

X-ray Photoelectron Spectroscopy

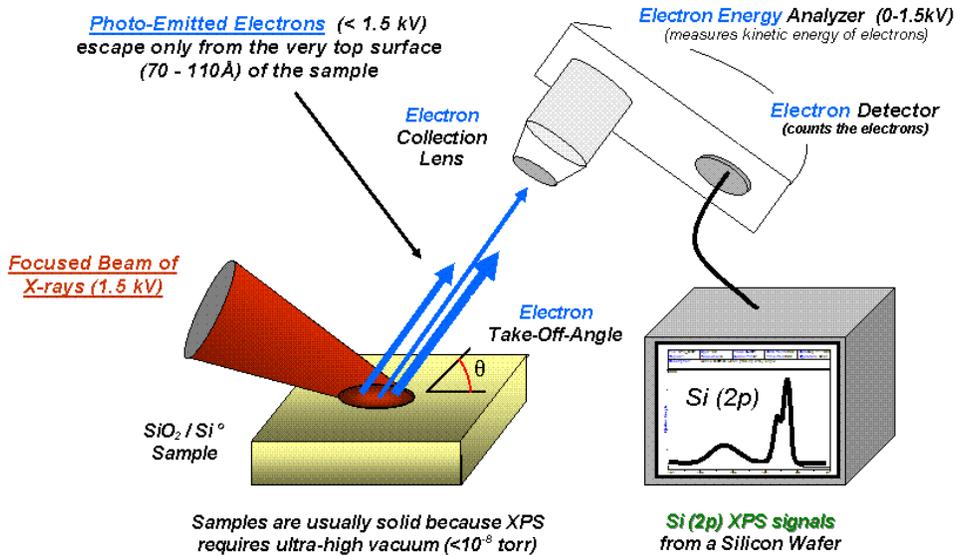


Figure 1: A silicon sample is analyzed using XPS. Source: <http://en.wikipedia.org/wiki/File:System2.gif>

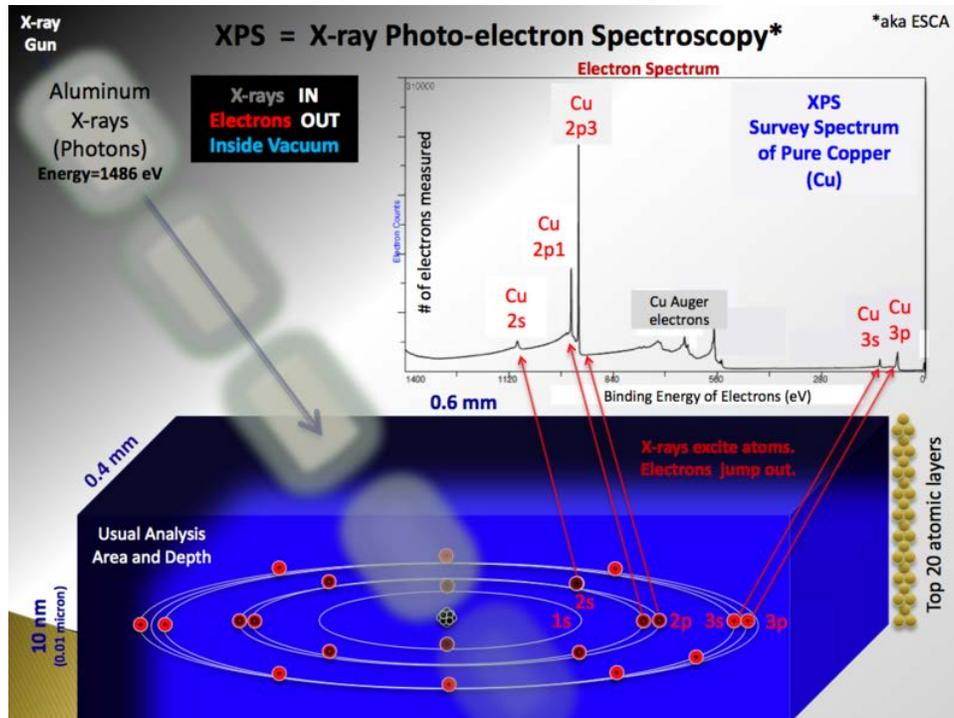


Figure 2: Another depiction of XPS, which is used to analyze the electronic structure of atoms. Source: http://en.wikipedia.org/wiki/File:XPS_PHYSICS.png

