

X-Ray Photoelectron Spectroscopy

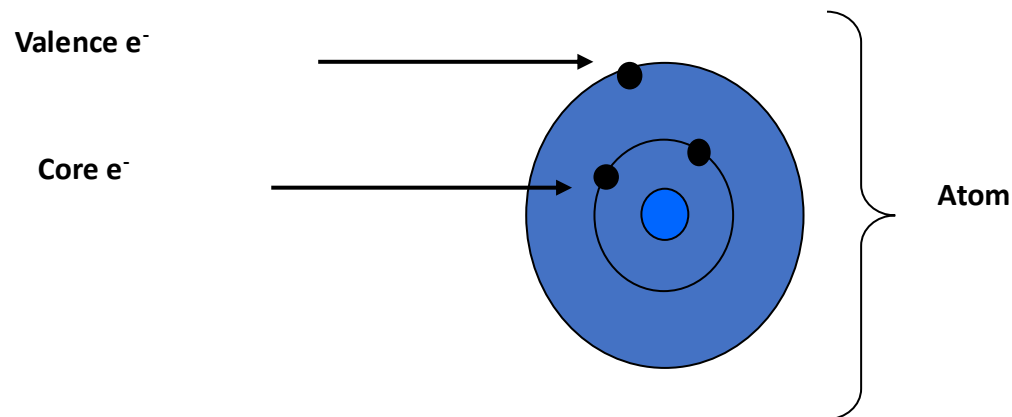
- ❑ XPS technique is based on Einstein's idea about the photoelectric effect, developed around 1905
- ❑ The concept of photons was used to describe the ejection of electrons from a surface when photons were impinged upon it
- ❑ During the mid 1960's Dr. Siegbahn and his research group developed the XPS technique.
- ❑ In 1981, Dr. Siegbahn was awarded the Nobel Prize in Physics for the development of the XPS technique

X-Rays

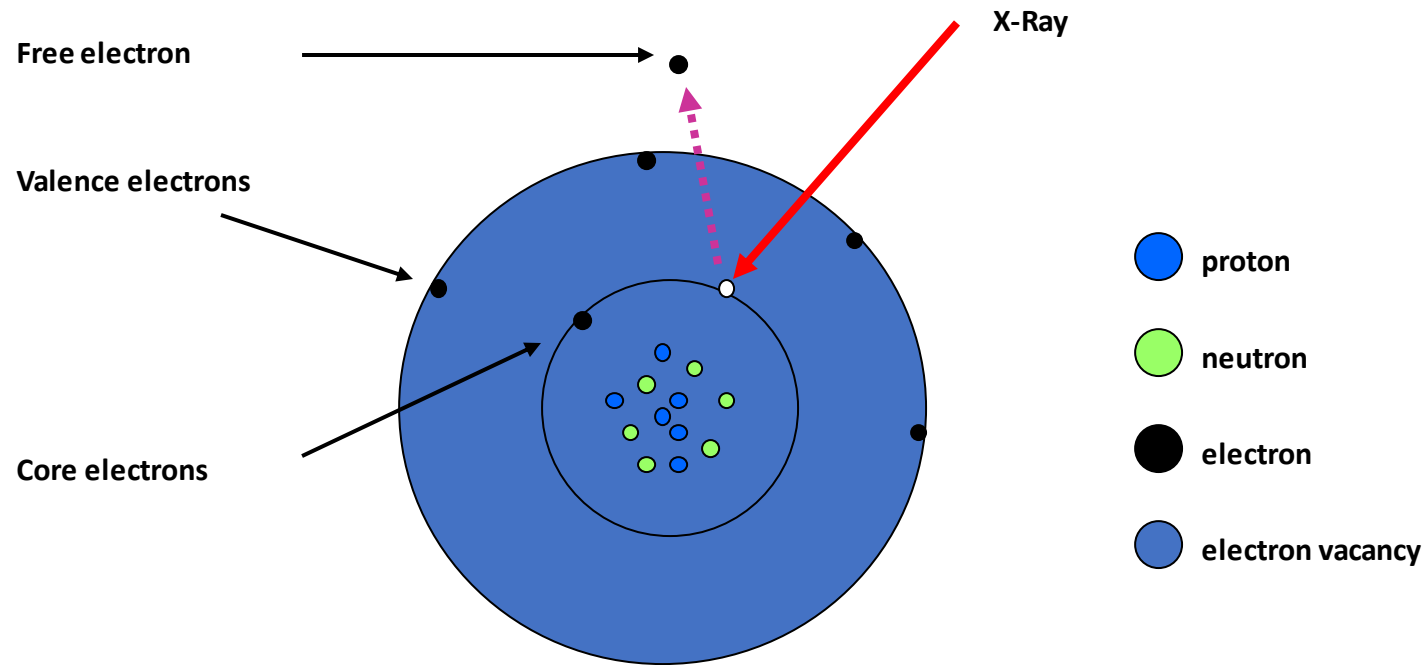
- ❑ Irradiate the sample surface, hitting the core electrons (e-) of the atoms.
- ❑ The X-Rays penetrate the sample to a depth on the order of a micrometer.
- ❑ Useful e- signal is obtained only from a depth of around 10 to 100 Å on the surface.
- ❑ The X-Ray source produces photons with certain energies:
 - MgK α photon with an energy of 1253.6 eV
 - AlK α photon with an energy of 1486.6 eV
- ❑ Normally, the sample will be radiated with photons of a single energy (MgK α or AlK α). This is known as a monoenergetic X-Ray beam.

