Photoelectric Effect

To understand the principles of photoelectron spectroscopy, the photoelectric effect must be applied. The photoelectric effect states that electrons can be pushed off the surface of a solid by electromagnetic radiation. The ejected electrons are called photoelectrons.

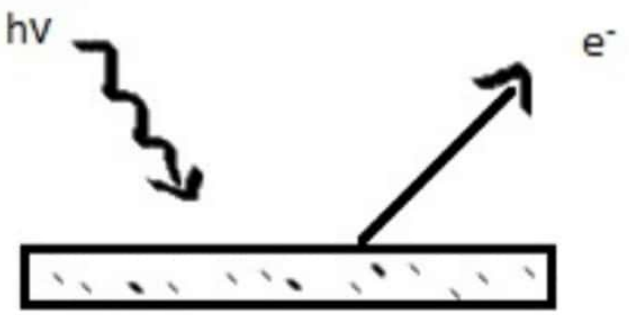

Figure 2. Scheme of photoelectric effect. Incoming light hits the surface of a solid causing the ejection of a photoelectron.

Originally, known as the Hertz effect, the photoelectric effect was first observed by Heinrich Hertz in 1887, when Hertz noticed that sparks would more readily jump between two charged surfaces that were illuminated with light. Hertz's observation would ultimately lead to Einstein's photoelectric law; the kinetic energy of an emitted photoelectron is given by

$$E_k = h\nu - E_I$$

where h is Planck's constant, v is the frequency of the ionizing light, and E_I is the ionization energy, which is synonymous with electron binding energy, of the electron. The term photoelectric effect is only considered when discussing solids, exclusively. As PES can be used for energy measurements of solids, liquids, and gases the term photoionization or photoemission better represents the principles of PES. Photoionization is the process in which molecule (M) is ionized by a beam of photons, in which the molecule will lose an electron:

$$M + h\nu \rightarrow M^{+}(E_{int}) + e$$

This process of photoionization follows the three-step model. The three-step model breaks down the process of photoionization into three independent steps:

1. The molecule will absorb the photon, causing the energy of the photon to be transferred to the molecule's electrons, which will become excited.
2. The excited electron will travel to the surface of the molecule. During this step, the excited electron travels it may or may not collide with other particles. Any excited electrons which do collide with a particle will loss energy.
3. The excited electron will escape the surface of the molecule into the vacuum where it will be detected.