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

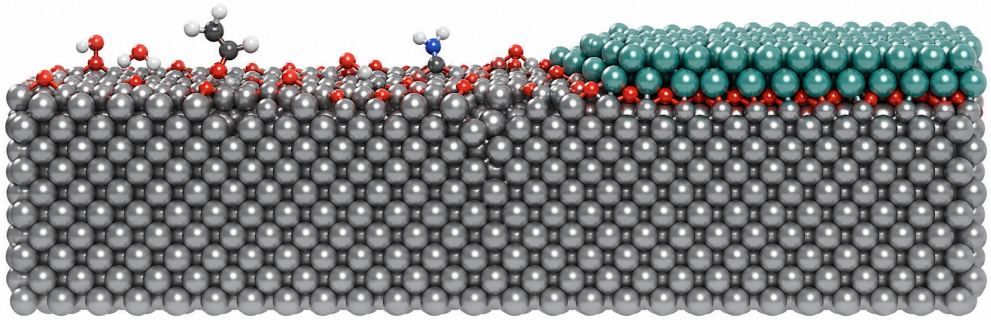
Electron Spectroscopy for Chemical Analysis

Why surfaces dominate materials performance

Reactions begin where atoms meet gases, l
iquids, electrodes, or another solid.

A native oxide, adsorbate, defect, or ultr
hin coating can control the behavior of
he whole device.

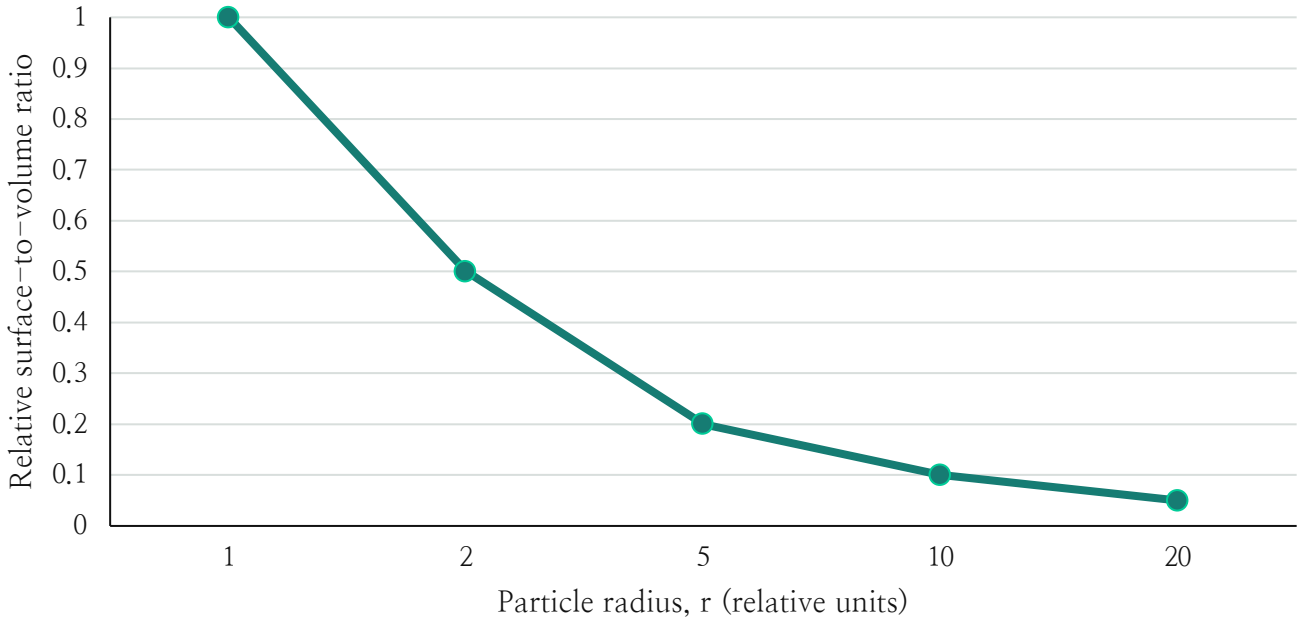
Nanomaterials amplify this effect becaus
their surface–to–volume ratio is large.



Surface chemistry can differ sh
arply from bulk composition.

Surface-to-volume scaling at the nanoscale

For a spherical particle, surface area scales with r^2 while volume scales with r^3. Therefore, S/V = 3/r.



Smaller particles expose more surface per unit volume.

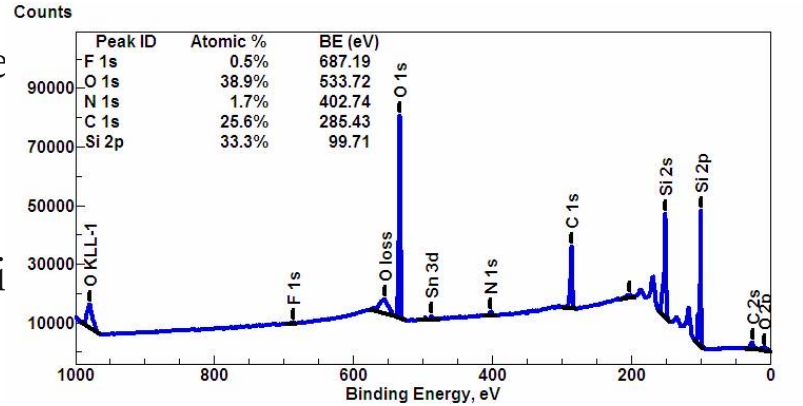
What ESCA measures

ESCA is X-ray photoelectron spectroscopy (XPS).

A known X-ray photon energy excites core-level electrons.

The analyzer measures electron kinetic energy.