Why the Core Electrons?

- ❑ An electron near the Fermi level is far from the nucleus, moving in different directions all over the place, and will not carry information about any single atom.
 - Fermi level is the highest energy level occupied by an electron in a neutral solid at absolute 0 temperature.
 - Electron binding energy (BE) is calculated with respect to the Fermi level.
- ❑ The core e-s are local close to the nucleus and have binding energies characteristic of their particular element.
- ❑ The core e-s have a higher probability of matching the energies of $AlK\alpha$ and $MgK\alpha$.



The Atom and the X-Ray

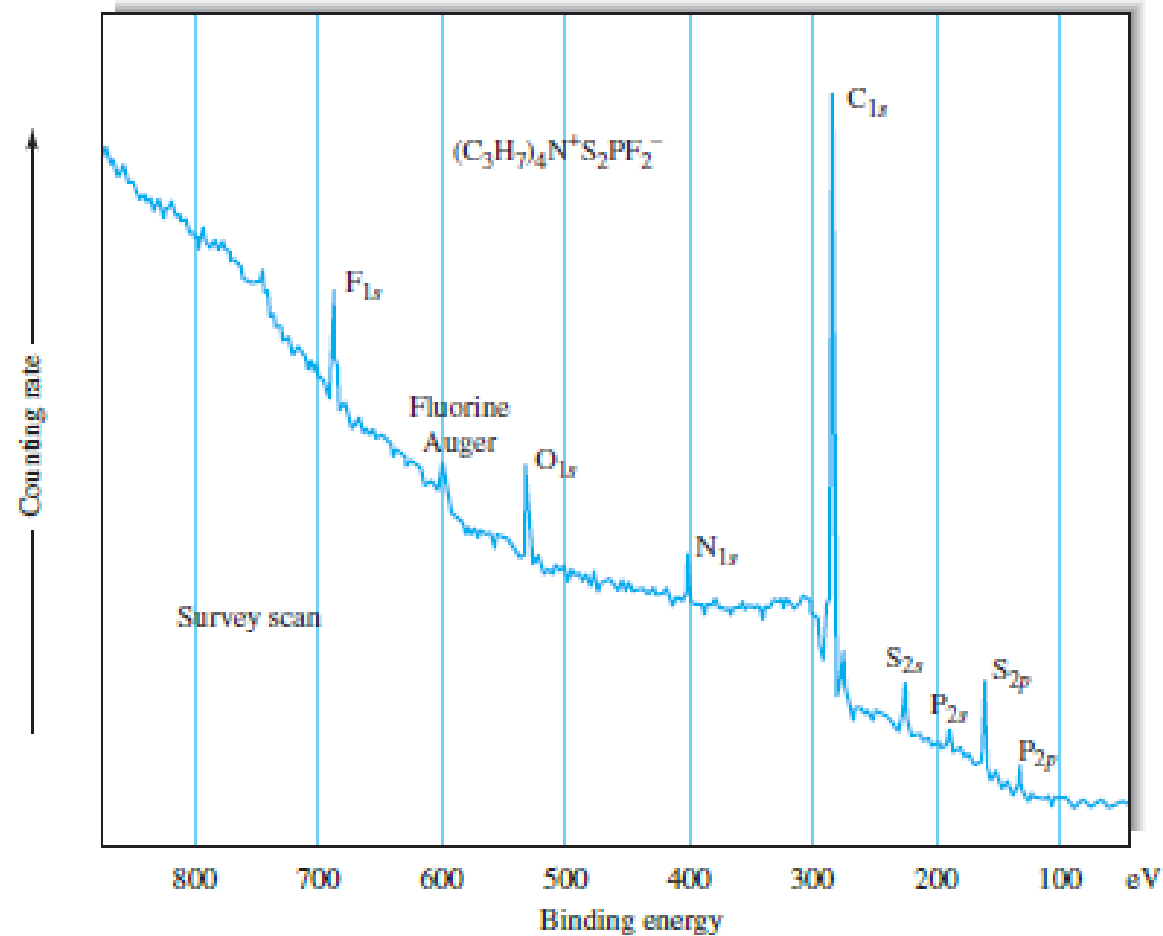


The core electrons respond very well to the X-Ray energy

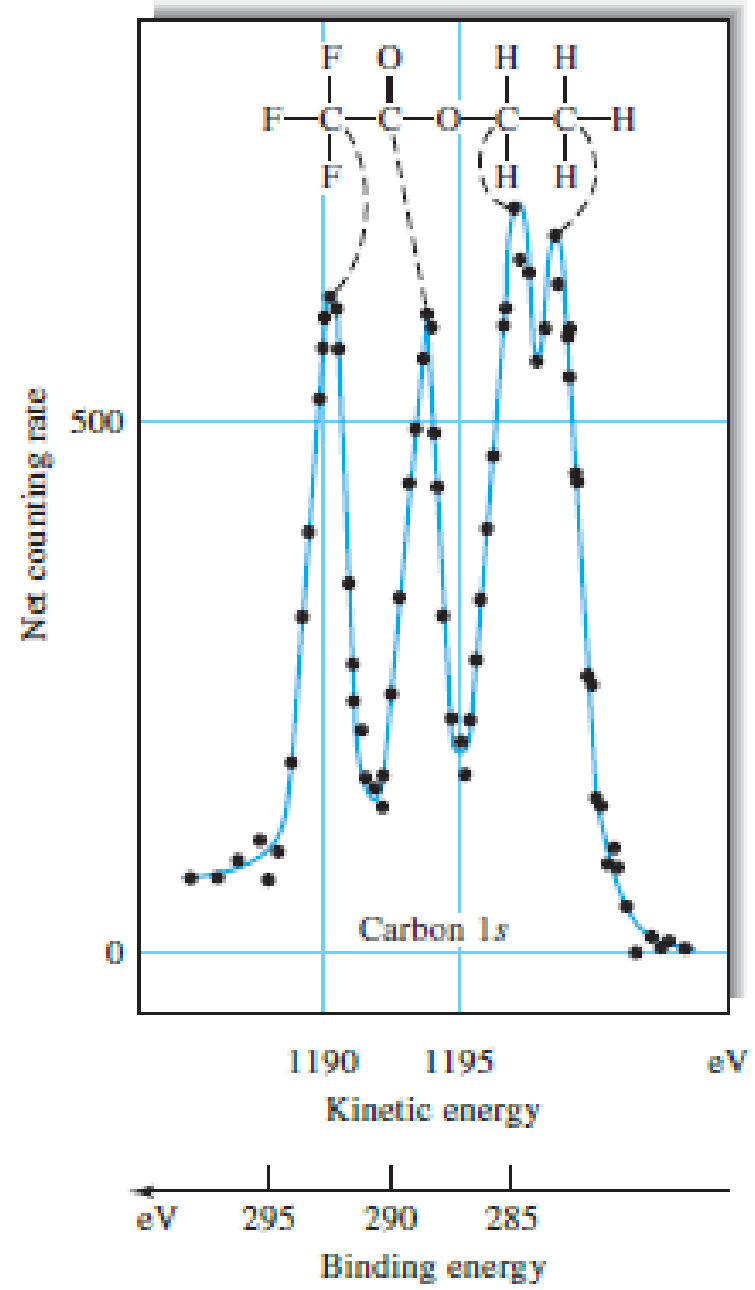
X-ray Photoelectron Spectroscopy (XPS)

