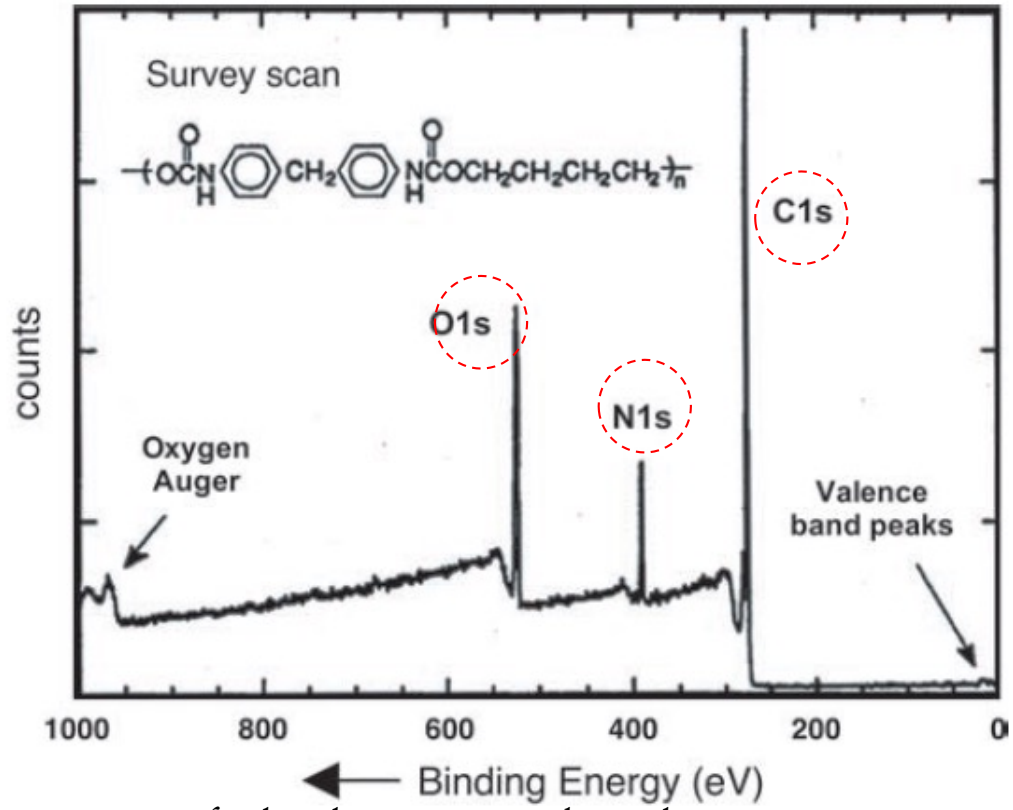
2. Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis

Spectral Features

The understanding and analysis of ESCA spectra

First, ESCA analyses are typically performed by taking a wide scan or survey scan spectrum, often covering a range of 1100 eV.



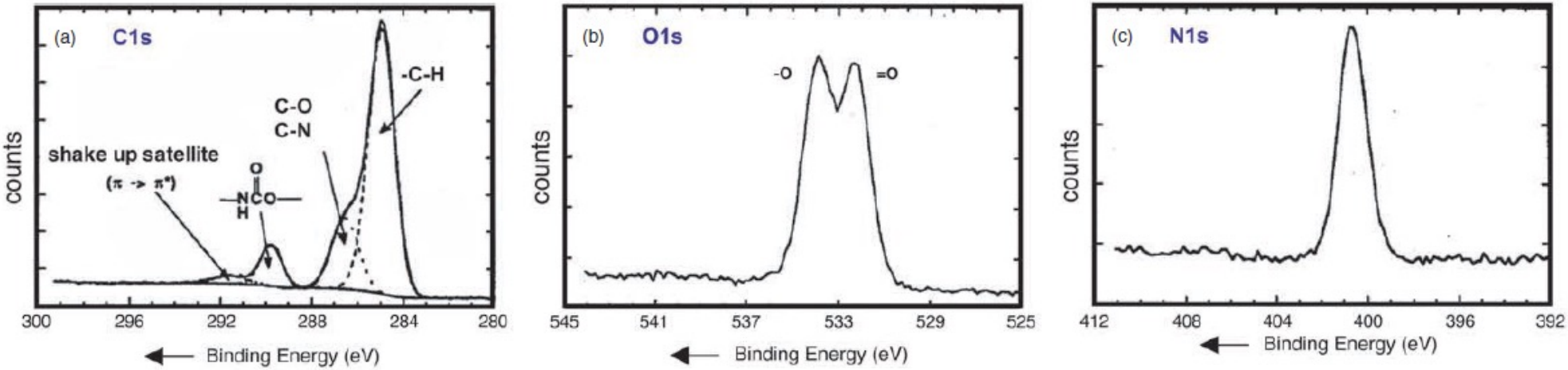
The ESCA survey scan of a hard-segment polyurethane

More detail scans
-> Oxygen
-> Carbon
-> Nitrogen

Electron Spectroscopy for Chemical Analysis

Spectral Features

Looking in more detail over smaller ranges (perhaps 20 eV) at specific features found in the wide scan spectrum

