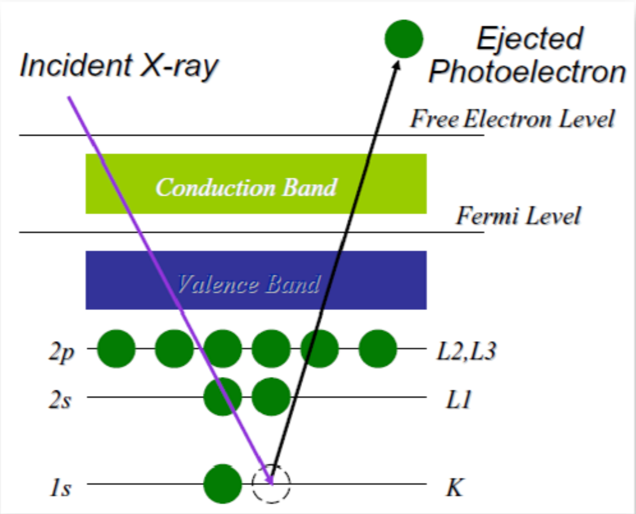
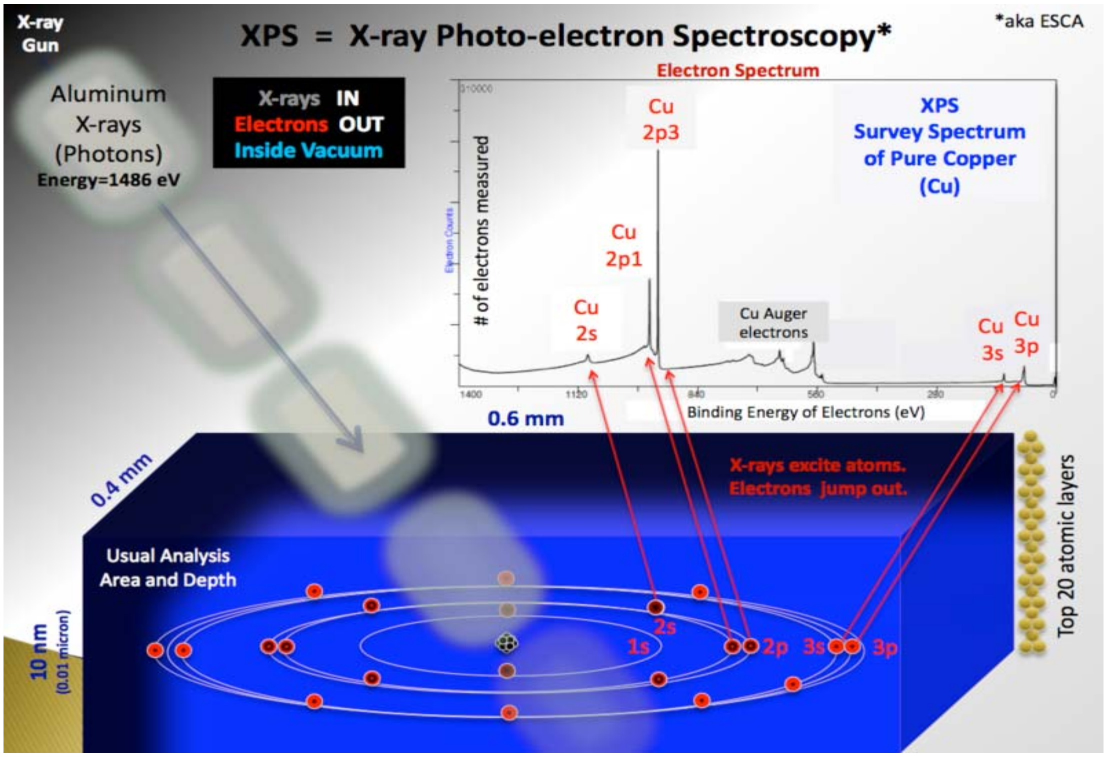
Chapter Four: X Ray Photoelectron Spectroscopy



X ray photoelectron spectroscopy (XPS) is the implementation of the photoelectric effect to study materials. It was developed in the 1960s by the Swedish Kai Siegbahn who earned the Nobel Prize in 1981 for his work; the technique is also known as Electron Spectroscopy for Chemical Analysis (ESCA).

As explained in the section "Photoelectric effect" and depicted in the figure, in XPS an incident x ray (of energy hf, f being the frequency) knocks an electron (with binding energy BE) out of the atom which escapes with an energy equal to $E = hf - BE - \Phi$, where Φ is the work function of the spectrometer (of the order of a few eV). Knowing Φ, the energy of the incident x ray and capturing the electron to measure its kinetic energy allows the determination of the binding energy of the electron and thus the identification of the element. The figure below (from Dr. B. Vincent Crist) shows a beautiful description of the complete XPS process from x ray irradiation to compilation of the electron energy spectra.

