

Topic 1.6: Photoelectron Spectroscopy

Revision Notes · AP Chemistry

UNIT 1 · ATOMIC STRUCTURE AND PROPERTIES

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What a Photoelectron Spectrum Is

Photoelectron spectroscopy, PES, is an experimental technique that reads an element's electron configuration directly. A sample is hit with high energy photons, and the photons knock electrons out of the atom.

Each photon gives up its energy to free one electron. Whatever energy is left over becomes the kinetic energy of the electron flying out, and that is what the instrument measures.

The energy balance. Photon energy = binding energy + kinetic energy of the ejected electron.
Rearranged: binding energy = photon energy – kinetic energy.

The binding energy is the energy that was holding that electron in the atom. An electron deep inside, close to a strong nuclear pull, has a high binding energy and leaves slowly. An electron far out, well shielded, has a low binding energy and leaves fast.

Why Each Subshell Gives One Peak

All electrons in the same subshell sit at the same average distance from the nucleus and feel roughly the same attraction. They therefore share the same binding energy, and they appear together as a single peak on the spectrum.

The horizontal position of a peak is the binding energy of that subshell. Peaks far to the left, at high binding energy, are subshells close to the nucleus. Peaks to the right, at low binding energy, are the outer subshells.

The height, or area, of a peak is proportional to the number of electrons in that subshell. A 2p peak for a full subshell stands three times as tall as a 2s peak, because 2p⁶ holds six electrons and 2s² holds two.

A PES spectrum is therefore a picture of the configuration itself: one peak per occupied subshell, positioned by how tightly it is held, sized by how many electrons it holds.

Worked Example: Reading a Spectrum

An element's spectrum (simplified teaching values, in MJ/mol) shows four peaks: at binding energy 1200 with relative height 2, at 110 with height 2, at 45 with height 6, and at 6 with height 2.

Count the electrons. The heights sum: $2 + 2 + 6 + 2 = 12$ electrons. The element is magnesium, $Z = 12$.

Assign the peaks. Highest binding energy is the subshell closest to the nucleus: 1200 is $1s^2$. Next, 110 is $2s^2$, then 45 is $2p^6$, and the small peak far right at 6 is $3s^2$, the loosely held valence electrons.

The spectrum confirms the configuration $1s^2 2s^2 2p^6 3s^2$ without any chemical test at all. Notice the large gaps: between 1s and 2s there is a jump of more than tenfold, because those electrons live in different shells.

Comparing Spectra Between Elements

Nuclear charge. Moving across a period adds protons. Every subshell is pulled in harder, so every peak shifts to higher binding energy. Chlorine's 1s peak sits at a higher binding energy than sulfur's, and its 3p peak does too.

Shielding and shells. Moving down a group adds a whole shell. The valence electrons of potassium are farther out and screened by more inner electrons than sodium's, so the outermost peak of potassium appears at lower binding energy than sodium's, even though potassium has the larger nucleus.

Peak patterns identify elements. Two elements in the same group have the same pattern of outer peaks. Sodium and potassium both end in a single low peak of height 1 for their lone ns^1 electron, which is the spectral fingerprint of Group 1.

From Spectrum to Configuration and Back

Given a spectrum, work in a fixed order. First, sum the peak heights to get the electron count and the element. Second, assign peaks from highest binding energy inward as 1s, 2s, 2p, 3s, 3p, and so on, checking each height against the subshell capacity. Third, write the configuration the peaks describe.

Given a configuration, predict the spectrum. Count the occupied subshells to get the number of peaks. Order them by binding energy, innermost highest. Set the heights in proportion to the electrons in each subshell.

Calcium, $[\text{Ar}] 4s^2$, occupies six subshells (1s, 2s, 2p, 3s, 3p, 4s), so its spectrum has six peaks, with heights in the ratio 2 : 2 : 6 : 2 : 6 : 2.

Traps That Cost Marks in Topic 1.6

Reading the axis backwards. Binding energy increases to the left in the standard AP presentation. The leftmost peak is the most tightly bound, never the valence shell. Check the axis labels before assigning anything.

Treating peak height as energy. Height counts electrons; position gives energy. A tall peak is a full subshell, not a strongly bound one. The 2p peak is often the tallest on the page and sits nowhere near the highest binding energy.

Expecting one peak per electron or per shell. Peaks count subshells. Twelve electrons in magnesium give four peaks, not twelve, and not three (one per shell).

Forgetting that ion spectra shift. Removing electrons reduces electron-electron repulsion and shielding, so the remaining electrons in an ion are held more tightly: the peaks of Mg^{2+} sit at higher binding energies than those of Mg, with the 3s peak gone entirely.

Comparing only one feature. Asked which of two spectra belongs to which element, use position and height together: the element with more protons has its peaks shifted to higher binding energy, and the heights fix the electron count.

Key Relationships to Remember

- Binding energy = photon energy – kinetic energy of the ejected electron
- One peak per occupied subshell; peak position = binding energy of that subshell; peak height $\propto$ number of electrons in the subshell
- Binding energy increases as electrons sit closer to the nucleus and as nuclear charge increases; it decreases with distance and shielding
- Peaks are read from highest binding energy (1s) to lowest (outermost subshell); heights sum to the total electron count
- Across a period, all peaks shift to higher binding energy; down a group, outer peaks shift lower as new shells are added

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