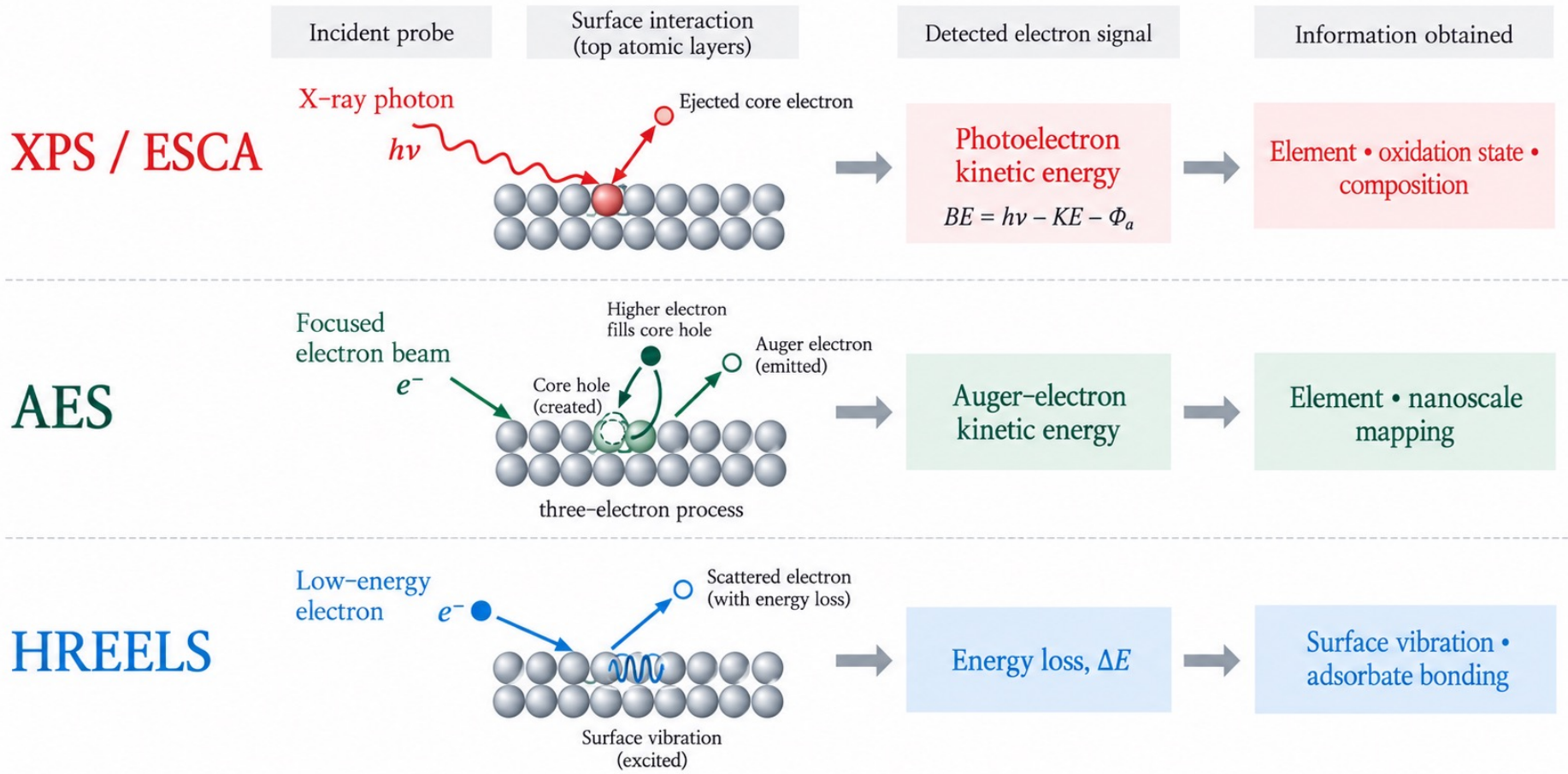
The spectrum reports elemental identity, chemical state, and surface composition.



A survey spectrum records photoelectron intensity across a broad binding-energy range.

Electron Spectroscopy for Chemical Analysis

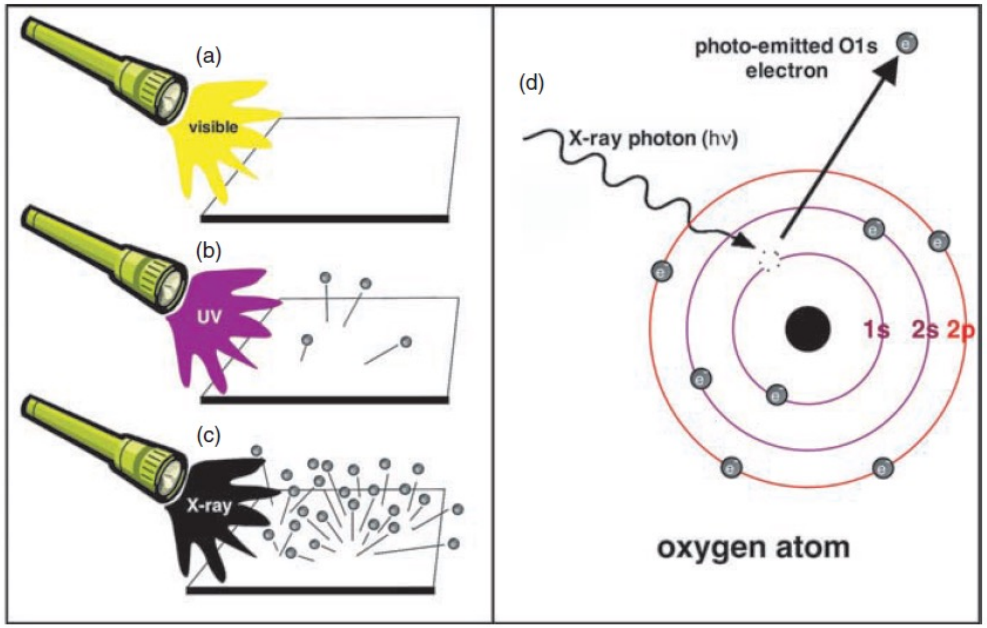
Electron spectroscopies for surface analysis



Same strategy: measure electron energy. Different excitation and energy-transfer pathways reveal different surface properties.

Electron Spectroscopy for Chemical Analysis

Basic ESCA experiment



Place the specimen in vacuum.

Irradiate the surface with mono chromatic X-rays.

