Photoelectron Spectroscopy

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<http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Photoelectron_Spectroscopy/Photoelectron_Spectroscopy%3A_Theory>

<http://www.youtube.com/watch?v=vANbxozsRSA>

Photoelectron spectroscopy is a technique that is used to gather information about the electrons in an atom.

An atom is bombarded with photons.  Some of the photons are absorbed and electrons are emitted.  The electrons are collected and their energy is analyzed.  Since we can know the energy of the photons, and we know that energy is conserved we know that the difference in energy between the photons sent into the atom and the energy of the electrons emitted will be the potential energy of the electrons when they are attached to the atom.  Remember that the potential energy of the electron in the atom is the work needed to remove the electron from the atom.

Energy of emitted electron = energy of photon - work needed to remove electron from atom

Visit this URL:

<http://www.chem.arizona.edu/chemt/Flash/photoelectron.html>

Select the button labeled mono.

Select the element hydrogen.

You will see a graph with two numbers.  The whole number is the integration of the number of electrons in the spectrum.  The decimal number is the work needed to remove the electron from the atom in MJ/mol.

Now select helium.  You’ll see that the integration is 2 and the energy is higher than hydrogen.  That’s because He has 2 electrons and H has 1.  Also, H and He have the same level of shielding (none) while He has 2 protons and H has 1.  That makes it harder to remove the electrons from He than from H.

Look at Li.  There are two sets of electrons.  1 electron has lower energy, the 2 have higher energy.  Let’s think about terminology.  We have said that electrons in 1s have lower potential energy than 2s.  When we look at the PES spectrum, we see 1 electron at a low number, and 2 electrons at a high number.  How can this be if the 2 electrons in 1s have lower energy than the 1 electron is 2s?

The answer is semantics.  Low, high, high, low.  Don’t worry about it.  The energy on the spectrum is the work needed to remove the electron from the atom.  Once the electron is removed, we can say the potential energy is infinite.  If the electron hit the nucleus, the potential energy would be 0.

On the PES spectra, a high energy number means the electron is closer to the nucleus, a low number means it is farther from the nucleus.  Note that the peak for an electron farther from the nucleus is closer to the beginning of the graph while the peak for an electron closer to the nucleus is farther from the beginning of the graph.

Think of the energy number on the graph as how hard it is to take the electron away from the atom.

Now look at boron.  The 2 electrons at 19.3 are the 1s electrons.  There are 2 electrons at 1.36 and 1 electron at .80.  The 2 electrons are 2s and the 1 electron is 2p.  Why are they different?  They are both in the same energy level (shell), so why do they have different potential energies.

The reason the 2s and 2p orbitals have different energy is that s penetrates better than p.  An s orbital can overcome the effect of shielding better than p.  Remember that penetration ability is:

s>p>d>f

So, it is easier to remove an electron from the 2p orbital in B than from the 2s.  That’s why the 2s are at 1.36 and the 2p are at .8.

Look at scandium.  The filling order has 3d after 4s because 3d does not penetrate as well as 4s.  However, in the spectrum for scandium we can see that there are 2 electrons at .63 and 1 at .77.  This suggests that it is easier to remove the 4s than the 3d.  This is because n = 3 shields n = 4.  This raises the energy of 4s once 3d starts to fill.

You can look at other elements and see how they work.