For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study - furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a quantitative analysis of the surface composition and is sometimes known by the alternative acronym, ESCA (Electron Spectroscopy for Chemical Analysis).



X-ray photoelectron spectrum of tetrapropyl ammonium difluoride thiophosphate. The peaks are labeled according to the element and orbital from which the emitted electrons originate.



The following X-ray sources are commonly employed:

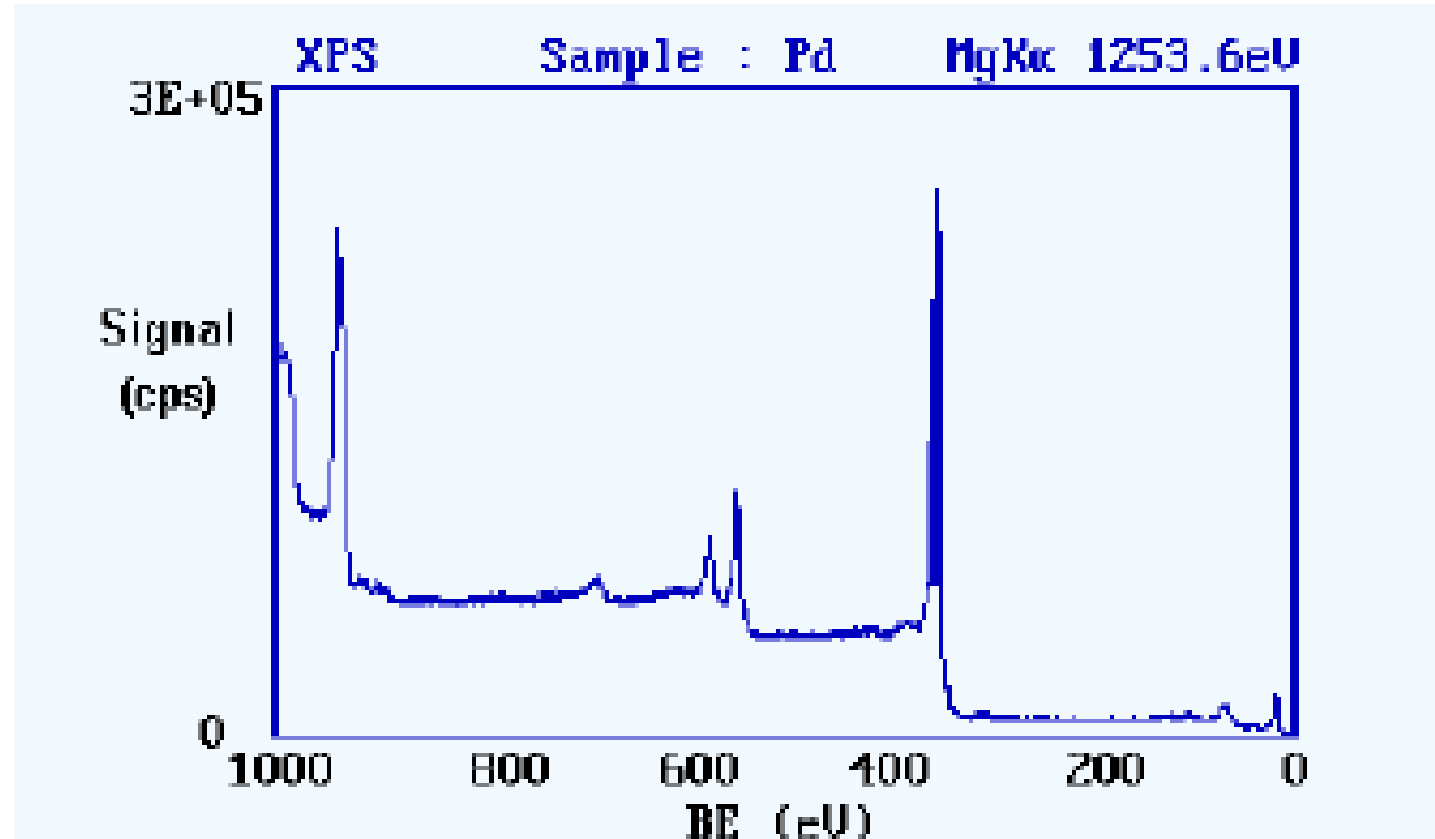
X-ray source	$h\nu$ (eV)
Mg K_{α} radiation	1253.6
Al K_{α} radiation	1486.6
Cu K_{α} radiation	5414.7