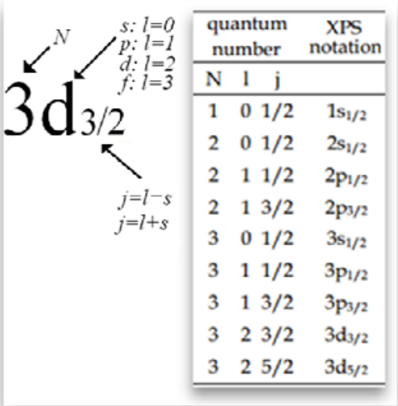


XPS is used to study the elemental composition, chemical state and electronic state of a material. Normally it helps to explore the top 10 nm or top 20 layers of a surface. To avoid scattering of the XPS electrons with air, XPS is performed in a ultra-high vacuum (UHV) chamber. Samples can be studied without any preparation other than normal cleaning, but some applications can benefit from being sputtered with ions to clean off surface contamination.

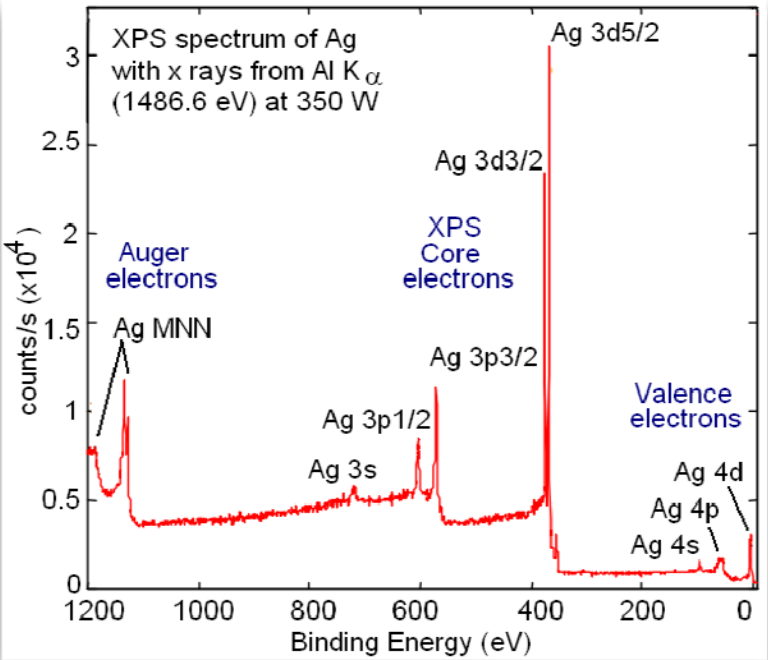
XPS can detect elements starting from Li (Z=3) and higher; hydrogen (Z = 1) and helium (Z = 2) cannot be detected due to the low probability of electron emission. Detection limits for most of the elements are in the parts per thousand range, but it can be increased to parts per million (ppm) for large concentrations or through long collection times (overnight). XPS is applicable to inorganic compounds, metals, semiconductors, organic material, bio-materials, as well as oils and gases under special conditions. XPS is non-destructive and can be safely used in the study of works of art.

XPS Spectra

Once the XPS electrons are captured and their kinetic energy measured, the binding energy of the electron can be estimated and used to produce the XPS spectrum, which is a histogram of the number of electrons captured as a function of their binding energy. Since the binding energy is different for every atomic energy level, the electron energy spectrum will show peaks at these levels and, depending on the energy resolution of the electron detector (usually of the order of an eV or smaller), at the sublevels within shells.



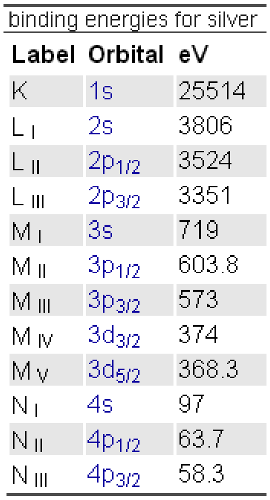
quantum number			XPS notation
N	l	j	
1	0	1/2	$1s_{1/2}$
2	0	1/2	$2s_{1/2}$
2	1	1/2	$2p_{1/2}$
2	1	3/2	$2p_{3/2}$
3	0	1/2	$3s_{1/2}$
3	1	1/2	$3p_{1/2}$
3	1	3/2	$3p_{3/2}$
3	2	3/2	$3d_{3/2}$
3	2	5/2	$3d_{5/2}$



The notation used in XPS to identify the energy levels follows the standards set by quantum mechanics. As mentioned in Chapter One, the binding energy of an atomic electron depends not only on the energy shell of the level they occupy, but also on the magnetic interaction between its intrinsic spin and the orbital angular momentum. Thus the energy levels are characterized by the orbital, and total and orbital angular momentum quantum numbers, N, j and l, respectively, and these are used in the nomenclature shown in the figure. The accompanying table shows the most common energy states encountered in XPS.

