

Ion and Atom Photoelectron Spectroscopy

We've previously gone over the importance of spectroscopy, and the role it plays in determining sample characteristics and identity. In that lesson, we went over the four types of spectroscopy that are covered on the AP Chemistry exam, and what you need to know for each of them. If you haven't already, see that lesson here! However, spectroscopy is a concept that doesn't go away as you advance into higher-level chemistry courses. It just so happens that Photoelectron Spectroscopy is one of the most mentioned on the AP Chemistry exam. Therefore, we think it's worthwhile to take a deeper look at the theory behind how PES operates, and what happens when certain ions and molecules are tested.

Overview

- In this lesson, you'll learn the fundamental chemistry behind **Photoelectron Spectroscopy**.
- Then, we'll discuss the two types of PES: **UV and X-ray**, and how they function and differ.
- In each PES section, we'll review different **applications** of PES for each respective type.
- Lastly, you'll learn what a **PES graph** looks like, and we'll walk through how to read a more complicated spectrum (similar to one that you may encounter on the AP exam).

Photoelectron Spectroscopy Chemistry

Let's begin with the theory behind Photoelectron Spectroscopy. What purpose does PES have, what qualities does it attempt to detect in samples, and how does it try to do that? Let's start with the first question.

Definition

As defined in our Spectroscopy lesson, Photoelectron Spectroscopy detects the ionization energy from removing electrons one by one with X-ray or UV radiation. This reveals information about individual atoms and their orbitals in samples that are gaseous or solid.

So, photoelectron spectroscopy plucks electrons off of an atom or molecule to reveal the structure of the sample. It broadly does this through two different methods: UV radiation and X-ray radiation. It should be noted that X-ray photons have a significantly higher energy level than UV photons.

Deep dive

If you need a refresher on the electromagnetic spectrum, refer to our general lesson on Spectroscopy. Photoelectron Spectroscopy is also rooted in something called the Photoelectric Effect. We'll have a lesson on that coming out soon as well!



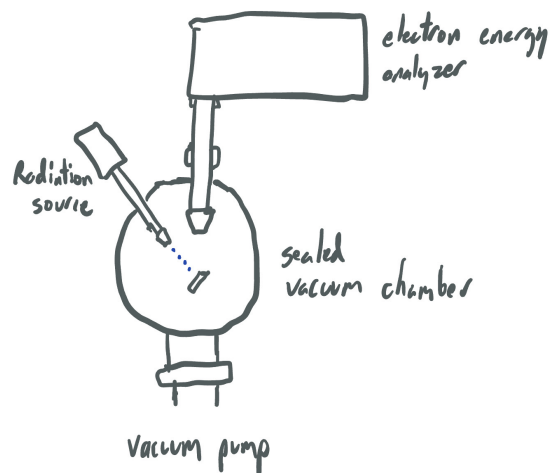
But what is this useful for? This is where the two main types of PES come into play.

Types of PES

For both types of photoelectron spectroscopy, three fundamental features allow chemists to probe a sample.

- First, a high-energy EM radiation source. Obviously, for UV PES a source of ultraviolet radiation is used, and for X-ray PES, X-ray radiation is used.
- Second, a detector that can pick up the kinetic energy given off by plucked-off electrons. This kinetic energy is proportional to the ionization energy needed to remove the electron.
- Third, this has to take place within a vacuum to prevent any atmospheric noise.

A typical PES experiment would be set up like this:



Drawn example of a Photoelectron Spectrometer

But of course, these different variables can change based on what kind of PES experiment you want to perform.

If you're thinking about the structure of an atom, there are traditionally two different regions: the nucleus and the electron cloud. The second has been represented as shells previously, and while the reality of the situation might be a bit different, this model is useful for visualizing how PES operates. We know that PES plucks off electrons from an atom. But from what shell? Are these electrons picked at random, or is there some order to their selection?

This reveals a key difference between UV PES and X-ray PES, and why there are multiple types of PES, to begin with. The higher the energy the EM source has, the more subshells can be probed and the closer chemists can get to the nucleus.



If you recall from the electromagnetic spectrum, UV radiation has less energy than X-ray radiation. This means that UV PES is used to target electrons on valence shells, while X-ray PES can reach shells closer in proximity to the nucleus.

Ultraviolet Photoelectron Spectroscopy and Applications

Let's start with describing UV PES, as its purpose and mechanisms are much more simple than X-ray PES. UV radiation has significantly less energy (typically measured in eV) than X-ray radiation. To give a visualization of this, UV photons typically have energy in a range of 1 eV to 100 eV. X-ray photons can have energy from 100 eV up to 100,000 eV! That's *1000x* more strong! It's clear from this comparison why X-ray PES has far more atomic penetration than UV.

Using this less powerful UV radiation source, chemists can probe and study the valence orbital of electrons in a sample on its own.

Example

But why would chemists want to isolate the valence electrons of a sample? There are a few good reasons they might want to do this.

- To analyze samples that might be radicals (molecules that contain one free electron.)
- To help facilitate reactions that are highly sensitive to valence electron count.
- The former two applications can be used to deduce the structure of a sample.
- Lastly, it can be used to gather valence orbital binding data to compare to predicted calculated values.