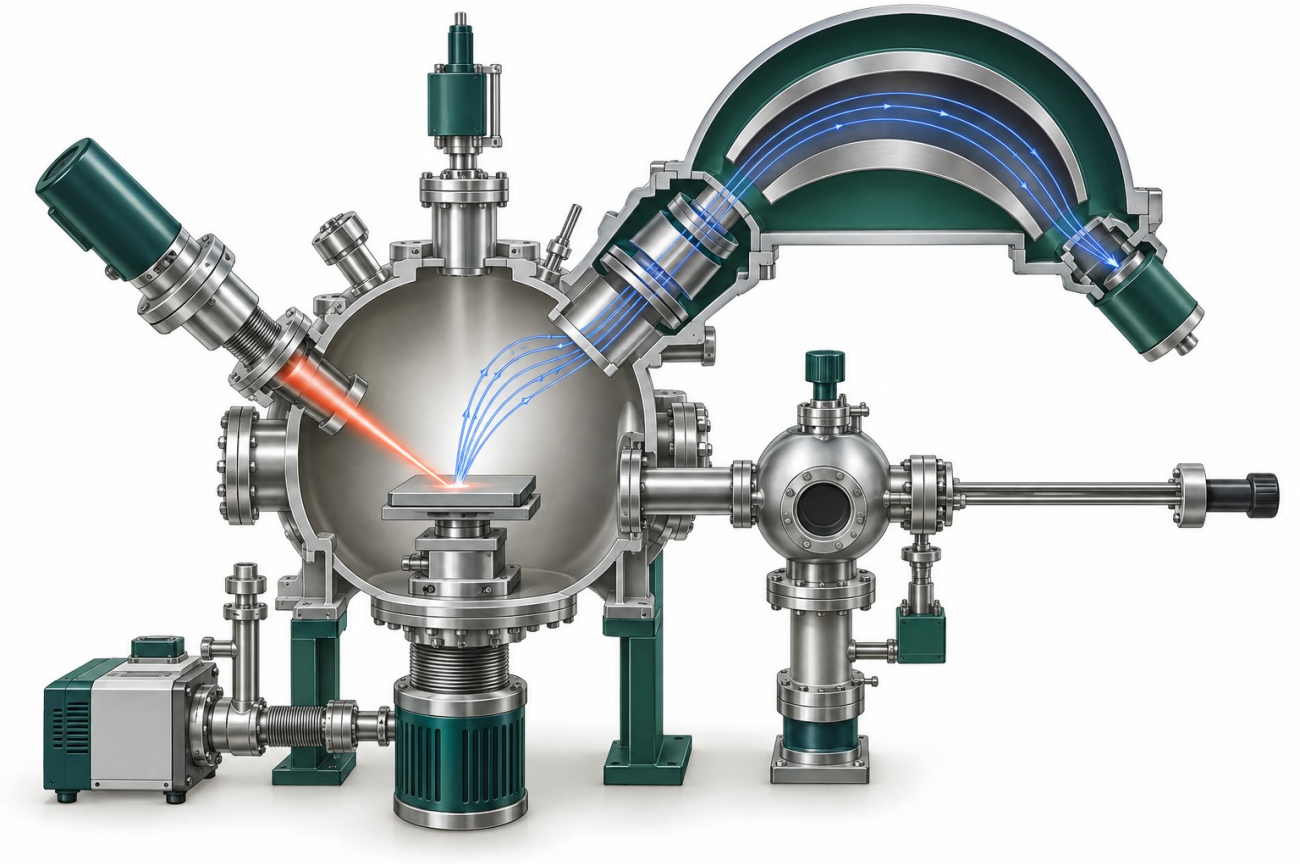
Collect emitted photoelectrons and separate them by kinetic e nergy.

Count electrons to form a spect rum.

Only X-rays carry enough energy to eject deep core-level electrons.

Electron Spectroscopy for Chemical Analysis

The XPS measurement chain



1 X-ray source

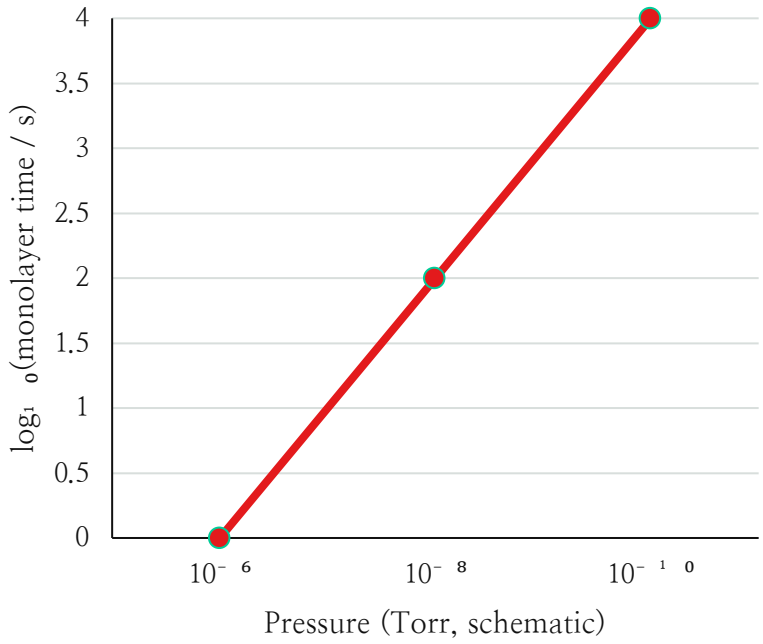
2 UHV chamber and sample stage

3 Electrostatic lens

4 Hemispherical anal yzer and detector

Why ultrahigh vacuum matters

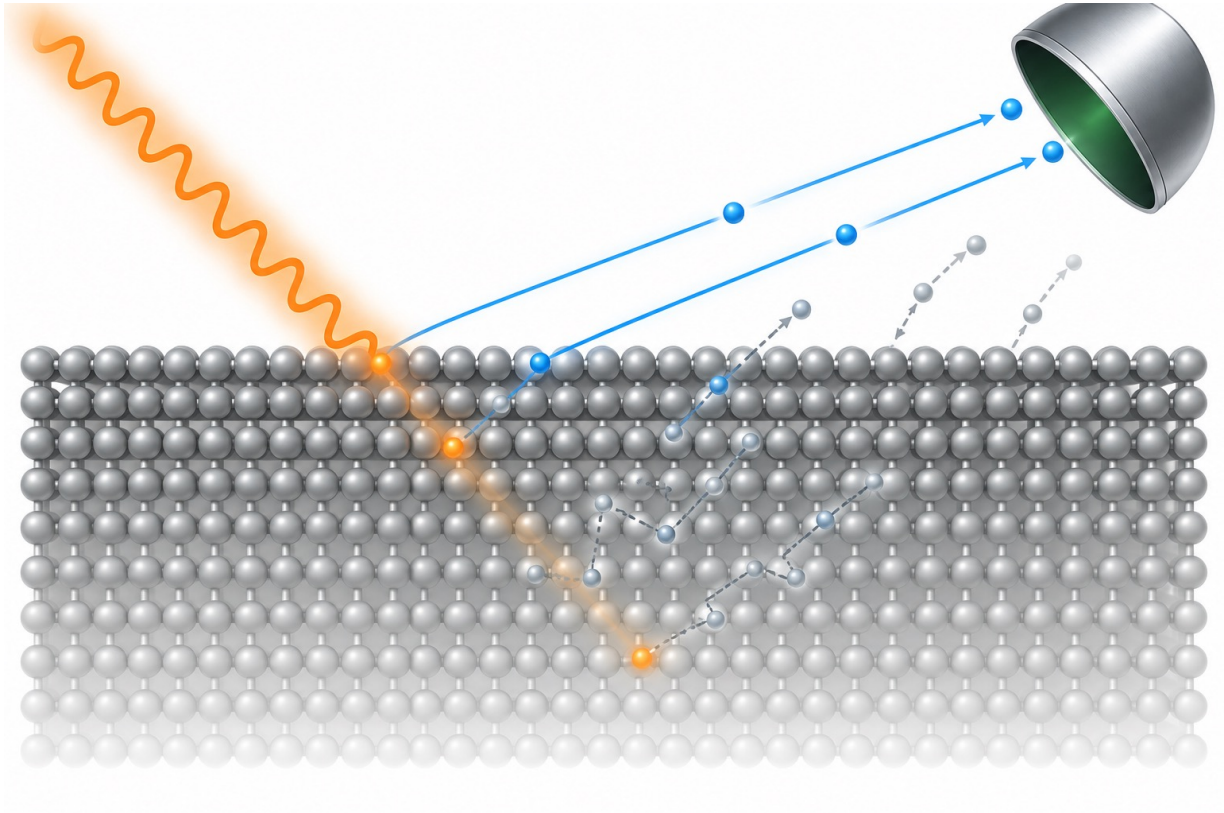
- Gas-phase collisions would scatter low-energy photoelectrons before they reach the analyzer.
- Residual gases can rapidly adsorb and change the outermost atomic layers.
- Clean-surface experiments therefore operate near 10^{-9} to 10^{-10} mbar when practical.