The figure shows an example of XPS spectra (adapted from Dr. Janssens work) obtained by irradiating an Ag target with Ag Kα x rays of 1486.6 eV. As it will be explained in the next section, the captured electrons have different origins; here it suffices to mention that the main peaks are from the XPS electrons emitted from the core levels. The background is produced by electrons that scatter inelastically with other atoms on their way out and suffer energy loss; since those electrons arrive at the detector with smaller kinetic energies, they are counted as electrons with a higher binding energies thus increasing the noise at higher binding energy and producing the stepped background. The intensity of all peaks is proportional to the intensity of the x ray beam.

The following chart shows the binding energies of the electrons in the different energy levels as a function of the charge (Z) of the atoms. Notice that in all cases the "s" levels have only one curve while there are two "p", "d" or "f" curves; this split of energy levels is due to the interaction energy between the particle spin and their orbital angular momentum.



binding energies for silver

Label	Orbital	eV
K	1s	25514
L_{I}	2s	3806
L_{II}	$2p_{1/2}$	3524
L_{III}	$2p_{3/2}$	3351
M_{I}	3s	719
M_{II}	$3p_{1/2}$	603.8
M_{III}	$3p_{3/2}$	573
M_{IV}	$3d_{3/2}$	374
M_{V}	$3d_{5/2}$	368.3
N_{I}	4s	97
N_{II}	$4p_{1/2}$	63.7
N_{III}	$4p_{3/2}$	58.3

Exercise 4.1

Use the spectra of an Ag target irradiated with Ag Kα x rays of 1486.6 eV to
A) determine the kinetic energies the photoelectrons had when they were captured. Assume that the spectrometer work function is negligible and use the exact Ag binding energies listed in the table (adapted from http://www.webelements.com) or from the tables in the Appendix.
B) Show that the peaks labeled as Auger peaks cannot indeed be XPS peaks.

Solution

A) Some examples:

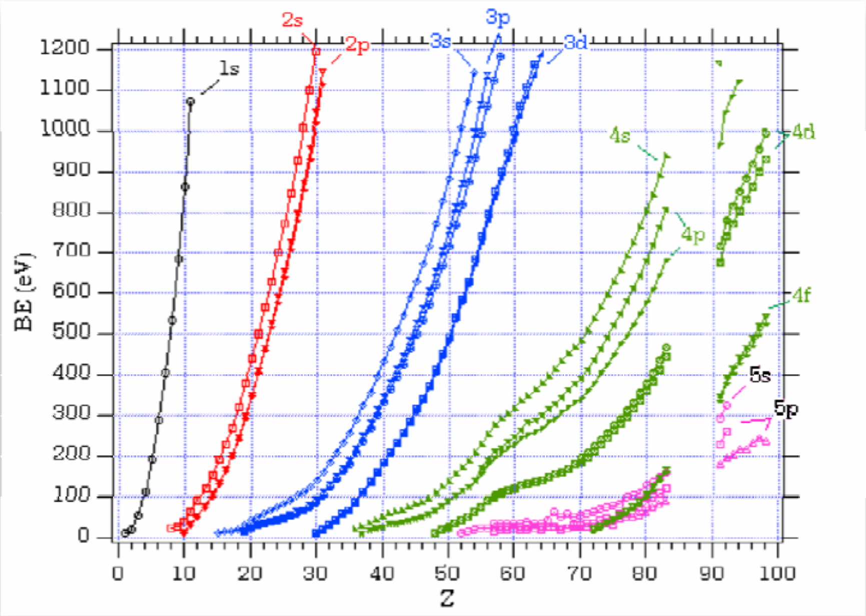
Ag $3d_{5/2}$: $E = hf – BE - \Phi = 1486.6 – 368.3 – 0 = 1118.3$ eV

Ag $3p_{3/2}$: $E = hf – BE - \Phi = 1486.6 – 573 – 0 = 913.6$ eV

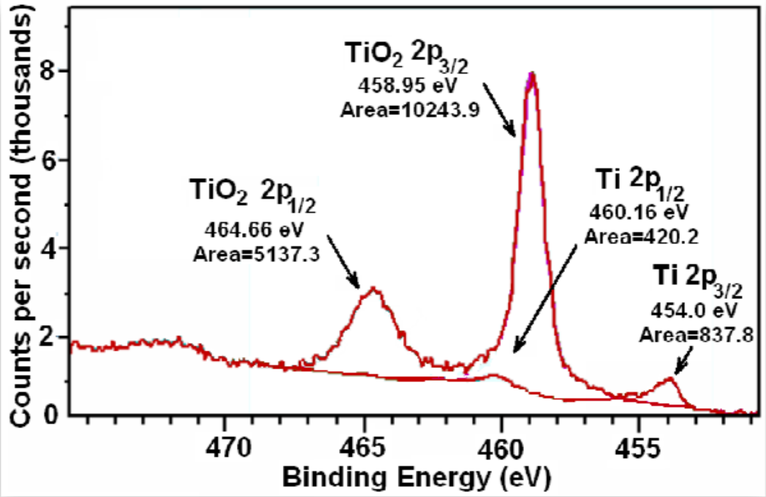
Ag 4s: $E = hf – BE - \Phi = 1486.6 – 97 – 0 = 1389.6$ eV

Etc. Notice that BE increases to the left while E increases to the right.