The most commonly employed x-ray sources are those giving rise to :

Mg K radiation : $h\nu = 1253.6$ eV

Al K radiation : $h\nu = 1486.6$ eV

The emitted photoelectrons will therefore have kinetic energies in the range of ca. 0 - 1250 eV or 0 - 1480 eV. Since such electrons have very short IMFPs in solids, the technique is necessarily surface sensitive.



XPS spectrum obtained from a Pd metal sample using Mg K radiation
- the main peaks occur at kinetic energies of ca. 330, 690, 720, 910 and 920 eV.

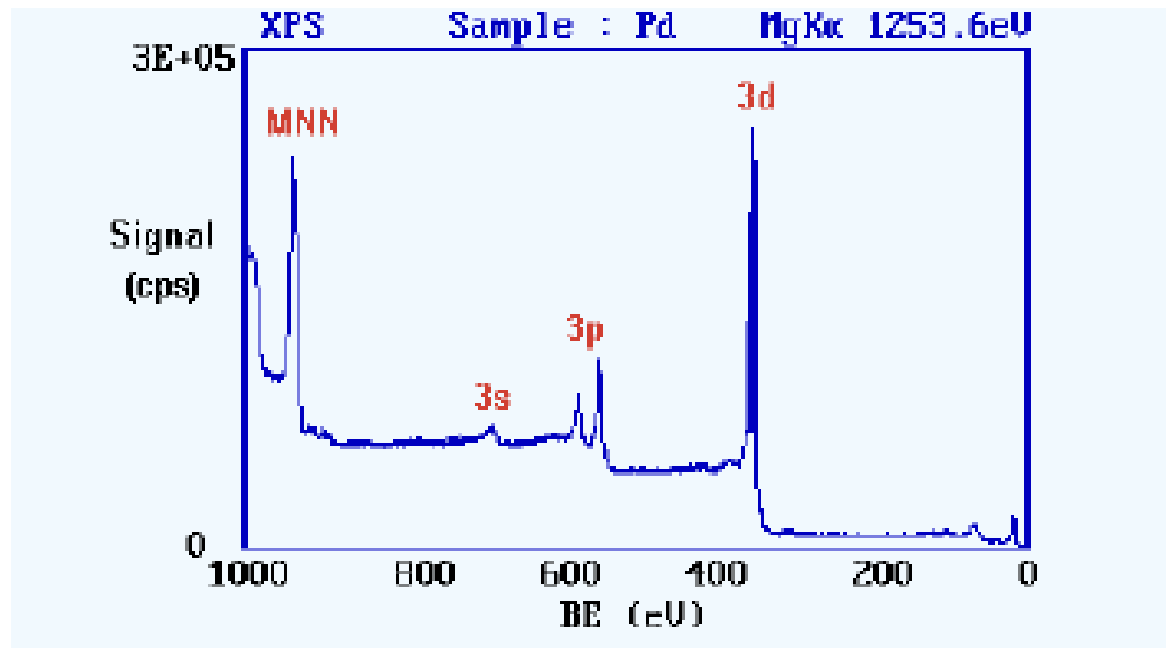
The most intense peak is now seen to occur at a binding energy of ca. 335 eV