Approximate times: 1 s, 100 s, and 10,000 s. One Langmuir = 10^{-6} Torr·s when the sticking coefficient is near 1.

Electron Spectroscopy for Chemical Analysis

Why XPS is surface sensitive



X-rays penetrate much deeper than the detected information depth.

Only electrons that escape without inelastic energy loss contribute to a sharp photoelectron peak.

For common XPS conditions, useful information usually comes from the top few nanometers.

Information depth and emission angle

$$I(z,\ \theta) = I_0 \exp[-z/(\lambda\ \cos\ \theta)]$$

θ is measured from the surface normal.

Normal emission

Longer effective path through the solid
Greater sampling depth

Grazing emission

Shorter effective escape depth
Greater surface sensitivity

Angle-resolved XPS changes depth sensitivity without sputtering the sample.

Electron Spectroscopy for Chemical Analysis

Information provided by ESCA

Elemental identification for all elements except H and He.

Semi-quantitative surface composition after sensitivity-factor correction.

Chemical-state information from binding-energy shifts and spectral shape.

Depth trends from angle-resolved analysis or sputter profiling.

Lateral chemical maps when the instrument provides focused analysis.

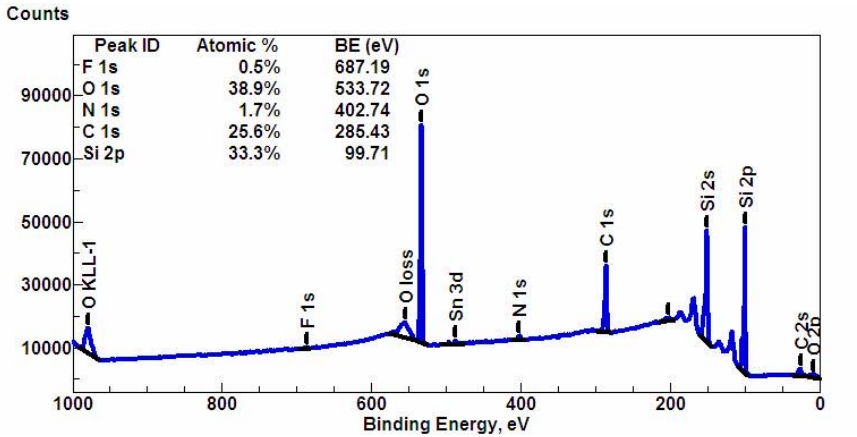
Table 3.1 Information derived from an ESCA experiment

In the outermost 10 nm of a surface, ESCA can provide the following:

- Identification of all elements (except H and He) present at concentrations >0.1 atomic %.
- Semiquantitative determination of the approximate elemental surface composition (error $< \pm 10\%$).
- Information about the molecular environment (oxidation state, covalently bonded atoms, etc.).
- Information about aromatic or unsaturated structures or paramagnetic species from shake-up ($\pi^* \rightarrow \pi$) transitions.
- Identification of organic groups using derivatization reactions.
- Non-destructive elemental depth profiles 10 nm into the sample and surface heterogeneity assessment using (1) angular-dependent ESCA studies and (2) photoelectrons with differing escape depths.
- Destructive elemental depth profiles several hundred nanometers into the sample using ion etching.
- Lateral variations in surface composition (spatial resolutions down to 5 μm for laboratory instruments and spatial resolutions down to 40 nm for sychrotron-based instruments).
- 'Fingerprinting' of materials using valence band spectra and identification of bonding orbitals.
- Studies on hydrated (frozen) surfaces.

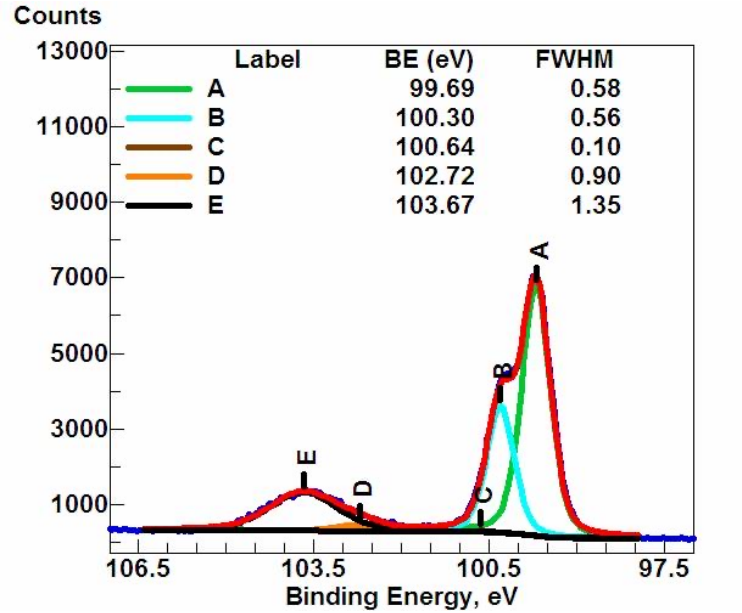
Electron Spectroscopy for Chemical Analysis

Survey scans and high-resolution scans



Survey scan

Which elements are present?



High-resolution region

Which chemical states produce the pe ak?

The photoelectric effect: Hertz and Hallwachs

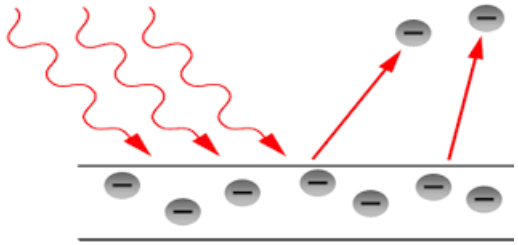
Heinrich Hertz

1880s

Heinrich Hertz observed that ultraviolet illumination m ade electrical sparks occur more readily.