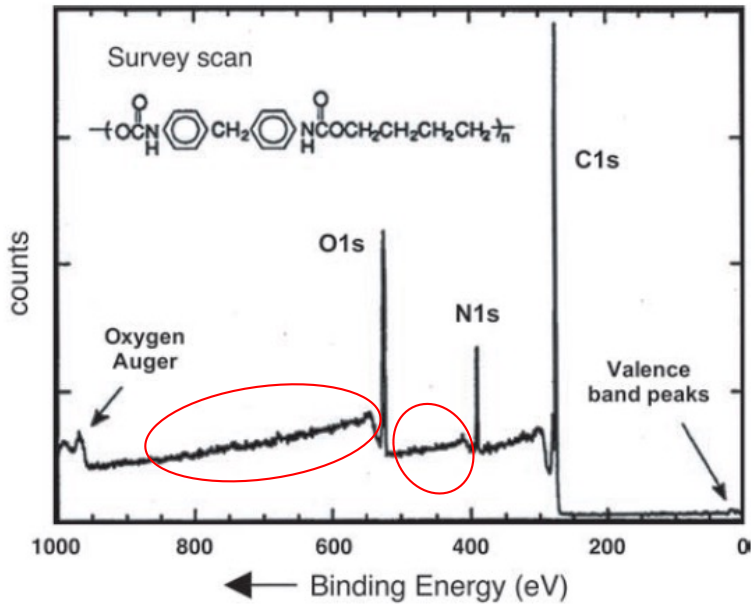


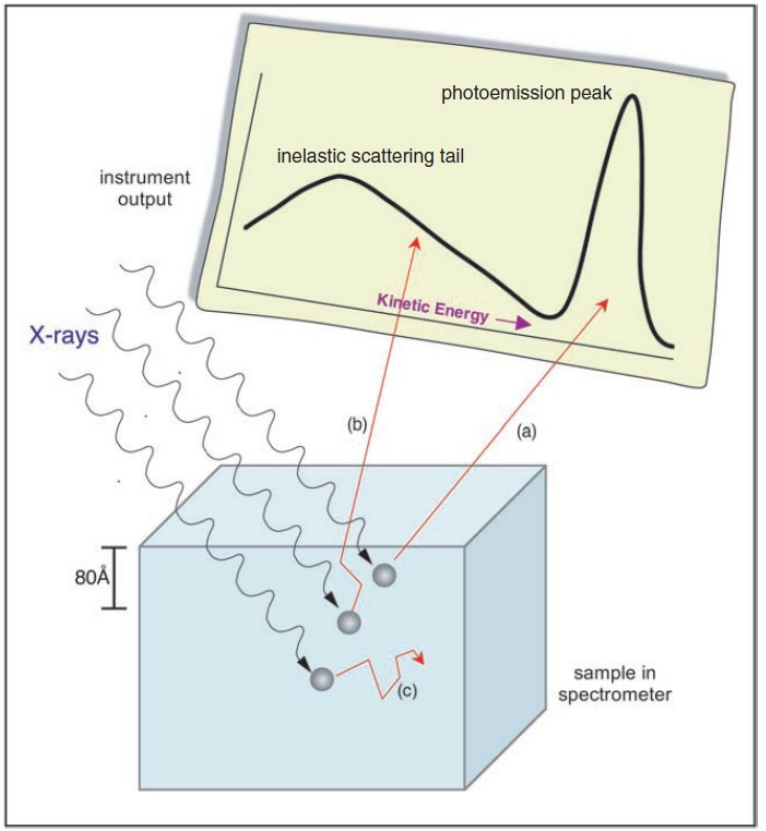
- From the Einstein equation, it is apparent that we could also plot it in terms of KE
- The KE of the emitted photoelectron is a precisely measured value. The binding energy is a calculated value computed from the KE
- The binding energy is a calculated value computed from the KE, the energy of the X-ray photon, the work function of the surface, and a correction term due to electrical charge accumulation on the surface.

Electron Spectroscopy for Chemical Analysis

Spectral Features

The background



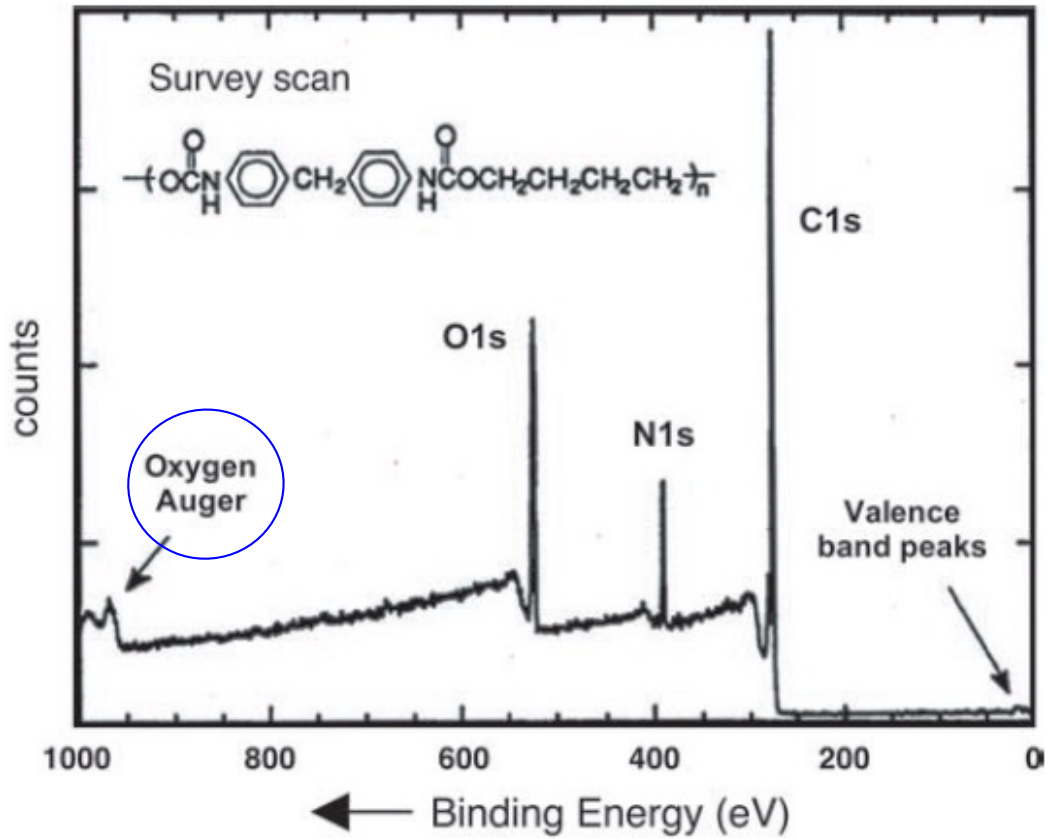


The number of counts attributed to the background will typically first increase abruptly and then decrease slowly with increasing binding energy (decreasing kinetic energy) above the photoemission peak → inelastic scattering

Electron Spectroscopy for Chemical Analysis

Spectral Features

The background



- Photoemission peaks associated with **core-level photoionization** events and X-ray-induced **Auger electron emission** peaks.
- If binding energy referencing has been performed, peaks can be readily identified from their positions using **tabulations** of binding energy values

Electron Spectroscopy for Chemical Analysis

Spectral Features

Table 3.5 Select photoelectron binding energies (eV) and Scofield photoemission cross-sections from [62][a] with permission from John Wiley & Sons, Ltd.