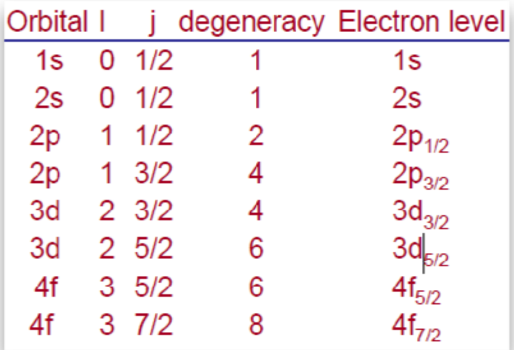
B) The two Auger peaks shown appear to have binding energies of, say, 1150 eV and 1180 eV, looking at the table of Ag energies, no levels with those energies are found, consequently the peaks do not correspond to XPS electrons.



The energy of a level varies according to the total angular momentum, $j = l + s$. States with $l > 0$ can have two possible j values: $j = 1 - ½, 1 + ½$ for $l = 1$ (p), or $j = 2 - ½$, or $j = 2 + ½$ for $l = 2$ (d), etc. In the XPS spectra this results in pairs of peaks with relatively close values as illustrated in the following figure (adapted from www.casaxps.com) which shows a superposition of two spectra from Ti and TiO_2.



A useful feature of these pairs of peaks is that they have a well defined ratio of intensities. Since different energy levels can be occupied by a different number of electrons, an x ray will have a larger probability of hitting an electron in a high occupancy level; thus levels with higher electron occupancy produce more intense XPS peaks. Thus, the ratio of the intensities of a given pair of peaks equals the ratio of the occupancies of such energy levels; such occupancy is given by the *degeneracy* which equals $2j+1$, the accompanying table shows the degeneracy of several energy levels.



Orbital	l	j	degeneracy	Electron level
1s	0	1/2	1	1s
2s	0	1/2	1	2s
2p	1	1/2	2	$2p_{1/2}$
2p	1	3/2	4	$2p_{3/2}$
3d	2	3/2	4	$3d_{3/2}$
3d	2	5/2	6	$3d_{5/2}$
4f	3	5/2	6	$4f_{5/2}$
4f	3	7/2	8	$4f_{7/2}$

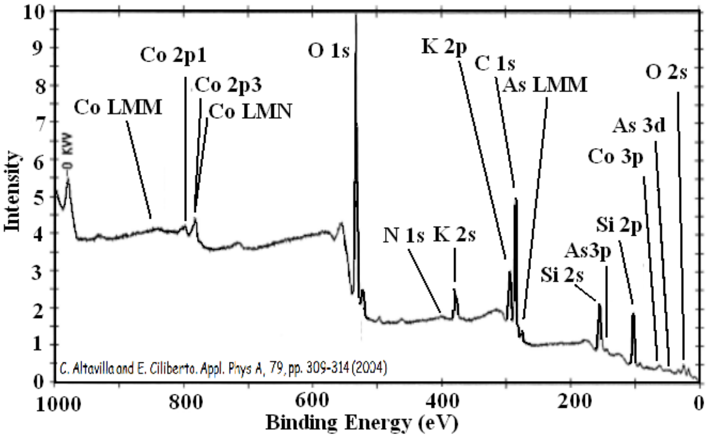
For instance, all pairs composed by the 2p3/2 and 2p1/2 peaks will have a degeneracy ratio of 4 to 2 i.e. a ratio of 4/2 = 2; quantifying the intensity of such peaks in the previous TiO_2 spectrum by the area under the peaks (as measured with respect to the background), we find the ratio of the areas to yield 10243.9/5137.3=1.994. Repeating the estimation with the 2p3/2 and 2p1/2 peaks of Ti we also find a ratio of 837.8/420.2=1.9938 in close agreement with the expected value. In general, all p peaks ($p_{1/2}$, $p_{3/2}$) will have an area ratio of 1:2, d peaks ($d_{3/2}$, $d_{5/2}$) of 2:3, f peaks ($f_{5/2}$, $f_{7/2}$) of 3:4, etc.

Relationship to Auger electrons

As studied before, after the XPS electron is emitted, another electron will occupy its place in the atom emitting a photon in the transition, photon which either will escape the material or will in turn kick a second electron out in a process known as Auger effect.

Thus, for every XPS electron emitted there will be either a photon or a second (Auger) electron being emitted. Although the emitted photon and Auger electron carry information that can aid in the identification of the element, XPS, strictly speaking, refers only to the analyses based on the first photoelectron emitted. Although the x rays and Auger electrons tend to contaminate the XPS spectra, such signals can be identified and filtered out of the analysis.