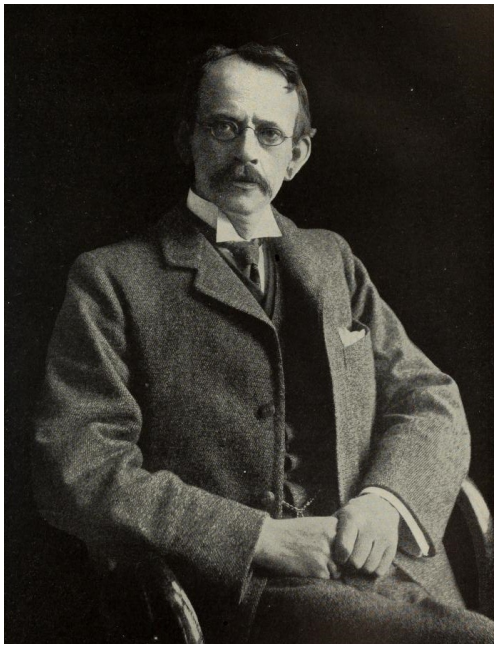
1888

Wilhelm Hallwachs showed tha t ultraviolet light discharged a n egatively charged zinc plate.



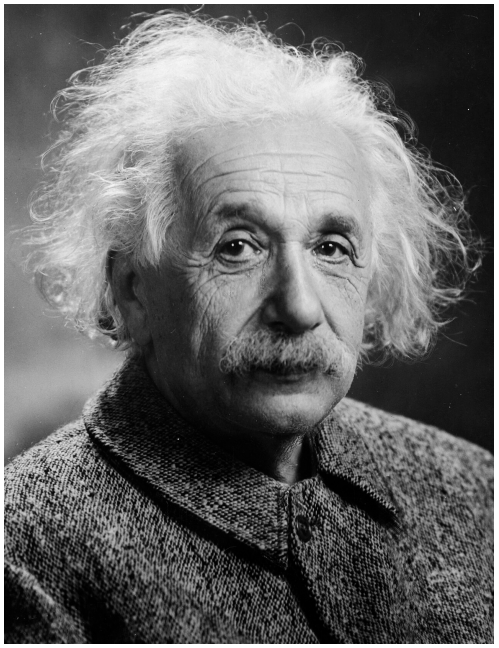
Electron Spectroscopy for Chemical Analysis

The photoelectric effect: electrons and light quanta



1899

J. J. Thomson identified the emitted particles as electrons.

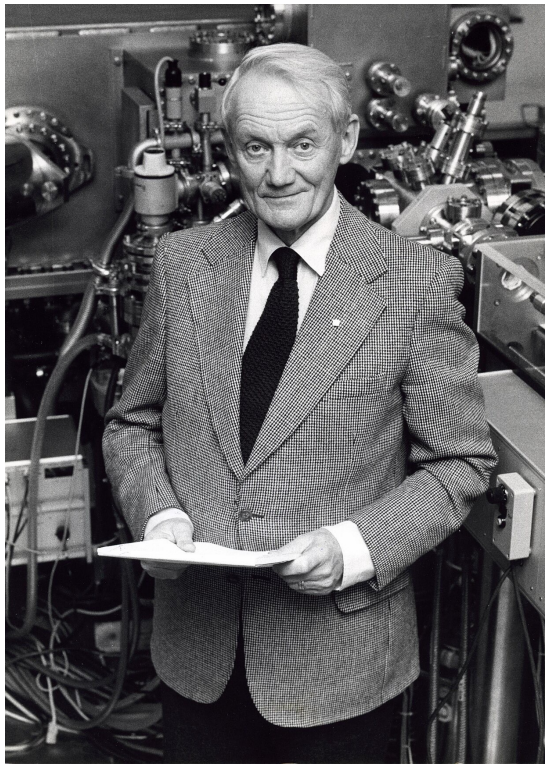


1905

Albert Einstein related electron emission to discrete photon energy.

Electron Spectroscopy for Chemical Analysis

From photoemission physics to ESCA



Kai M. Siegbahn

1914 Robinson and Rawlinson recorded the energy distribution of photoelectrons from X-ray-irradiated gold.

1950s – 1960s Kai Siegbahn developed high-resolution instrumentation and established ESCA as an analytical method.

1981 Nobel Prize in Physics

Electron Spectroscopy for Chemical Analysis

X-ray interactions with matter

1

Transmission

The photon passes t hrough without inter acting.

2

Scattering

The photon transfers only part of its energ y and changes direct ion.

3

Photoemission

The photon transfers it s energy to an electron, which can leave the at om.

ESCA uses the third outcome.

Electron Spectroscopy for Chemical Analysis

Partial and complete energy transfer

Compton scattering

A photon transfers part of its energy to an electron. The scattered photon continues with lower energy and a changed direction.