the valence band (4d, 5s) emission occurs at a binding energy of ca. 0 - 8 eV (measured with respect to the Fermi level, or alternatively at ca. 4 - 12 eV if measured with respect to the vacuum level).

the emission from the 4p and 4s levels gives rise to very weak peaks at 54 eV and 88 eV respectively

the most intense peak at ca. 335 eV is due to emission from the 3d levels of the Pd atoms, whilst the 3p and 3s levels give rise to the peaks at ca. 534/561 eV and 673 eV respectively.

the remaining peak is not an XPS peak at all ! - it is an Auger peak arising from x-ray induced Auger emission. It occurs at a kinetic energy of ca. 330 eV (in this case it is really meaningless to refer to an associated binding energy).



Spin-Orbit Splitting

Closer inspection of the spectrum shows that emission from some levels (most obviously 3p and 3d) does not give rise to a single photoemission peak, but a closely spaced doublet. We can see this more clearly if, for example, we expand the spectrum in the region of the 3d emission ...

The 3d photoemission is in fact split between two peaks, one at 334.9 eV BE and the other at 340.2 eV BE, with an intensity ratio of 3:2 . This arises from spin-orbit coupling effects in the final state. The inner core electronic configuration of the initial state of the Pd is :

$(1s)^2 (2s)^2 (2p)^2 (3s)^2 (3p)^2 (3d)^{10}$ with all sub-shells completely full.

The removal of an electron from the $3d$ sub-shell by photo-ionization leads to a $(3d)$ configuration for the final state -

since the d -orbitals ($l = 2$) have non-zero orbital angular momentum, there will be coupling between the unpaired spin and orbital angular momenta. Spin-orbit coupling is generally treated using one of two models which correspond to the two limiting ways in which the coupling can occur - these being the LS (or Russell-Saunders) coupling approximation and the $j-j$ coupling approximation. If we consider the final ionised state of Pd within the [Russell-Saunders coupling](#) approximation, the $(3d)$ configuration gives rise to two states (ignoring any coupling with valence levels) which differ slightly in energy and in their degeneracy ...