One example of such problem was shown in the Janssens XPS spectrum presented before (see Example 4.1). Another example is presented in the accompanying figure produced by an XPS study of glassy pigments which shows the Co LMM, LMN and As LMM Auger peaks in addition to the XPS spectrum; the nomenclature used for the Auger electrons is based on the shells involved in the transition.



C. Altavilla and E. Ciliberto. Appl. Phys A, 79, pp. 309-314 (2004)

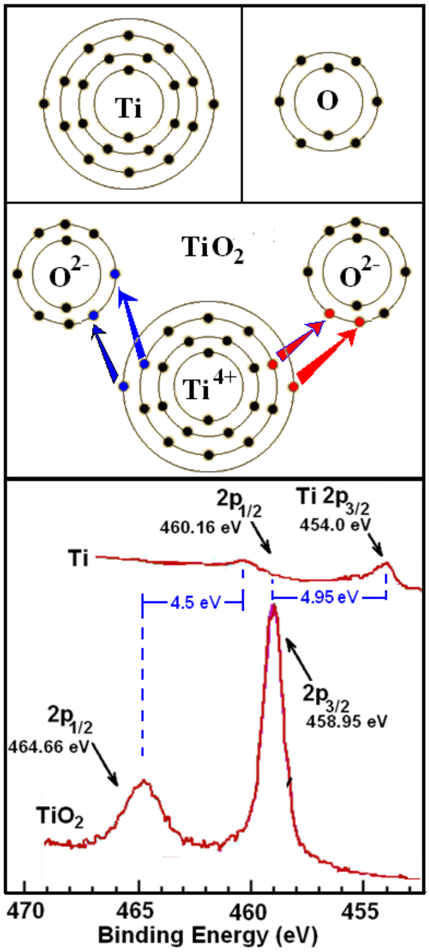
It must be mentioned that Auger electrons obtained through XPS apparatus appear with the wrong binding energy as they are taken as photoelectrons by the data analysis system. Auger spectroscopy will be discussed at length in the following chapter.

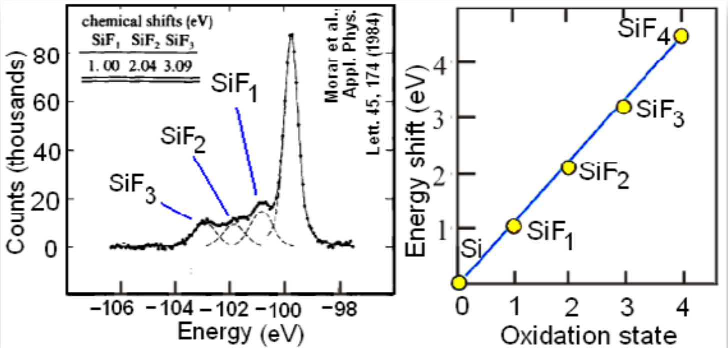
Chemical shifts

The possibility of determining accurate electron binding energies allows XPS to quantify small variations of binding energy due to, for instance, the binding of the atom to another atom (e.g. such as in the formation of compounds). Such variations are known as *chemical shifts* and produce small changes in the location of the peak positions; in oxidation, for instance, atoms lose electrons which in turn increase the binding energy of the photoelectron. XPS is specially suited for detecting the chemical shifts due to the fact that, being a one-electron process, the emitted electrons have a very small energy dispersion, especially in comparison to other processes, such as Auger emission.

One example is titanium which exhibits a very large chemical shifts between different oxidation states. The figure shows the electronic configurations of both neutral Ti and O as well as of TiO2 with the titanium atom losing 4 electrons and the two oxygen atoms receiving them. The lower panel shows the spectrum from a pure Ti sample (Ti^0) compared with that of titanium dioxide (Ti^{4+}); as it can be observed, the energy shifts are 4.5 eV for the 2p1/2 and 4.95 eV for the 2p3/2.

A more quantitative example of the change in binding energy due to oxidation is illustrated in the XPS spectra of fluorine attached to a silicon surface forming layers of SiF_1, SiF_2 and SiF_3. The left panel of the figure shows the spectra of SiF_x showing the shifted peaks, and the right panel presents the energy shift for four oxidation states. Again, oxidation (i.e. the removal of a valence electron) increases the binding energy, while the addition of an electron decreases the binding energy.

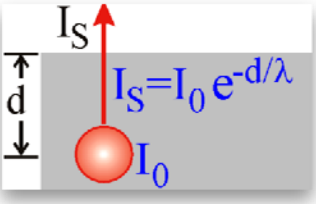




The ability of XPS to resolve chemical shifts depends mainly on the magnitude of the shift, the sharpness of the incident radiation as well as on the energy resolution of the electron detector. Samples with various components that overlap their photoelectron binding energies produce broad XPS peaks, which cannot be resolved for chemical shifts. Chemical shifts are usually in the range of a fraction of an eV to about 10 eV.