XPS – the simplified story for AP Chemistry students

1. A type of PES (photoelectron spectroscopy)
2. It is used to understand the electron configuration of electrons in an atom; it can be used to determine the number and energy of electrons in the core energy levels
3. Lots of energy is needed to remove an electron from the core energy levels of an atom
 - a. Infrared light (IR) can be used to make atoms within a molecule or a molecule itself move (translation, vibration, rotation).
 - i. IR light: enough energy to make atoms tremble, but not enough energy to remove core electrons
 - b. UV-Vis spectroscopy (near-ultraviolet and visible light) is used to excite the valence electrons of an atom. The light given off when the electron relaxes has energy proportional to the energy difference between the two states of the electron's transition.
 - i. UV-Vis light: enough energy to make the electrons hop up temporarily to higher-than-usual energy levels. Does not have enough energy to remove core electrons.
 - c. X-rays do not (as far as I know) significantly affect the motion of atoms/molecules nor does it cause temporary excitation/relaxation of valence electrons.
 - i. XPS is used to knock electrons out of the atom, especially the core electrons.
 - ii. When the electrons are knocked out, they can be counted with an analyzer. The bigger the signal that the analyzer reads out, then the bigger the peak on the XPS spectrum. Taller peak = more electrons ejected.
 - iii. FOR A GIVEN ATOM, the closer the electrons are to the nucleus, then the tougher it is to remove them. The greater the amount of energy (in eV) needed to remove an electron, then the closer that electrons was to the nucleus.
 - iv. When COMPARING TWO ATOMS, if one atom has a greater nuclear charge than the other, then similar electrons will require more energy to remove from the higher-charge nucleus than from the lower-charge nucleus.
 - v. Photoelectron emission spectra are displayed as number of electrons on the y-axis vs. energy needed to remove electrons on the x-axis.
 1. The energy is usually measured in electron volts (eV). An electron volt is a convenient, small unit of energy used in physics. $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