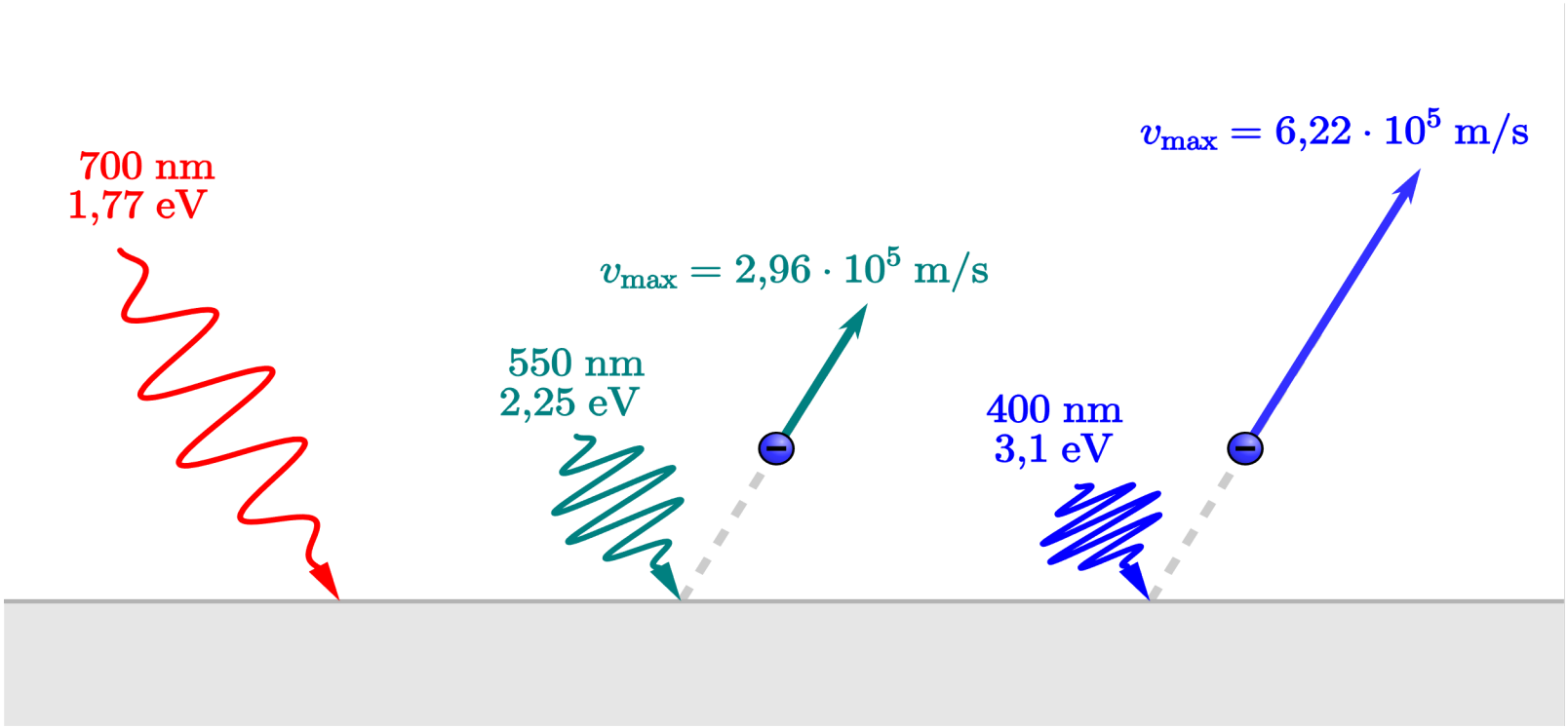
Photoemission

An electron absorbs the photon energy. If the energy exceeds the binding requirement, the electron escapes with measurable kinetic energy.

The energy analyzer converts this kinetic-energy distribution into an XPS spectrum.

Electron Spectroscopy for Chemical Analysis

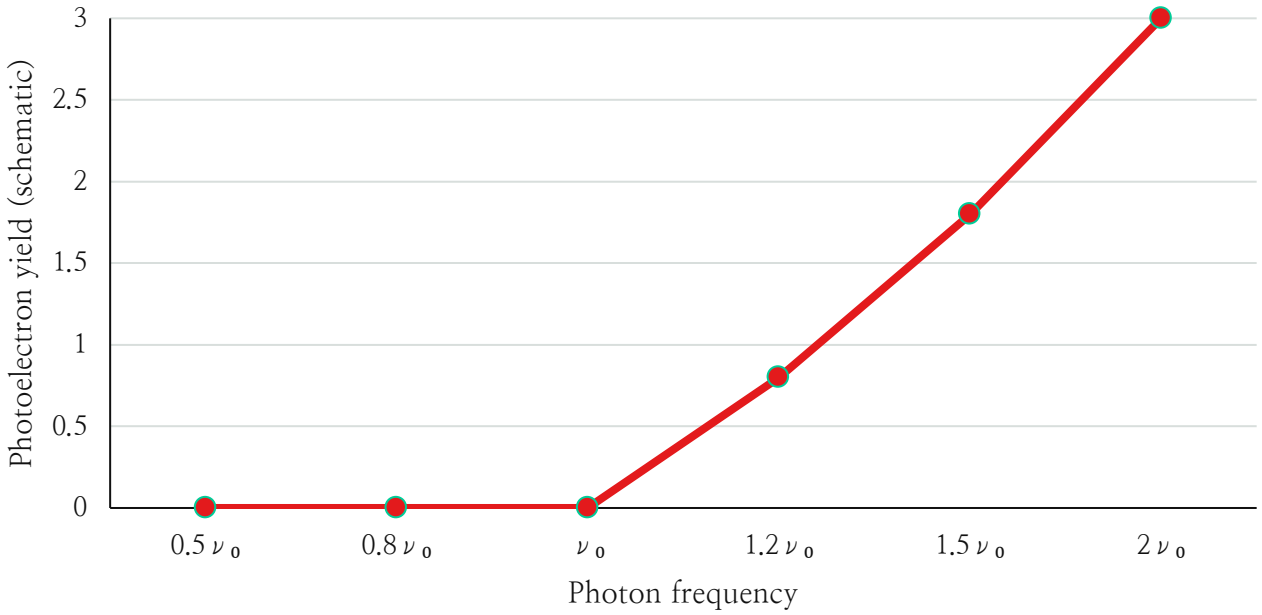
Photoemission from a bound electron



Emission requires photon energy above a threshold set by the electron bindi ng energy and the surface work function.

Photoelectric observation 1: threshold frequency

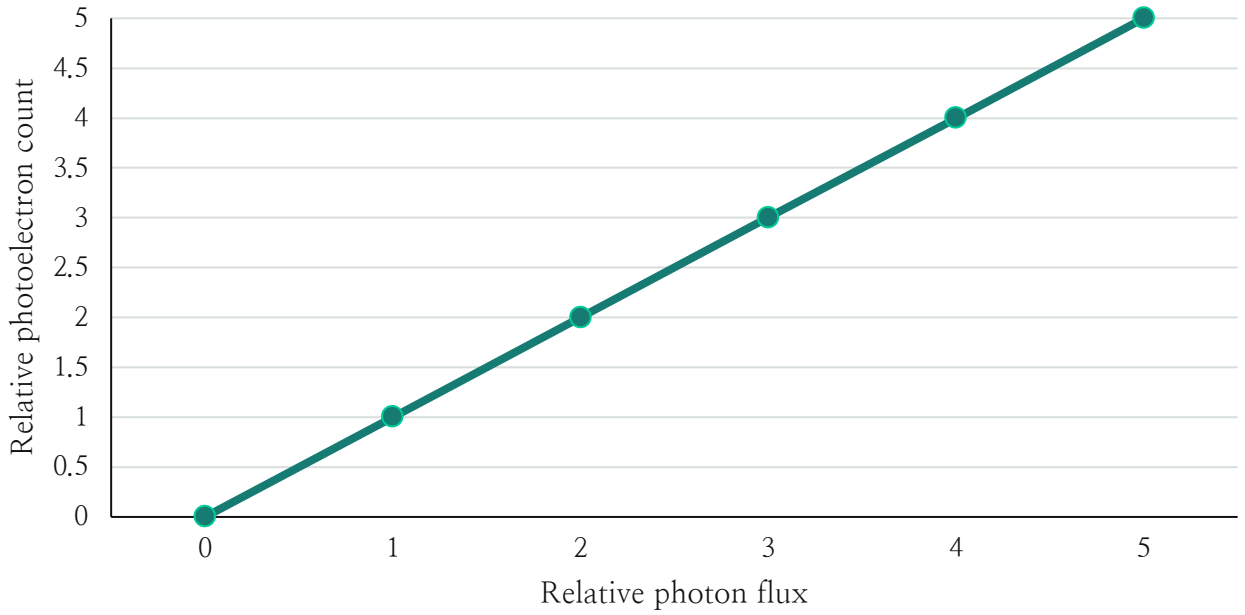
Below the threshold frequency, increasing light intensity still produces no photoelectrons.