XPS Sampling Depth

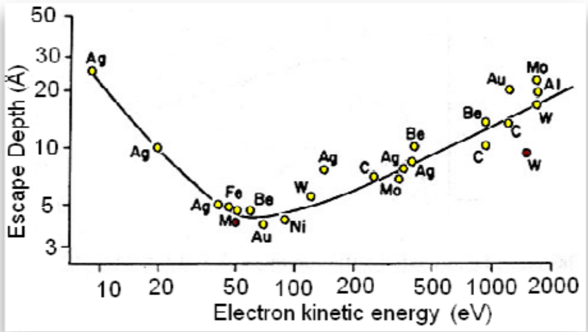
The XPS process is obscured by a several factors, but most importantly by the absorption properties of the material both for the incident x rays and the emitted electrons; although the penetration depth of an x ray is of several µm, the mean free path of an electron is of the order of a few nm, thus strongly limiting the sampling depth of XPS. An accurate description of the absorption of electrons by the medium is a complex process that depends on the kinetic energy of the photoelectron and the properties of the material; in practical terms it is best to describe such absorption in terms of a phenomenological attenuation law known as the Beer-Lambert law.



In an XPS analysis the x rays free a number of electrons a depth d below, a fraction of which will move straight to the surface. If the number of electrons that move toward the surface per unit time is I_o, the number of electrons that will reach the surface per unit time, I_S, will be given by

$$I_S = I_0\, e^{-d/\lambda},$$

where λ is the electron mean free path in the medium. Notice that at depths of $d \approx 3\lambda$ the intensity at the surface is $I_S \approx 0.05 I_o$, i.e. 95% of electrons produced at distances of 3λ will be absorbed; this fact is used to define the “sampling depth” as 3λ.

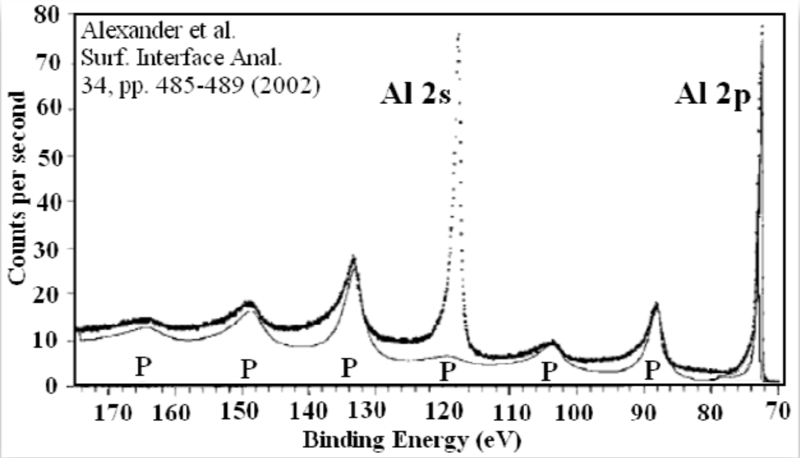


Luckily, the mean free path, λ, has a behavior that is similar for a large class of materials and can be characterized in terms of the so-called “Universal Curve” shown in the figure (adapted from the investigation of Seah and Dench). Experimental measurements presented there for a variety of media show that the sampling depth (or escape depth) of electrons is always in the range of 3 to 30 nm or so, this puts λ in the range of 1 to 10 nm. In summary XPS can gather information from the top 30 nm of material which corresponds to about 20 atomic layers.

Plasmon peaks

Other effects that modify the XPS spectra are the so called plasmon peaks which are produced by the interaction of the photoelectrons with collective excitations of the electrons in the valence band known as *plasmons*.

The plasmon excitations are fluctuations of the electron density produced either by the photoelectron itself while it propagates through the solid (extrinsic plasmon), or by the valence electrons in response to the presence of the core hole left by the emitted photoelectron (intrinsic plasmon). Interactions of the photoelectron with the plasmons reduce the kinetic energy of the electron making it appear with a larger binding energy in the XPS spectrum. Due to the repetitive spatial pattern of the plasmon waves, the photoelectron-plasmon interactions can occur more than once producing several “plasmon” peaks in the XPS spectrum at regular energy intervals. The figure shows the Al 2s and Al 2p XPS peaks along with several plasmon peaks.



The energy intervals of the plasmon "satellite" peaks are dictated by the material and can provide useful chemical information. Plasmons are noticeable mainly in Al, Mg and Si and are absent in non-metals.

A similar effect is produced when the photoelectron excites a valence electron into a higher energy level (i.e. it "shakes up" the electron). As before, the electron kinetic energy is reduced and the electron is counted in the spectra as with a larger binding energy. Due to the narrowness of the valence energy band, these shake ups tend to reduce the kinetic energy by a fixed amount thus producing regular distinct "shake up" peaks at binding energies a few eV larger than the real one.