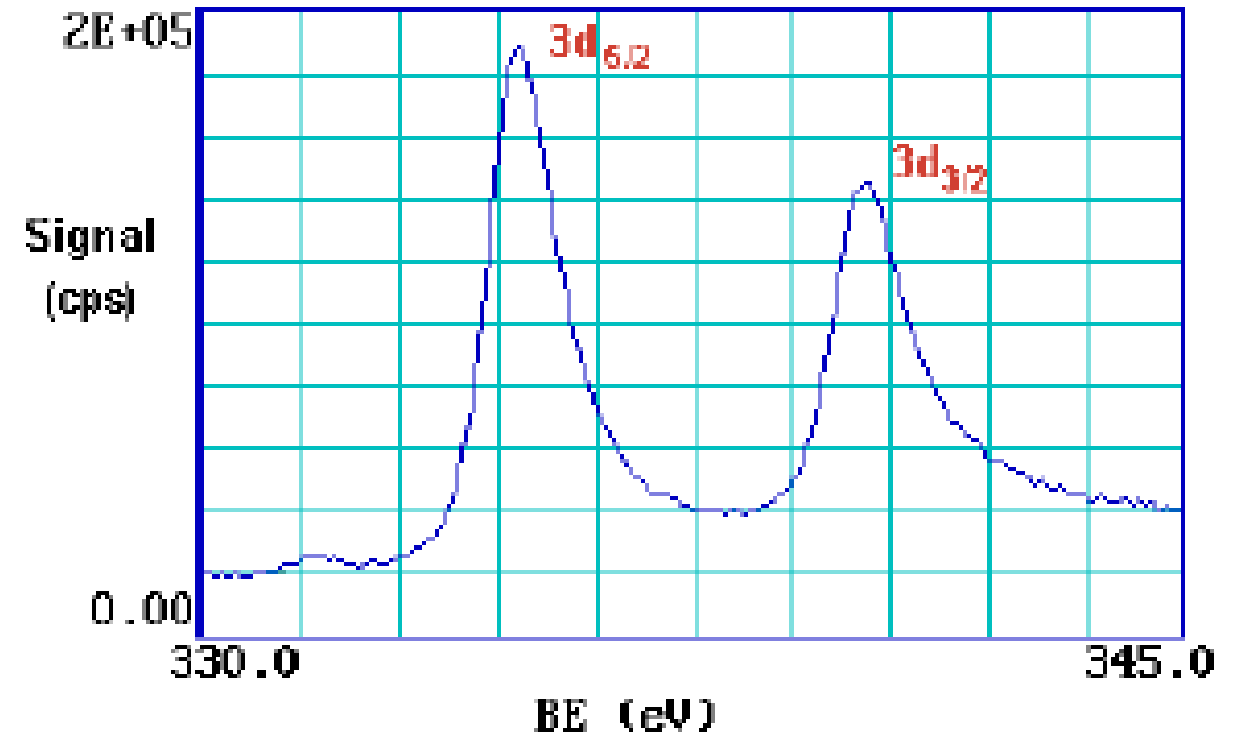
These two states arise from the coupling of the $L = 2$ and $S = 1/2$ vectors to give permitted J values of $3/2$ and $5/2$. The lowest energy final state is the one with maximum J (since the shell is more than half-full), i.e. $J = 5/2$, hence this gives rise to the "lower binding energy" peak.

The relative intensities of the two peaks reflects the degeneracies of the final states ($g = 2J + 1$), which in turn determines the probability of transition to such a state during photoionization.

The Russell-Saunders coupling approximation is best applied only to light atoms and this splitting can alternatively be described using individual electron l - s coupling. In this case the resultant angular momenta arise from the single hole in the d -shell; a d -shell electron (or hole) has $l = 2$ and $s = 1/2$, which again gives permitted j -values of $3/2$ and $5/2$ with the latter being lower in energy.