X-Ray Photoelectron Spectroscopy and Applications

But what if we want to look deeper into a sample? This is where X-ray PES comes into play. At this point in your AP Chemistry studies, you've most certainly been familiarized with atomic orbitals, and how every element has a unique electron configuration. As it turns out, X-ray PES attempts to turn this principle into a tangible, detectable property. X-ray PES is primarily used to determine the elemental composition of a sample by analyzing the orbitals that are present- which correlates to the aforementioned electron configuration.

Example

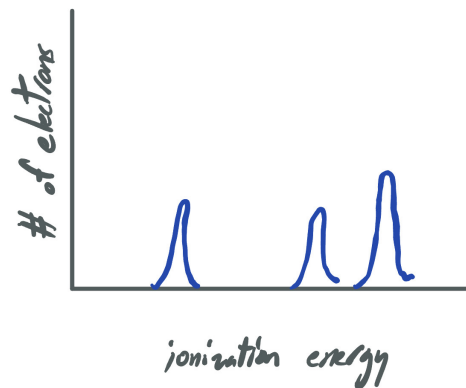
What can chemists do with the power of X-ray PES? The range of applications is much more than UV PES!

- Determine the composition of a sample's elements or formula
- Deduce information regarding the electronic or chemical state of the sample
- Lastly, they can determine binding energy from each orbital.

Photoelectron Spectroscopy Graphs and Calculations



To familiarize yourself with what a PES spectrum looks like, here's the example that was provided in our general Spectroscopy article.



Drawn example of nitrogen under Photoelectron Spectroscopy.

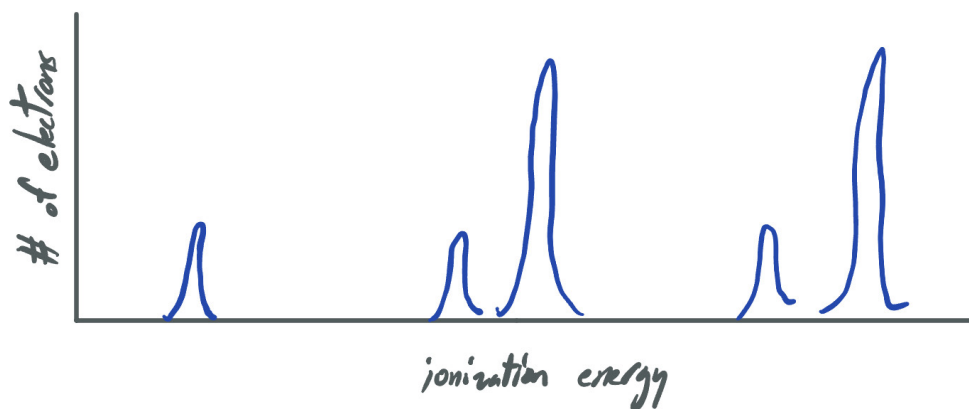
Example

Above, there is a PES spectrum of a pure, idealized sample of nitrogen. We know that nitrogen has an electron configuration of $1s^2 2s^2 2p$ in its ground state. Analyzing the PES of our nitrogen gas sample, we can see that we have three peaks that correspond with the three discrete levels of energy. We can also see that the height of the peaks is relative to how many electrons are in each subshell. For example, the first two peaks are equal in height because $1s^2$ and $2s^2$ both have 2 electrons. The third peak, which represents $2p$ is half in height because there is only one electron in its subshell. This technique can be applied to the PES spectrum to determine what element is being analyzed.

For an easy example such as a sample of pure nitrogen, the PES spectrum is pretty easy to analyze. If you can recall a problem that involves a complicated electron configuration, however, it's pretty easy to see how quickly things can get complicated. But, as long as you keep track of the relative size of each peak and write down the associated orbital that goes with them, you should be able to keep things clear.

Let's try to walk through an additional, more complicated PES graph. Go ahead and try to read the spectrum below, and once you've finished your attempt, we can walk through it together.





Drawn example of a mystery element under Photoelectron Spectroscopy.

This PES spectrum is representative of Argon! We know that the electron configuration of argon is $1s^2 2s^2 2p^6 3s^2 3p^6$. These peaks can be correlated to their respective orbitals based on their relative heights. It should also be noted that these peaks are grouped relatively based on what their shell is. That means $1s^2$ is by itself, $2s^2$ and $2p^6$ are together in the 2nd group, and $3s^2$ and $3p^6$ are together in the 3rd group. This pattern would continue into higher-level shells.

Deep dive

For higher-level PES problems, chemists will integrate these peaks to determine elemental ratios. However, the AP Chemistry exam primarily focuses on spectrum identification and peak assignment.

We hope that this in-depth lesson about Photoelectron Spectroscopy helps you to understand why PES is useful to chemists, how PES might appear on the AP Chemistry exam, and how to interpret spectra problems.

Ion and Atom Photoelectron Spectroscopy - Key takeaways

- You learned the fundamental chemistry behind Photoelectron Spectroscopy and how it relates to the atomic model.
- We talked about the main objective of PES: to analyze the electron subshells of a sample.
- Then, we discussed the two types of PES: UV and X-ray, and how they function and differ.
- After, we went over different applications of PES, and how that objective helps to fulfill these experimental requirements.
- Lastly, we covered what a PES graph looks like and how to assign peaks