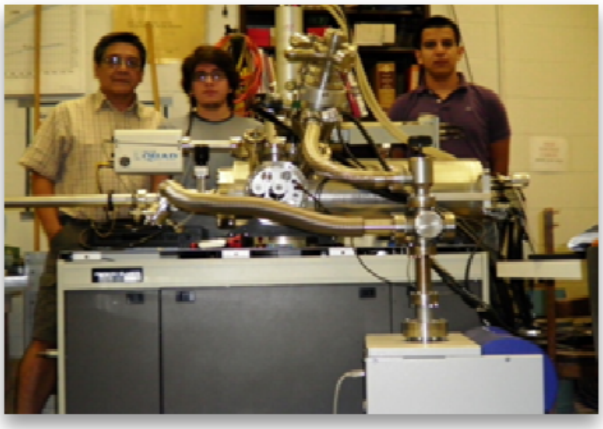
A related effect occurs when the photoelectron kicks out a valence electron ("shake off"). Since such inelastic collisions can reduce the electron kinetic energy by a wide range of energies, in the end the electrons appear at apparent larger binding energies –not a series of narrow peaks as before— but in a broad "shake off" peak.

Static charging

Yet another phenomenon that can affect the XPS spectrum arises due to the possible build up of positive charge on the surface of non-conducting samples. When thousands of photoelectrons are emitted and the sample is non-conducting, an excess of positive charge is created on the surface of the sample which, in turn, creates a surface electric field that will reduce the kinetic energy of the ejected electrons shifting the XPS peaks to higher energies. Fortunately, such effect can be eliminated by shifting the spectrum according to a well known reference point, such as the "adventitious carbon line" (C 1s line of 284.8 eV). Other -hardware based— approaches are depositing a thin layer of gold over the sample, or using of a low energy electron gun during the x ray irradiation to compensate the charge deficiency.

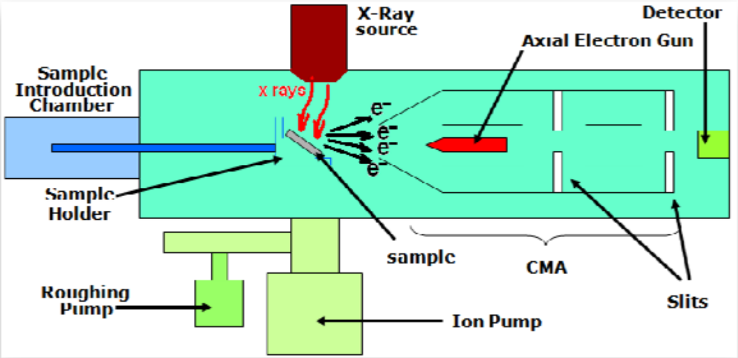
When the sample charges negatively (due e.g. to electron backscattering), the kinetic energy of the photoelectrons increases due to electric repulsion and thus the electrons are counted as with a lower binding energy. In such cases the XPS analysis is impossible.

XPS Spectrometer



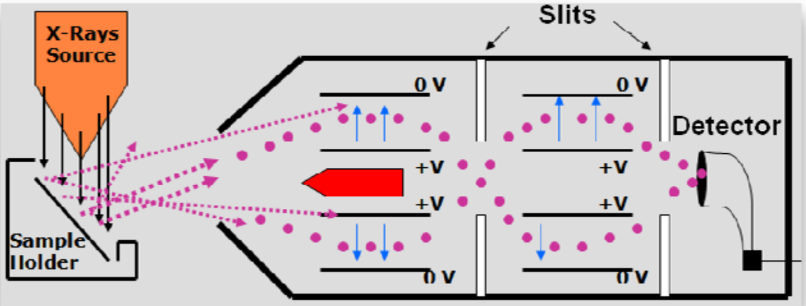
XPS is usually performed in commercially units or using synchrotron light sources. The picture shows the Perkin Elmer Φ560 XPS/AES/SIMS of the University of Texas at El Paso.

The main components of an XPS system are a source of x rays, an ultra-high vacuum (UHV) chamber with pumps, an electron collection lens and an electron energy analyzer. Other elements include an introduction vacuum chamber, sample mounts and a data collection system. A useful additional item is an ion gun used to bombard Ar or Ne gas ions to remove surface contaminants from the sample.



The diagram shows the main components of an XPS system such as the Φ560 which operates with either Al Kα (1486.6 eV) or Mg Kα (1253.6 eV) x rays and at a pressure smaller than 10^{-9} Torr.