Threshold condition: $h\nu \geq \Phi$

Photoelectric observation 2: intensity controls electron count

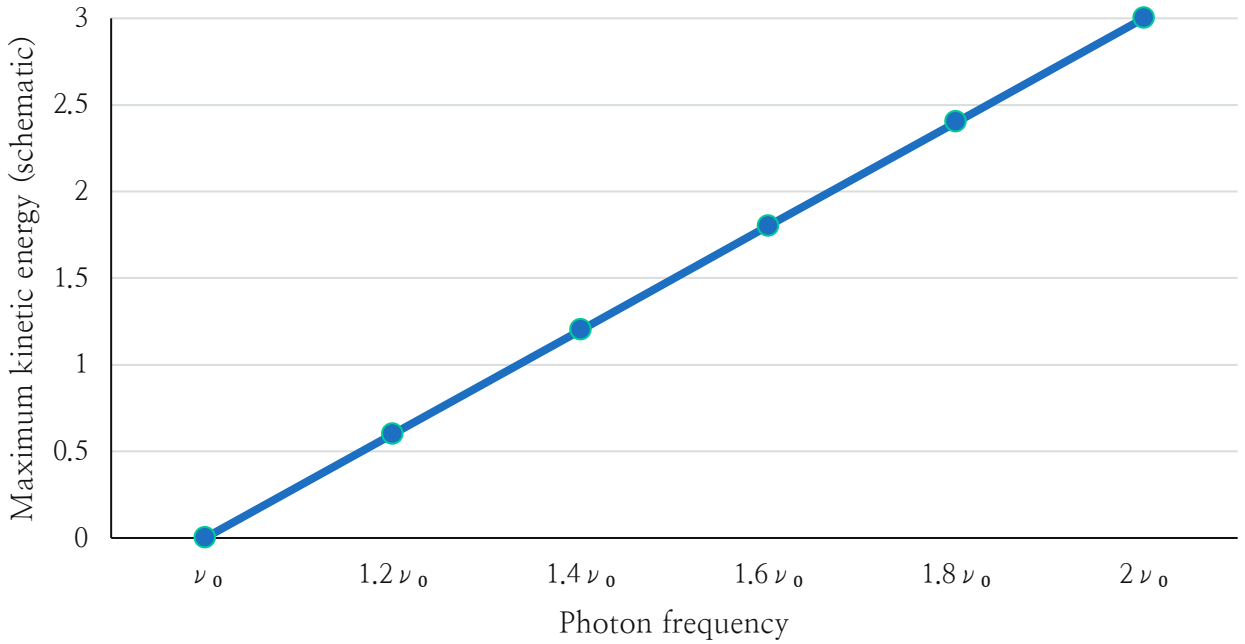
At fixed photon energy above threshold, higher photon flux produces more emitted electrons.



Intensity changes signal magnitude, not the maximum kinetic energy.

Photoelectric observation 3: photon energy controls kinetic energy

Once the threshold is exceeded, the maximum kinetic energy increases linearly with photon frequency.



$$KE_{max} = h\nu - \Phi$$

Photoelectric observation 4: emission is ultrafast

$$\sim 10^{-16}\ \mathrm{s}$$

The delay between photon absorption and electron emission is extremely short on laboratory time scales.

This rapid response allows photoelectron energy to be interpreted through energy conservation.

Electron Spectroscopy for Chemical Analysis

Radiation as waves and photons

Wave description

$$c = \lambda \nu$$

Wavelength λ and frequency ν describe the same electromagnetic radiation.

Photon description

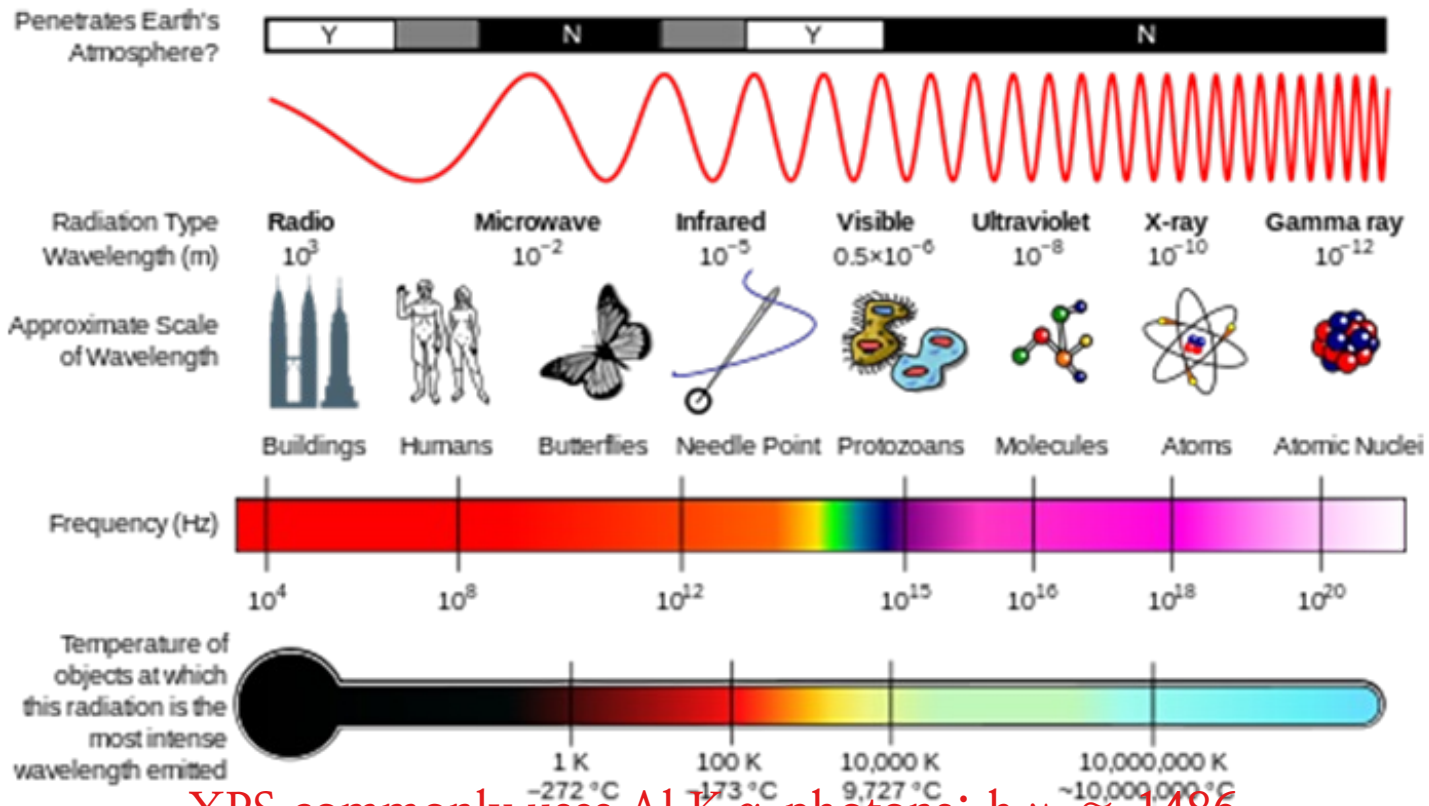
$$E = h \nu$$

A single photon carries discrete energy proportional to its frequency.