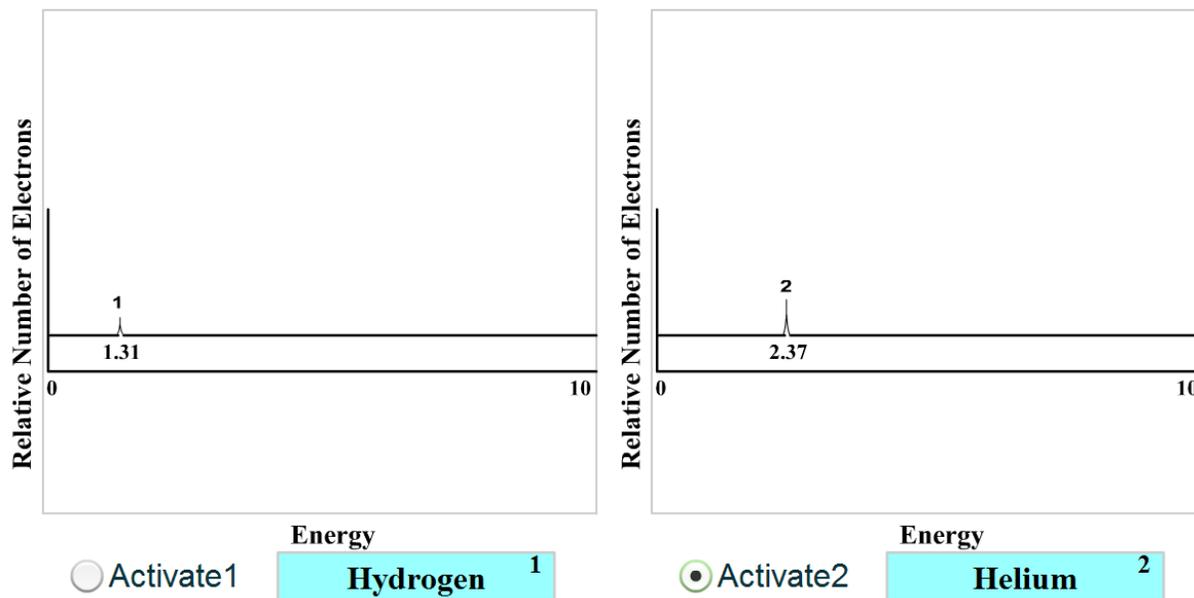
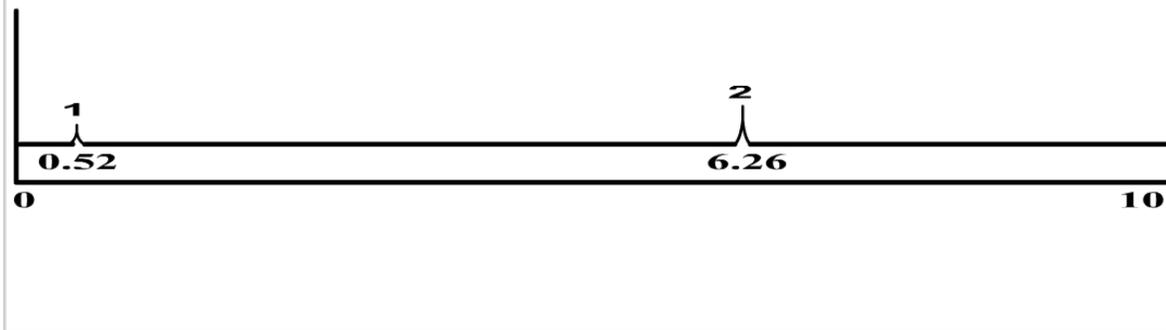


Figure 3: Photoelectron emission spectra for hydrogen ($Z=1$) and helium ($Z=2$). Source: <http://www.chem.arizona.edu/chemt/Flash/photoelectron.html>.

4. Let's analyze figure 3.
 - a. The peak for He is TWICE AS HIGH as that of H. This is because there are TWICE AS MANY ELECTRONS in the 1s sublevel in He as there are in H.
 - b. The peak for He is HIGHER IN ENERGY (2.37 eV) than that of H (only 1.31 eV) because the NUCLEAR CHARGE of He is higher ($Z=2$) for He than that of H ($Z=1$). ("Z" is the nuclear charge, and we use it as "atomic number" in our class.)
 - c. Can you justify the peak heights and binding energies in the two spectra below? Which peaks represent 1s electrons? 2s electrons? How could answer these questions for Be if you did not have the spectrum of Li available for comparison?

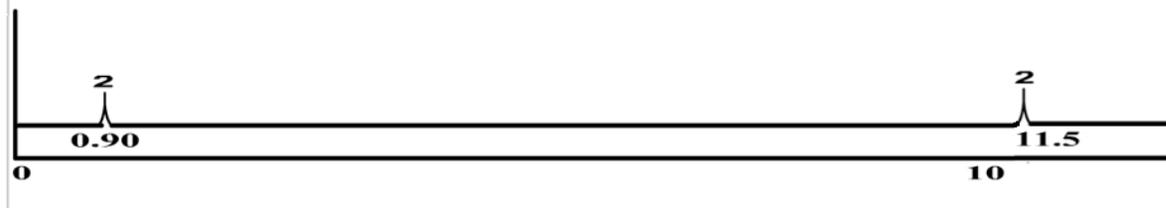
Relative Number of Electrons



Energy

Lithium 3

Relative Number of Electrons



Energy

Beryllium 4