Element	1s	2s	$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$
C	284 [1.00]															
N	399 [1.80]															
O	532 [2.93]	24 [0.141]														
F	686 [4.43]	31 [0.210]														
Al		118 [0.753]	73 [0.181]	73 [0.356]												
Si		149 [0.955]	100 [0.276]	99 [0.541]												
P		189 [1.18]	136 [0.430]	135 [0.789]	16 [0.112]											
S		229 [1.43]	165 [0.567]	164 [1.11]	16 [0.147]											
Ti		564 [3.24]	461 [2.69]	455 [5.22]	59 [0.473]	34 [0.276]	34 [0.537]									
Cu		1096 [5.46]	951 [8.66]	932 [16.73]	120 [0.957]	74 [0.848]	74 [1.63]									
Ag					717 [2.93]	602 [4.03]	571 [8.06]	373 [7.38]	367 [10.66]	95 [0.644]	62 [0.700]	56 [1.36]				
I					1072 [3.53]	931 [5.06]	875 [10.62]	631 [13.77]	620 [19.87]	186 [0.959]	123 [1.11]	123 [2.23]	50 [1.69]	50 [2.44]		
Au										759 [1.92]	644 [2.14]	546 [5.89]	352 [8.06]	334 [11.74]	87 [7.54]	84 [9.58]

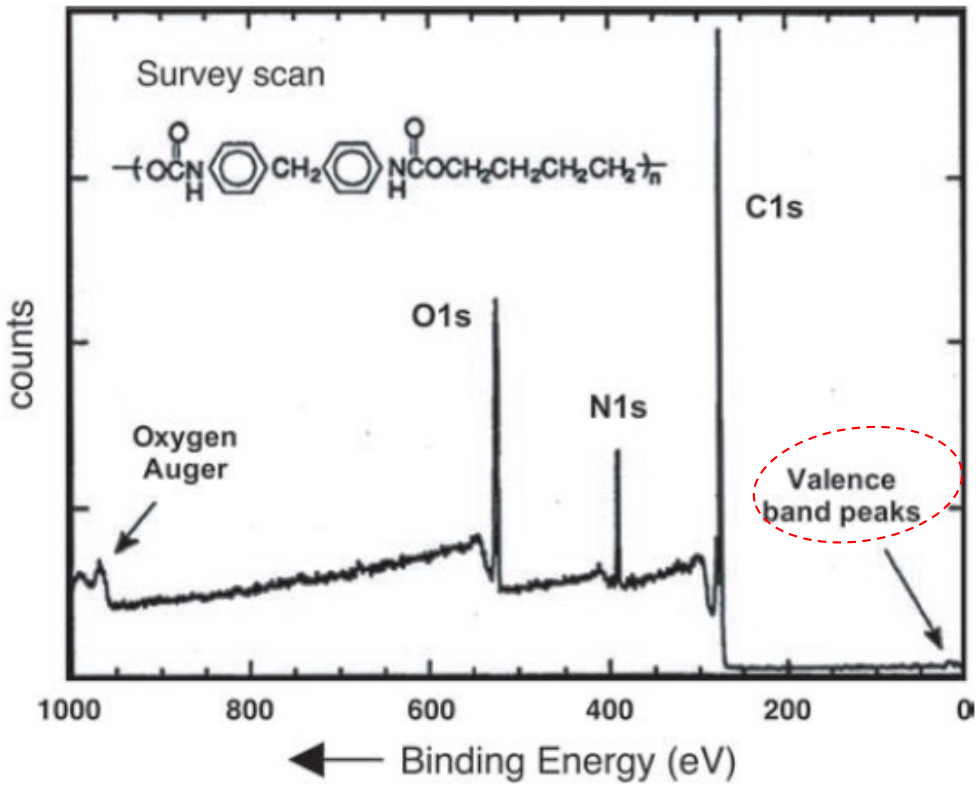
[a] Cross-sections listed in brackets.

The binding energies of photoemission lines produced with Al Kα irradiation (1486.6 eV)

Electron Spectroscopy for Chemical Analysis

Spectral Features

The background

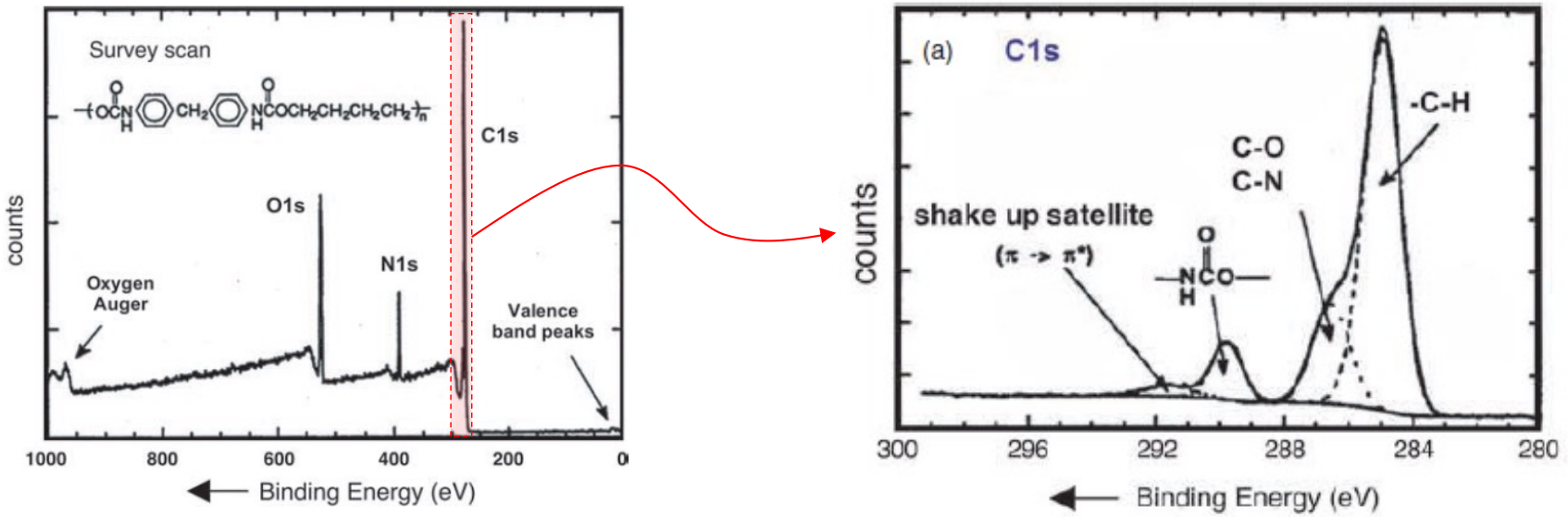


- The final feature to be discussed in thiswide scan spectrum is observed at low binding energies. The low-intensity features seen between 0 and 30 eV are due to photoemission of valence (outer shell) electrons
- Interpretation of these spectral features is often more complex than the core-level lines -> we will discuss this later.