For XPS, photon energy must exceed the core-level binding energy.

Electron Spectroscopy for Chemical Analysis

The X-ray region of the electromagnetic spectrum



XPS commonly uses Al Kα photons: hν ≈ 1486.6 eV.

Photon energy and wavelength

$$E = h\nu = hc/\lambda$$

$$h = 6.626 \times 10^{-34} J \cdot s$$

$$c = 2.998 \times 10^{8}\ m \cdot s^{-1}$$

$$E(eV) \approx 1239.84 / \lambda\,(nm)$$

$$E = \frac{hc}{\lambda} = \frac{1.986 \times 10^{-16}\ \text{J nm photon}^{-1}}{\lambda}$$

Electron Spectroscopy for Chemical Analysis

Photoelectric energy balance in XPS

$$BE = h\nu - KE - \Phi_a$$

$h\nu$	KE	Φ_a
Known X-ray photon energy	Measured by the energy analyzer	Analyzer work-function term

Commercial instruments apply the work-function calibration when reporting binding energy.

Binding energy in ESCA

Binding energy is the energy required to remove an electron from a defined atomic or molecular state.

$$1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$$

Core-level binding energies primarily identify the element.

Small shifts reveal oxidation state and local bonding.

Peak area can support quantitative composition after calibration.

Electron Spectroscopy for Chemical Analysis

Binding energy and atomic identity

A negatively charged electron is bound by the positively charged nucleus.

Closer to the nucleus

Core electrons experience a larger effe ctive attraction and generally have hig her binding energies.

Farther from the nucleus

Valence electrons are less tightly bound and participate directly in chemical bon ding.

Isotopes have the same nuclear charge, so their ordinary XPS binding energie s are nearly identical.

Electron Spectroscopy for Chemical Analysis

The Binding Energy of an Electron in an Atom

A negatively charged electron will be bound to the atom by the positively charge d nucleus.

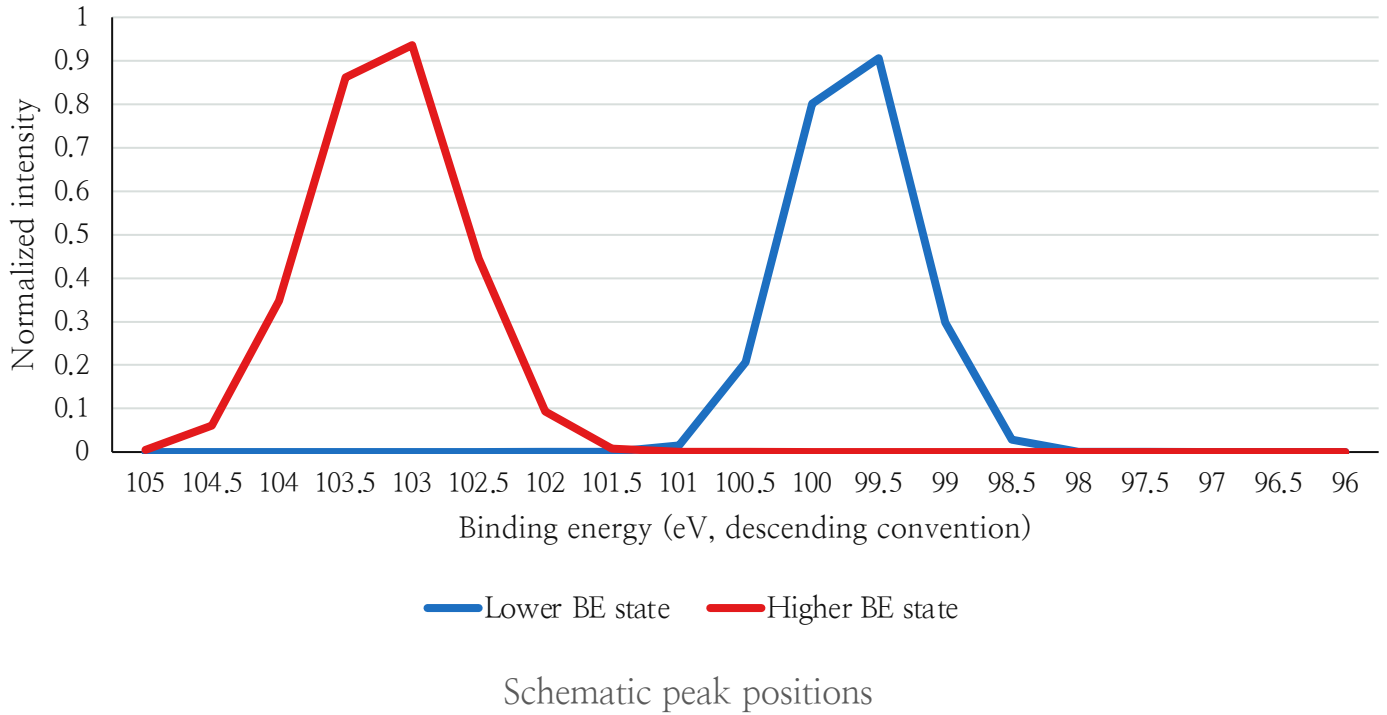
The closer the electron is to the nucleus, the more tightly we can expect it to be b ound.

Binding energy varies with elemental identity (nuclear charge) and with the chemi cal environment, because neighboring atoms alter the electron distribution around the atom of interest.

Different isotopes of a given element have different numbers of neutrons in the nu cleus, but the same nuclear charge. Changing the isotope will not appreciably affe ct the binding energy.

Chemical environment shifts core-level energies

Neighboring atoms redistribute electron density. More electron-withdrawing environments often shift a core level to higher binding energy.



Schematic peak positions

Electron Spectroscopy for Chemical Analysis

The Binding Energy of an Electron in an Atom

Weak interactions associated with crystallization or hydrogen bonding usually p roduce smaller binding-energy changes than covalent or ionic bonding.

The binding-energy variations that provide chemical information in ESCA are pri marily associated with covalent or ionic bonds between atoms.

→ These binding-energy changes are called binding-energy shifts or chemi cal shifts.

For gases, the binding energy of an electron in a given orbital is identical to its i onization energy, or first ionization potential.

In solids, surface and solid-state effects introduce additional energy terms that must be included when removing an electron from the surface.

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