Photoelectron Spectroscopy

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Introduction

- It is also known as photoemission spectroscopy.
- Measures the energy of electrons that emitted from solid, liquid or gases emitted after photoelectric emission and to determine the binding energy of the electrons.
- It can be divided on the basis of energy sources, as in XPES (X-Ray Photoelectron spectroscopy) ionization energy is provided by an X-ray photon and in simple UPES (Ultra-violet Photoelectron Spectroscopy) it is an EUV photon, or an ultraviolet photon.

PES calculates the following by measuring the Kinetic Energy of the emitted electron:

- binding energy
- intensity and angular distributions of electrons
- examine the electronic structure of molecules

X-ray photoelectron spectroscopy (XPS) was developed by Kai Siegbahn starting in 1957

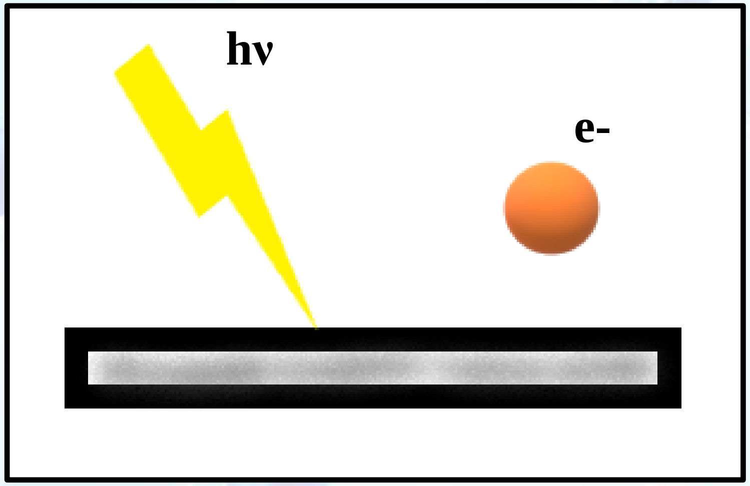
Ultraviolet photoelectron spectroscopy (UPS was developed originally for gas-phase molecules in 1961 by Feodor I. Vilesov and in 1962 by David W. Turner

Two-photon photoelectron spectroscopy (2PPE) is an extended technique in which optically excited electronic states are used and there is an introduction of a pump-and-probe scheme.

While other conventional methods involve studying the intensity of radiation for knowing the electronic configurations, this method depends on electron for calculations

Extreme-ultraviolet photoelectron spectroscopy (EUPS) is an intermediate of XPS and UPS and used to assess the valence band structure. It gives better energy resolution and ejected electrons are faster, resulting in less space charge and mitigated final state effects.

Photoelectric Effect



The emission of electron after a light radiation of high intensity falls on the surface. The emitted electrons are referred as photoelectrons. According to classical theory of electromagnetic energy, the electrons are emitted with the energy transferred from the incident radiation.

Emission mechanism

- **The energy of photon is proportional to the frequency of the light.**
- **When an electron in material absorbs energy of one photon and crosses the work function (binding energy) and electron is ejected.**
- **Higher the frequency of radiation, more is the probability of electron ejection. Hence, energy of the emitted electrons does not only depend on intensity of incident radiation, but on energy (equivalent frequency) of the individual photons.**
- **So, we can relate that photoemission is the result of an interaction between an incident photon and the innermost electrons of an atom. The movement of an outer electron in an atom to occupy the vacancy results in the emission of a photon.**

- **On irradiation the electrons absorb energy from photons. They follow an "all or nothing" principle. Either all energy from one photon is absorbed and one electron is emitted from atomic binding or the energy is re-emitted. The absorbed energy then releases electron from atom and also rest contributes to the Kinetic Energy of electron as a free particle.**
- **I*nternal photoemission* is used when the photoelectron is emitted into a solid rather than into a vacuum and emission into a vacuum distinguished as *external photoemission*.**

The photoionization follows *A three-step model* and it breaks down the process of photoionization into three independent steps:

- **In first step, the molecule absorbs a photon which results into the energy transfer from photon to the molecule's electrons and hence the electron will become excited.**
- **This excited electron travels to surface of the molecule. In this step, the excited electron may or may not collide with other particles or each other. Any excited electrons which do collide with a particle will loss energy.**
- **The excited electron then escapes the surface of molecule into the vacuum where it will be detected by a detector and used for further analysis.**

Photoelectron Spectroscopy Set up