Electron Spectroscopy for Chemical Analysis

Spectral Features

Additional Detail in the high-resolution ESCA spectra



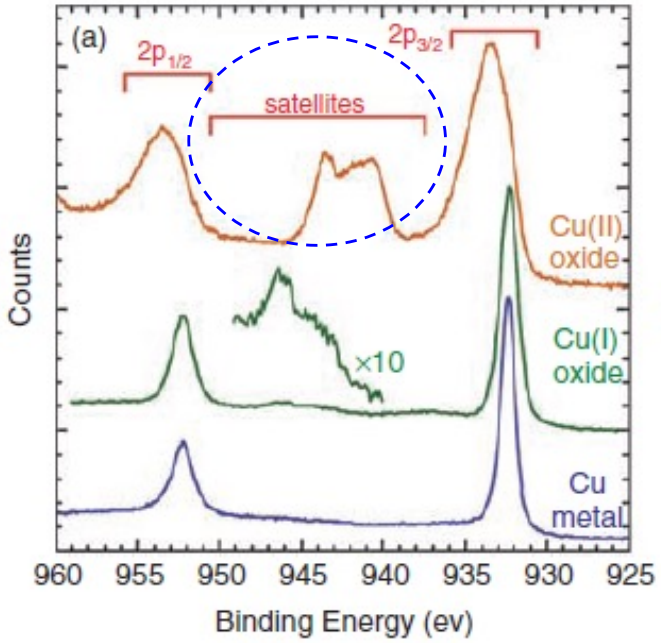
- From the peak shape, it is apparent that this spectrum is composed of a number of subpeaks. These subpeaks, attributed to chemical shifts from atoms and groups bound to the carbons
- Another feature is noted at 6.6 eV from the lowest binding energy (hydrocarbon) peak. This peak is referred to as a shake-up satellite. It represents photoelectrons that have lost energy through promotion of valence electrons from an occupied energy level (e.g. a π level) to an unoccupied higher level (e.g. a $\pi*$ level).

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Shake-up peaks"

- Shake-up peaks (also called 'loss peaks' because intensity is lost from the primary photoemission peak) are most apparent for systems with aromatic structures, unsaturated bonds or transition metal ions



Examples of the Cu_2O and CuO shake-up satellites

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Shake-off peak"

- If the departing photoelectron transfers sufficient energy into the valence electron to ionize it into the continuum, the photoemission loss peak is called a 'shake-off' peak

- The shake-off satellite peaks of the photoemission peak can have a wide range of possible energies (of course, always with a lower KE than the photoemission peak)

- This energetically broad feature is typically hidden within the background signal and is usually not detected or used analytically

Electron Spectroscopy for Chemical Analysis

"Shake-up" vs. "Shake-off"

1. Shake-up: Excitation of Another Electron

What happens?

1. An incident X-ray ejects a core electron (photoelectron).
2. The sudden creation of a core hole causes another electron, typically a valence electron, to become excited.
3. This electron moves to a higher, previously unoccupied energy level but remains bound to the atom or material.
4. Some energy is used for this excitation, reducing the photoelectron's kinetic energy.

XPS consequence:

A shake-up satellite peak appears at a higher apparent binding energy than the main photoelectron peak.

Example: CuO exhibits prominent shake-up satellite features in its Cu 2p XPS spectrum, associated with its electronic structure and Cu^{2+} states.

Electron Spectroscopy for Chemical Analysis

"Shake-up" vs. "Shake-off"

2. Shake-off: Complete Ejection of Another Electron

What happens?

1. An incident X-ray ejects a core electron.
2. The sudden change in the electronic potential causes another electron to be emitted into an unbound state.
3. Consequently, two electrons are emitted: the primary photoelectron and the shake-off electron.
4. Additional energy is required for the second electron to escape, reducing the kinetic energy of the primary photoelectron.

XPS consequence:

Shake-off typically produces broad satellite features or a continuous intensity distribution at higher apparent binding energies.

Electron Spectroscopy for Chemical Analysis

"Shake-up" vs. "Shake-off"

3. Comparison of Shake-up and Shake-off

Feature	Shake-up	Shake-off
Electron behavior	Excited to a higher energy level	Completely ejected
Final electronic state	Bound excited state	Ionized state
Additional electron emission	No	Yes
XPS spectral feature	Often a distinct satellite peak	Often a broad satellite or continuum
Apparent binding energy	Higher than main peak	Higher than main peak
Energy consumption	Electronic excitation energy	Additional ionization energy

Electron Spectroscopy for Chemical Analysis

"Shake-up" vs. "Shake-off"

4. Why Do Shake-up and Shake-off Appear at Higher Binding Energies?

The fundamental XPS equation is: $BE = h\nu - KE - \phi$

- BE : Binding energy
- $h\nu$: Incident X-ray photon energy
- KE : Measured photoelectron kinetic energy
- ϕ : Spectrometer work function

During shake-up or shake-off, additional energy is transferred to another electron.
Therefore,

$$\boxed{\text{Additional energy loss} \rightarrow KE \downarrow \rightarrow BE \uparrow}$$

As a result, satellite features appear on the higher binding energy side of the main photoelectron peak.

Electron Spectroscopy for Chemical Analysis

"Shake-up" vs. "Shake-off"

5. Simple Analogy



Shake-up

An electron moves to a higher floor but stays inside the building.