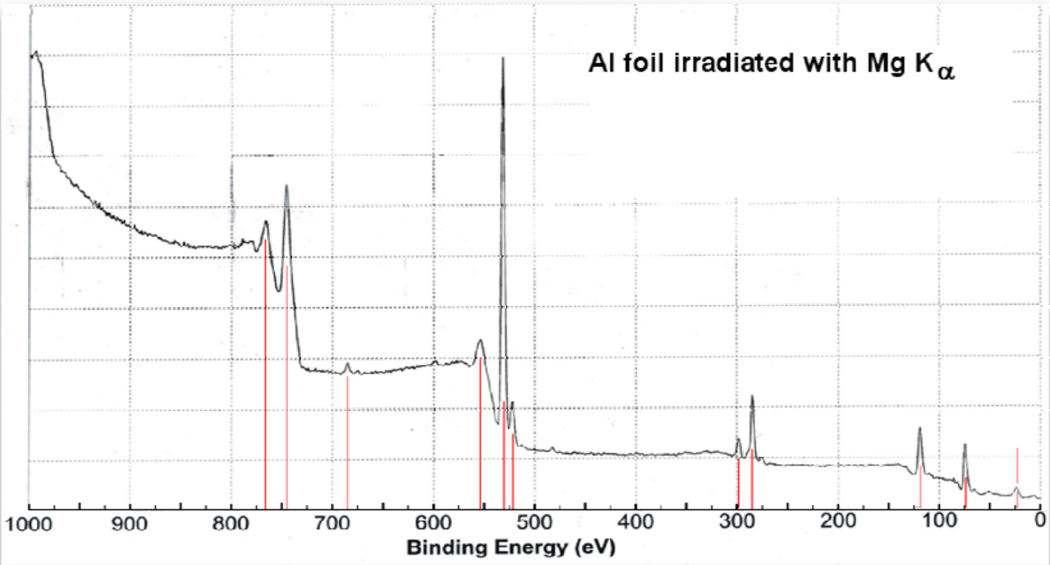
The next diagram illustrates the operation of the cylindrical mirror analyzer (CMA) which is used to collect and analyze the electrons. The CMA is composed of two concentric metallic cylinders maintained at different voltages. By using a combination of electric fields, the CMA captures and guides electrons of a given energy toward the detector while deflecting the rest towards the shield. By repeating the process at different values of the fields, electrons of different energies are captured and counted. The energy binning determines the resolution of the XPS peaks, which is normally an eV or less; analyses of chemical states (oxidation states, etc.) require finer resolutions.



Problems

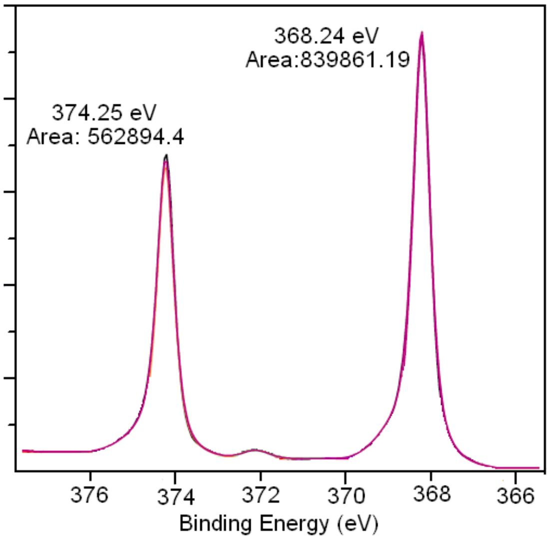
Problem 4.1

The spectra shown was obtained by irradiating Al foil with Mg x rays (1253.6 eV), use the tables of binding energies in the Appendix to identify the origin of the peaks signaled. Notice that the energy resolution of the spectrometer was 1 eV.



Problem 4.2

A clumsy student took the attached XPS spectra but forgot to identify the peaks. Please look the energies of the peaks, their relative areas and the binding energy tables of the Appendix to determine the element(s) and the energy levels to which the two peaks correspond.



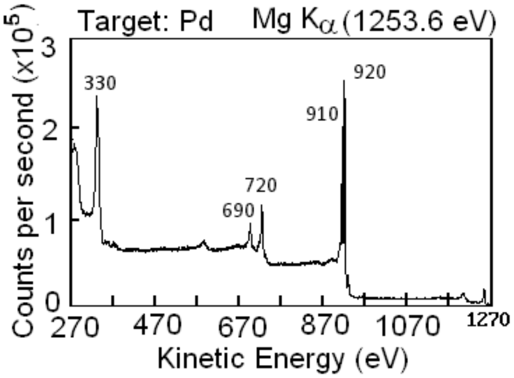
Problem 4.3

The XPS spectrum was obtained irradiating Mg K$_\alpha$ x rays on a Pd sample.

A) Determine the binding energy of the electrons that were collected on the five peaks shown.

B) Identify the energy levels of the peaks.

(Problem adapted from www.chem.qmul.ac.uk/surfaces/scc/scat5_3.htm).



Problem 4.4

You are about to perform a rare XPS study of NaCl using oxygen K$_\alpha$ x rays, what will be the kinetic energies of the 1s, 2s, 2p and 3s electrons?