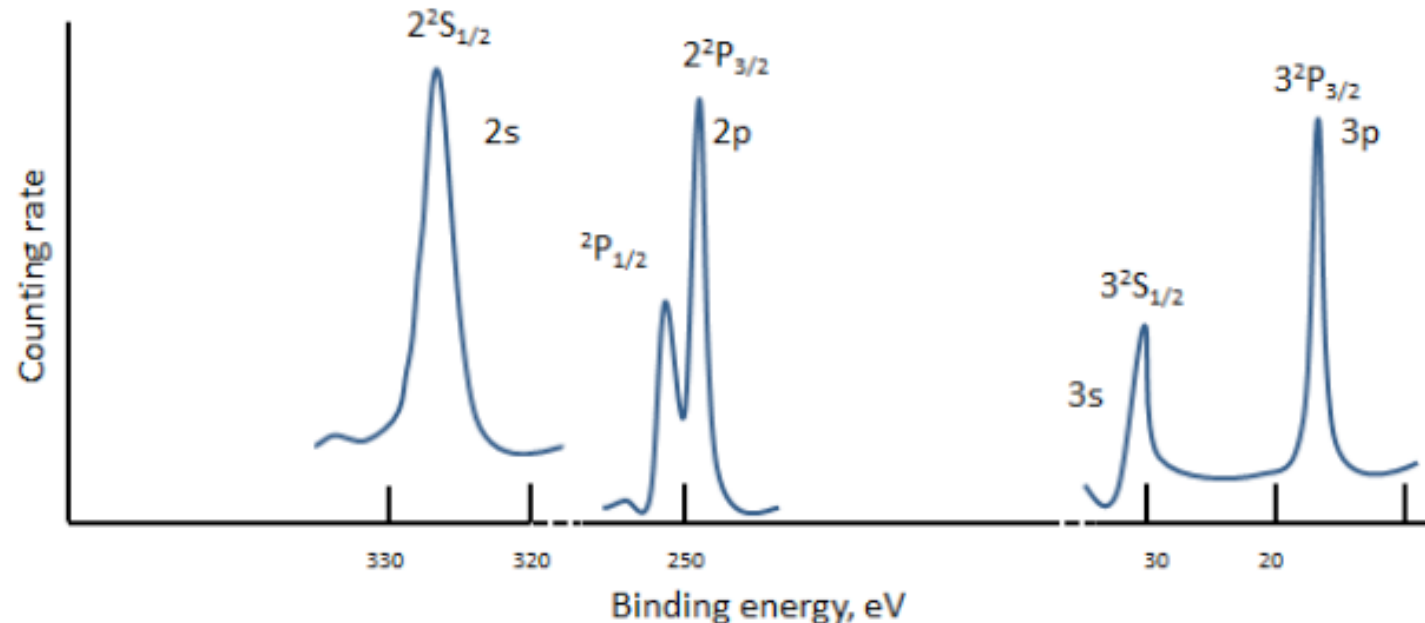
The peaks themselves are conventionally annotated as indicated - note the use of lower case lettering

This spin-orbit splitting is of course not evident with s -levels ($l = 0$), but is seen with p , d & f core-levels which all show characteristic spin-orbit doublets.



Effect of spin-orbit coupling

Closer look at the 2p peak at ~250 eV shows that it is actually a doublet with peaks at 248.4 and 250.6 eV. This is due to spin-orbit coupling because of which the $2p_5$ configuration gives rise to two states $2_2P_{3/2}$ and $2_2P_{1/2}$, of which the former is higher in energy because the 2p orbital is more than half-filled. The same splitting should also be observed for the 3p peak, but the two states $3_2P_{3/2}$ and $3_2P_{1/2}$ are close in binding energy (15.8 and 15.9 eV), and the compound peak merges to one.



Chemical Shifts

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon both the formal oxidation state of the atom and the local chemical and physical environment. Changes in either give rise to small shifts in the peak positions in the spectrum - so-called chemical shifts. Such shifts are readily observable and interpretable in XP spectra (unlike in Auger spectra) because the technique is of high intrinsic resolution (as core levels are discrete and generally of a well-defined energy) and is a one electron process (thus simplifying the interpretation).

Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulombic interaction between the photo-emitted electron and the ion core. This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of the XPS technique.

In practice, the ability to resolve between atoms exhibiting slightly different chemical shifts is limited by the peak widths which are governed by a combination of factors; especially the intrinsic width of the initial level and the lifetime of the final state the line-width of the incident radiation - which for traditional x-ray sources can only be improved by using x-ray monochromators the resolving power of the electron-energy analyser In most cases, the second factor is the major contribution to the overall line width.

Each element has a characteristic binding energy associated with each of its core atomic orbitals. Hence, each element gives rise to a characteristic photoelectron spectrum, which can be used to identify it. Moreover, there is a quantitative aspect, too. The intensity of the peaks is related to the concentration of the element in the sample. Thus, XPS is an important technique, providing both qualitative and quantitative information about the composition of a sample. For this reason, it is also known by the alternative acronym, ESCA (Electron Spectroscopy for Chemical Analysis).