Shake-off

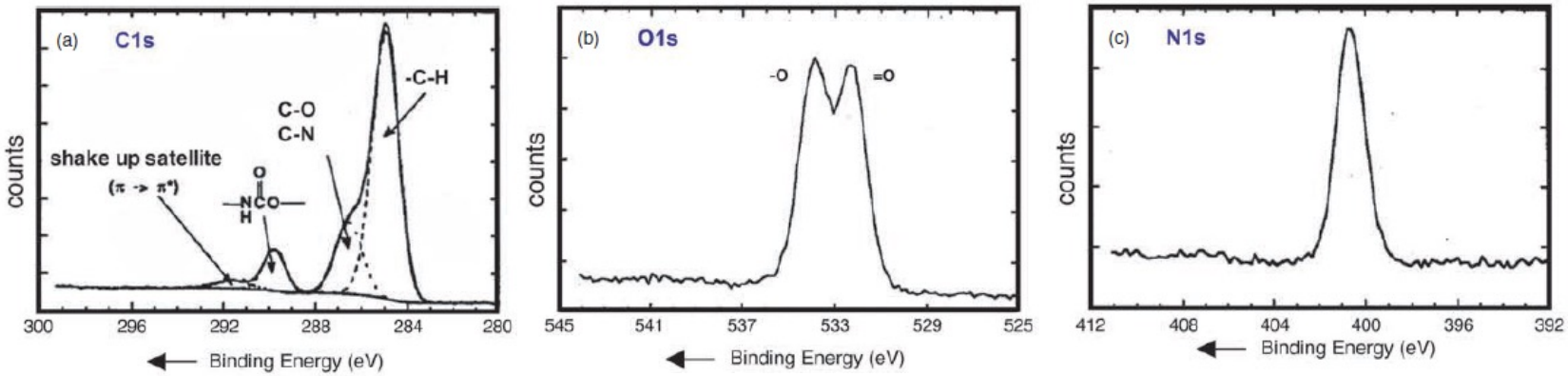
An electron leaves the building completely.

The energy required for either process reduces the kinetic energy of the primary photoelectron.

Electron Spectroscopy for Chemical Analysis

Spectral Features

- High-resolution spectra of each of the features found in the wide scan spectrum are examined to extract maximum information.



- The information from a complete dataset should be collaborative and not contradictory

- For example, where significant levels of oxygen are seen in a wide scan spectrum of an organic polymer, subpeaks associated with carbons bound to oxygen should be found in the high-resolution C_{1s} spectrum

- The subpeaks in the O1s spectrum should also have binding energies appropriate for oxygen – carbon functionalities

Electron Spectroscopy for Chemical Analysis

Spectral Features

About inorganic systems

⟶ Spin – orbit doublets, Multiplet splitting, Plasmon losses

What Is Spin – Orbit Splitting?

- Spin – orbit splitting occurs because of the interaction between an electron's orbital angular momentum and its intrinsic spin angular momentum.
- This interaction causes an electronic energy level to split into two states with slightly different energies, producing two peaks in an XPS spectrum, known as a spin – orbit doublet.

The total angular momentum quantum number (j) is given by: $\boxed{j = l \pm \frac{1}{2}}$

where:

- l: Orbital angular momentum quantum number
- $s = 1/2$: Electron spin quantum number
- j: Total angular momentum quantum number

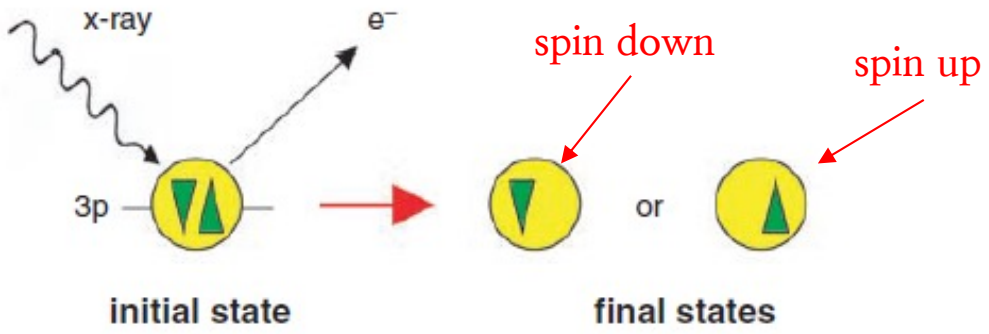
For orbitals with $l > 0$, two possible values of j exist.

Electron Spectroscopy for Chemical Analysis

Spectral Features

Formation of Spin – Orbit Doublets

"Spin – orbit doublets"



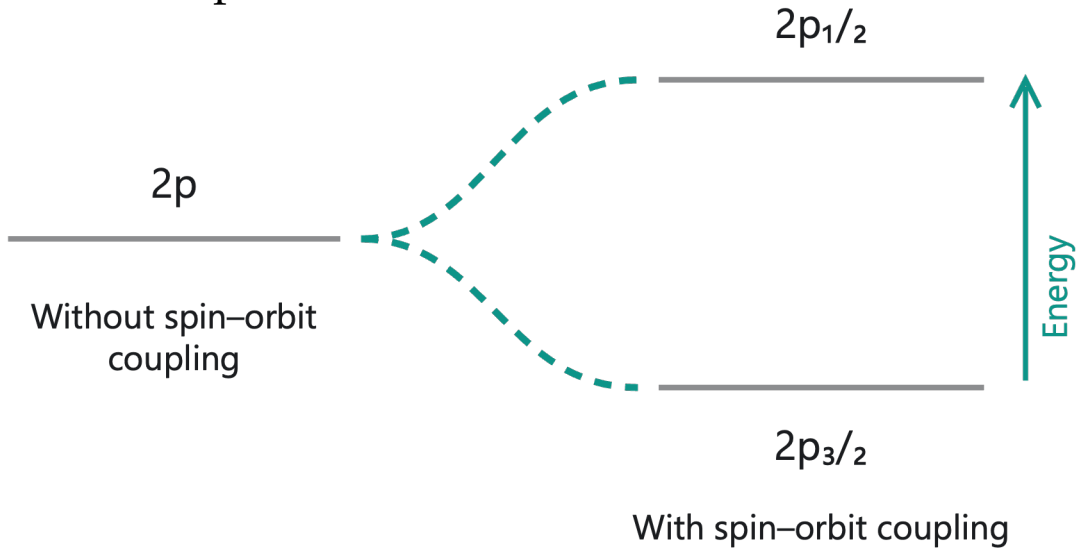
- The initial state and final states (after photoemission) for a pair of electrons in a 3p orbital

- Two energetically equivalent final states are possible, '**spin up**' or '**spin down**'

Electron Spectroscopy for Chemical Analysis

Spectral Features

Formation of Spin – Orbit Doublets



Schematic illustration of the splitting of a 2p energy level into $2p_{3/2}$ and $2p_{1/2}$ states.

For a p orbital ($l = 1$):

$$j = 1 + \frac{1}{2} = \frac{3}{2}$$

$$j = 1 - \frac{1}{2} = \frac{1}{2}$$

the 2p level splits into:

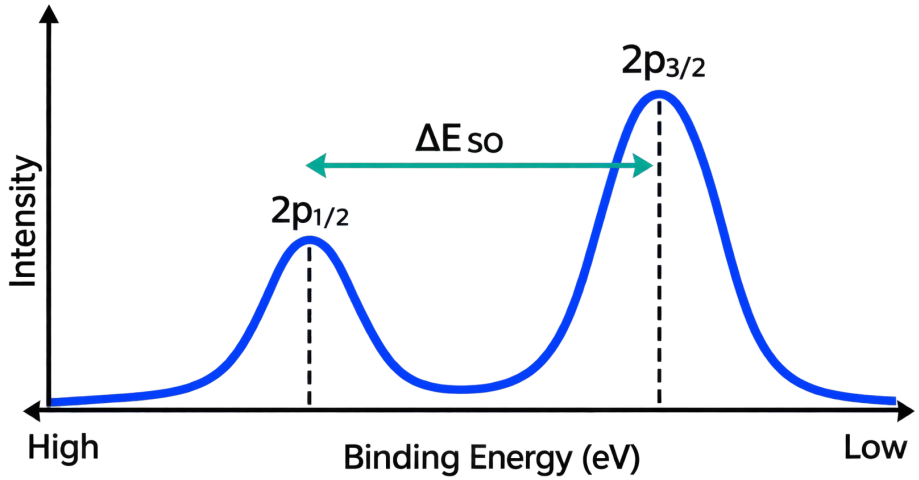
- $2p_{3/2}$: Lower binding energy
- $2p_{1/2}$: Higher binding energy

The energy difference between these two states is called the spin – orbit splitting energy (ΔE_{SO})

Electron Spectroscopy for Chemical Analysis

Spectral Features

Spin – Orbit Doublets in XPS Spectra



Schematic XPS spectrum of a 2p spin – orbit doublet

Important characteristics:

1. Two peaks originate from the same core-level orbital.
2. The peaks appear at different binding energies.
3. Their energy separation is characteristic of the element and core level.
4. Their relative intensities are determined approximately by the degeneracy of the corresponding states.

Electron Spectroscopy for Chemical Analysis

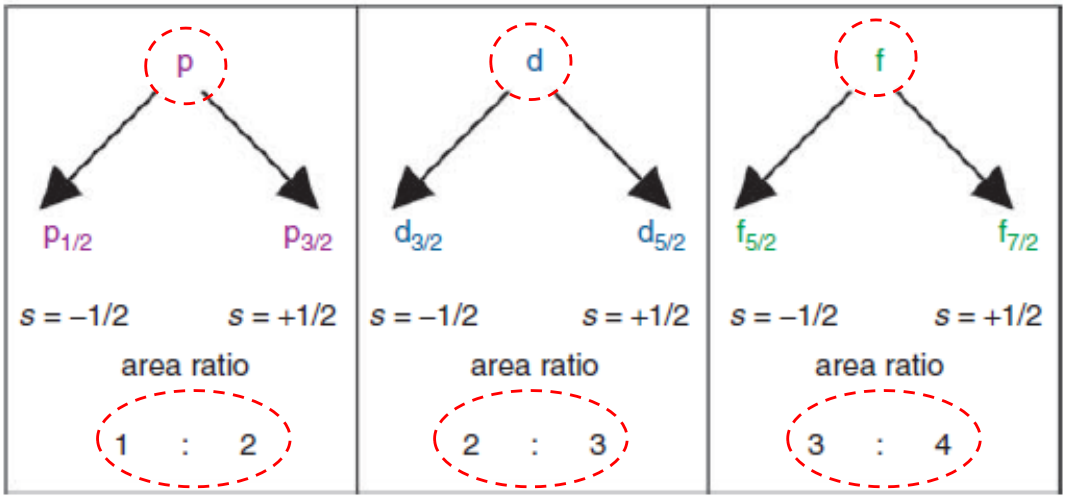
Spectral Features

Relative Peak Intensities

- If there is an open shell (quantum number $l > 0$, i.e. p, d, or f orbital) with two states of the same energy (orbital degeneracy), a magnetic interaction between the spin of the electron (up or down) and its orbital angular momentum may lead to a splitting of the degenerate state into two components

- This is called spin – orbit coupling or j – j coupling (j quantum number = l + s)

- The ratio of their respective degeneracies, $2j + 1$, determines the intensities of the components



Electron Spectroscopy for Chemical Analysis

Spectral Features

"Spin – orbit doublets"

Example, the $f_{5/2}$ and $f_{7/2}$ components of a gold 4f photoemission peak

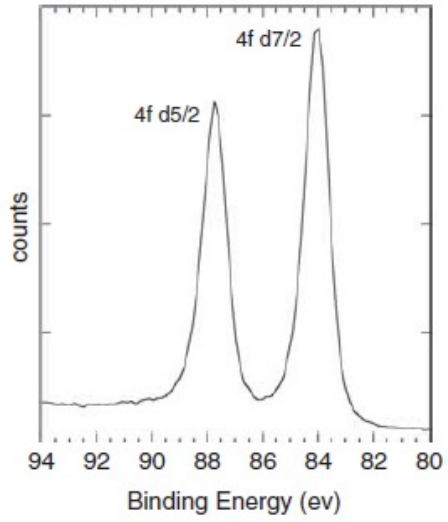


Figure 3.13 Spin–orbit coupling leads to a splitting of the gold 4f photoemission line into two subpeaks

The total 4f photoemission intensity for gold as used in quantitation is the sum of the two spin – orbit peaks. The trend for the doublet separation is p 〉 d 〉 f within a given atom.

Electron Spectroscopy for Chemical Analysis

Spectral Features

1. What Is Multiplet (electrostatic) splitting?

- Multiplet splitting occurs when an unpaired electron in an atom interacts electrostatically with the core hole created during photoemission.
- This interaction produces several possible final electronic states with slightly different energies, resulting in multiple peaks in an XPS spectrum.
- Multiplet splitting is particularly important in transition-metal compounds containing partially filled d orbitals, such as Mn, Fe, Co, and Ni oxides.

2. How Does Multiplet Splitting Occur?

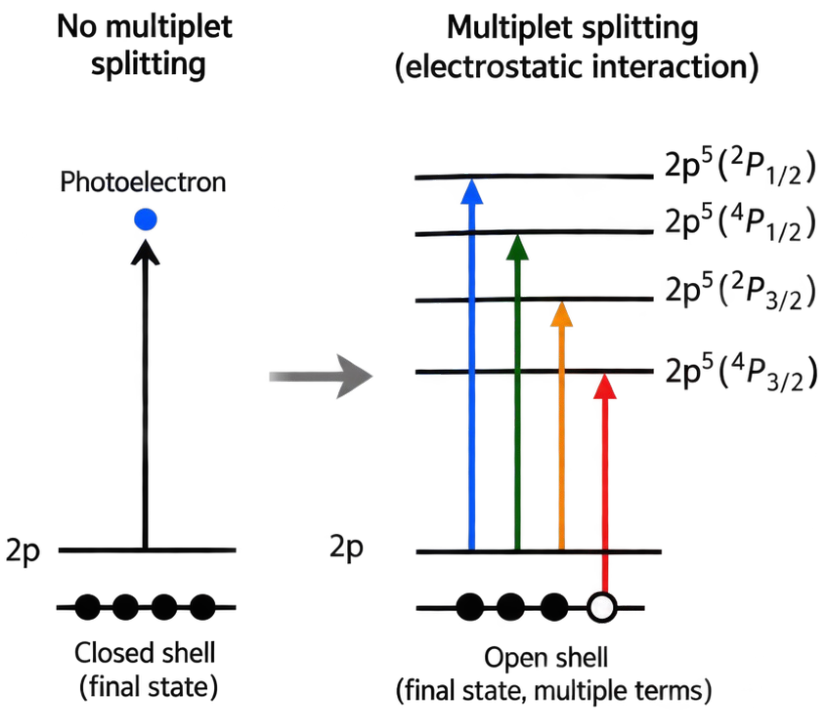
1. An incident X-ray ejects a core electron.
2. A core hole is created in the atom.
3. The remaining core and valence electrons interact through electrostatic and exchange interactions.
4. Different arrangements and couplings of the electrons produce multiple final states.
5. Each final state has a different energy, giving rise to multiple XPS peaks.

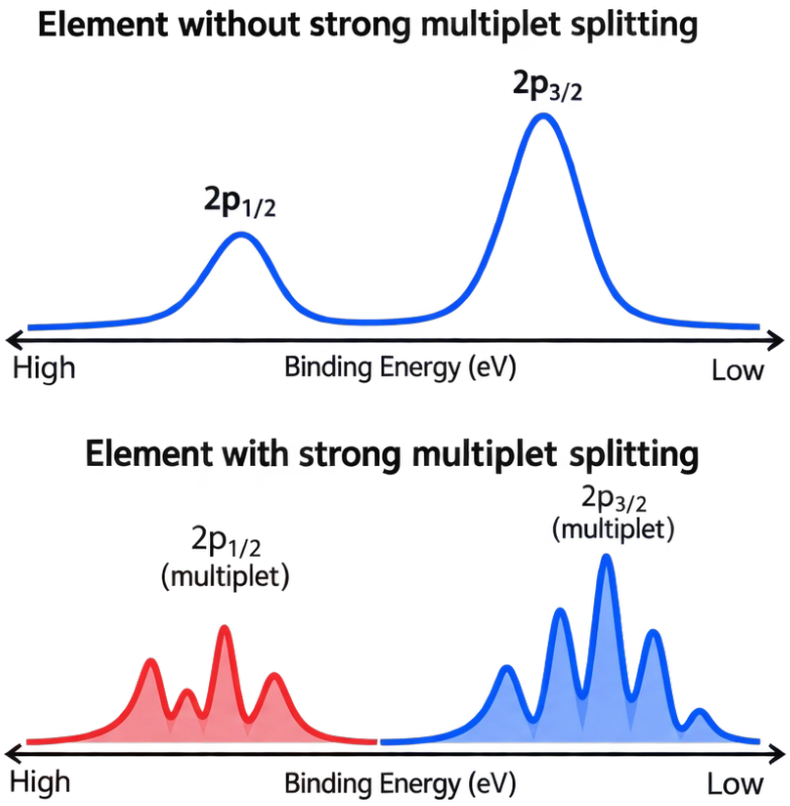
Key concept: One core-level photoemission process can produce several peaks because multiple final electronic states are possible.

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Multiplet (electrostatic) splitting"





Electron Spectroscopy for Chemical Analysis

Spectral Features

3. Multiplet Splitting vs. Spin – Orbit Splitting

Feature	Spin – Orbit Splitting	Multiplet Splitting
Main origin	Interaction between orbital and spin angular momentum	Electron – electron electrostatic and exchange interactions
Electronic structure	Core levels with nonzero orbital angular momentum	Especially important for open-shell atoms and ions
Spectral features	Typically a doublet	Multiple peaks or complex peak structures
Examples	Au 4f, Cu 2p	Mn 2p, Fe 2p, Ni 2p
Main significance	Core-level identification	Information about oxidation and electronic states

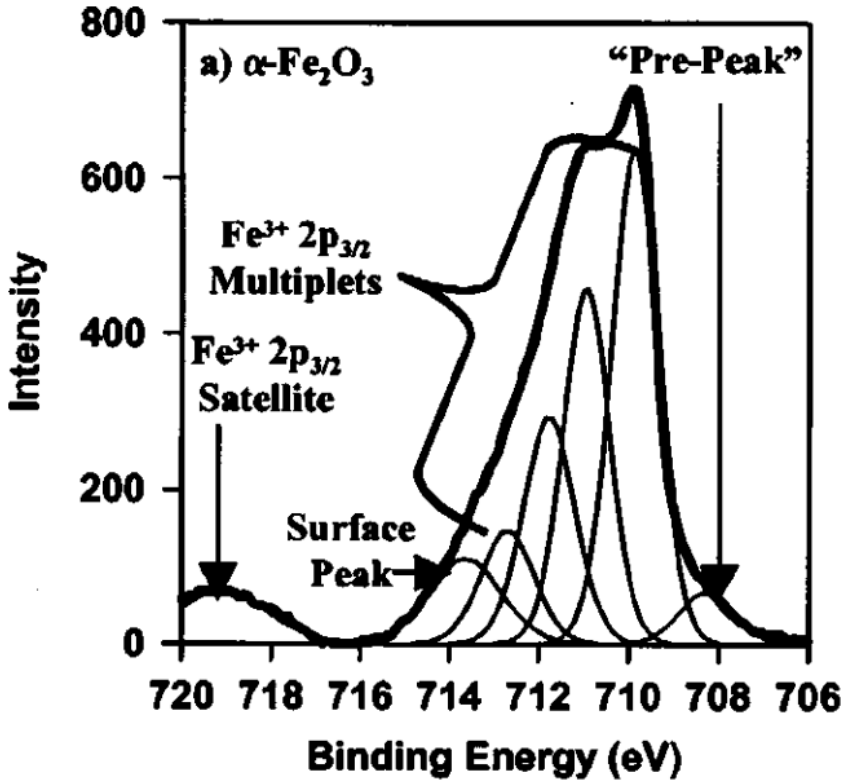
Importantly, spin – orbit and multiplet splitting can occur simultaneously, producing complex XPS spectra.

Electron Spectroscopy for Chemical Analysis

Spectral Features

Multiplet Splitting in Transition-Metal 2p XPS

Example: Fe_2O_3 (Fe^{3+})



Reference: Grosvenor et al., Surface and Interface Analysis 36, 1564 – 1574 (2004).

Origin of Multiplet Splitting

- Following Fe 2p photoemission, the 2p core hole interacts with unpaired Fe 3d electrons. Electrostatic and exchange interactions generate multiple final states with different energies.

Experimental Features

- The Fe $2p_{3/2}$ envelope contains several overlapping multiplet components. For α -Fe_2O_3, reported fitting components occur near 709.8, 710.7, 711.4, and 712.3 eV. Additional satellite structures must be distinguished from multiplet splitting.

Electron Spectroscopy for Chemical Analysis

Spectral Features

1. What Are Plasmon Losses?

- Plasmon losses occur when a photoelectron transfers part of its kinetic energy to the collective oscillation of electrons in a material.
- These collective electron oscillations are called plasmons.
- As a result, the photoelectron loses kinetic energy, producing additional peaks at higher apparent binding energies in the XPS spectrum.

Key concept: Plasmon losses are energy-loss features caused by collective electronic excitations, rather than additional chemical states.

2. How Do Plasmon Losses Occur?

1. An incident X-ray ejects a core electron from an atom.
2. The photoelectron travels through the material toward the surface.
3. The photoelectron can excite collective oscillations of electrons (plasmons).
4. Energy is transferred from the photoelectron to the plasmon.
5. The photoelectron reaches the detector with reduced kinetic energy.

The energy loss is approximately: $\Delta E_{\text{loss}} = \hbar\omega_p$

where $\hbar\omega_p$ is the plasmon angular frequency.

A photoelectron can excite one or more plasmons, producing a series of loss features.

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Plasmon losses"

- Characteristic **collective vibrations** have been noted for this continuum of electrons and are referred to as plasmon vibrations

- In some cases, the exiting photoelectron can couple with the plasmon vibrations leading to characteristic, periodic energy losses

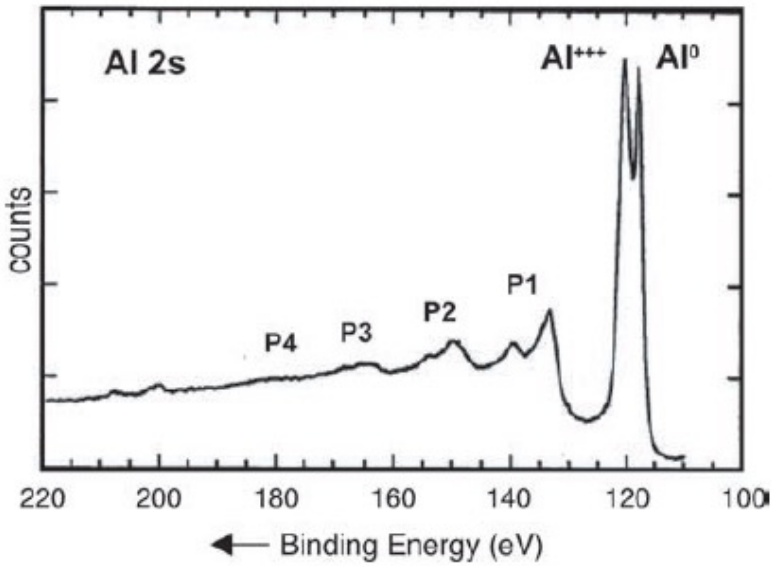


Figure 3.14 Plasmon loss peaks for the aluminum 2s photoemission peak

Electron Spectroscopy for Chemical Analysis

Spectral Features

A feature that is associated with the type of instrument is the **X-ray satellite**

Table (below) summarizes all features that are important both to understand the spectra obtained, and for enhancing the information content of the ESCA experiment

Table 3.10 Features observed in ESCA spectra

1. Photoemission peaks
   - Narrow
   - Nearly symmetric
   - Shifted by chemistry
   - Contain vibrational fine structure
2. X-ray satellite peaks
   - Not observed with a monochromatized source
   - Always the same energy shift from the photoemission peak
3. Shake-up satellites and shake-off satellites[a]
4. Photon-enduced Auger lines
5. Inelastic scattering background[a]
6. Valence band features
7. Spin–orbit coupling
8. Multiplet splitting
9. Plasmon loss peaks[a]

[a]Loss process.

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