A Short Primer on Inverse Photoelectron Spectroscopy (IPES)

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Inverse Photoelectron Spectroscopy (IPES) is a complementary technique to Photoemission spectroscopy (PES). While PES probes the occupied density of states in a sample through the photoelectric effect (ionizing photons in and electrons out), IPES does the reverse, i.e. the sample is exposed to an electron beam and the emitted photons are collected.

The most popular IPES mode is the "isochromat" mode, in which an UV detector with a narrow band pass is used to count emitted photons of a certain constant energy. Fig.1 illustrates this process for a metal. On the right hand side of the diagram, the electrons coming from the electron source (filament) of the electron gun are accelerated to E_{kin} relative to the equilibrated Fermi level of the sample/gun system (the sample and gun are in electrical contact). Once the electrons impinge on the sample, they recombine more or less randomly into all of the unoccupied states below their kinetic energy. This gives rise to a continuous Bremsstrahlung (x-ray) spectrum (essentially this is the exact same process that happens in any x-ray gun when the x-ray cathode is bombarded with electrons from a filament nearby). This

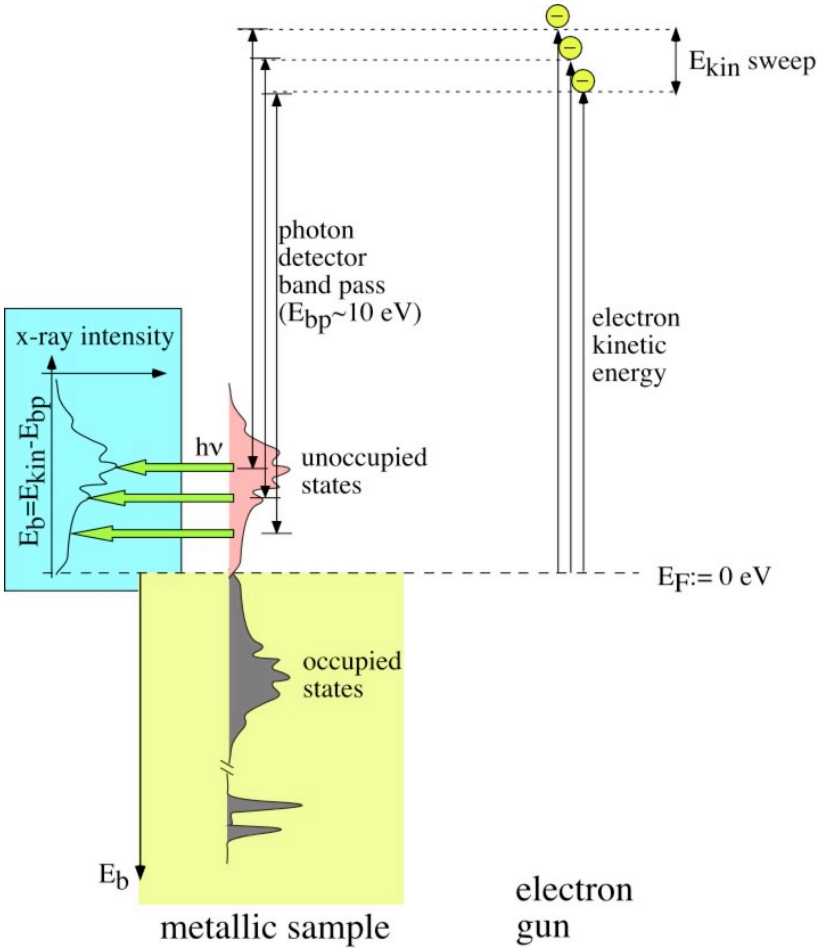

Fig.1: Schematic of IPES in "isochromat" mode. Electrons of a certain kinetic energy are emitted form the electron gun. At the sample surface they recombine into empty states above the Fermi level and photons (Bremsstrahlung) are emitted. A detector with a narrow (~0.6 eV) fixed energy window (~10 eV) counts emitted photons. Variation of the electron kinetic energy allows to scan through the unoccupied states, resulting in the IPES spectrum.

spectrum represents in a first order approximation the density of states of the unoccupied states. However, without an expensive (and signal attenuating) UV monochromator, this spectrum cannot be measured easily. However, ionizing radiation can fairly easily and inexpensively be quantified by using a (gas-based) Geiger-Müller counter or a solid state detector such as a photomultiplier. The problem with these detectors, however, is that they do not allow easily to quantify the energy of the impinging photons, i.e. they only count photons, but do not tell us much about their energy.

The "trick" in IPES, that allows the detailed measurement of the density of the unoccupied states, is to use a bandpass photon detector that only counts photons of a certain energy E_{bp} ("bp" for bandpass, i.e. the energy representing the center energy of the detected energy band width). This allows to specifically count only photons originating from recombination into a certain narrow band of states at E_{bp} below E_{kin} (see Fig.1). Sweeping of E_{kin} by adjusting the acceleration potential in the electron gun then allows to "push" this energy window across the range of interest of the unoccupied states, and a spectrum of photon count vs. binding energy above the Fermi level (see "blue box" in Fig.1) can be obtained. The photon intensity per binding energy is a first-order measure of the unoccupied density of states.

An example for a Geiger-Müller principle detector used in IPES is a dimethyl ether/ ethanol filled tube with a MgF_2 window[1] (there are several other gas/window combinations that can be used). The dimethyl ether ionizes above 10.1 eV while the MgF_2 window transmits below 10.97 eV (Transmission function: see Fig.2 in Ref.[1]). The ethanol serves to quench ions before they can hit the detector wall and create secondary electrons. The full width at half maximum (FWHM) band pass window of this detector is about 0.6 eV, defining the resolution of the measurement (electron guns have a comparably narrow energy distribution). The maximum sensitivity is at 10.6 eV.

An example for a solid state detector is a photomultiplier tube (where the first dynode is coated with KCl) and a CaF_2 window[2]. The KCl ionizes above ~7 eV while the CaF_2 window cuts off at about 10.1 eV. While this combination represents a fairly large window, the sensitivity spectrum shows a narrow peak at 9.8 eV (see Fig.1 in Ref. [2]), giving this detector essentially the same 0.6 eV FWHM resolution like the above Geiger-Müller detector.

The advantage of solid state detectors is that they do not need a gas filled chamber, i.e. they are more easily integrated into a ultra-high vacuum system (necessary to perform IPES) than Geiger-Müller type detectors, which need to seal off the ionization chamber relative to the vacuum system. On the other hand, it was shown by Hill and McLean[3] that Geiger-Müller detectors have a ~20x better sensitivity than solid state detectors. This is an important feature, since photon counts in IPES measurements are notoriously low (of the order of 100 cts/sec/Sr).

References:

[1]K. C. Prince: "Improved Inverse Photoemission Detector", Rev Sci Instrum 59 (5), pp. 741-742 (1988).

[2]N. Babbe, W. Drube, I. Schafer and M. Skibowski: “A Simple and Compact System for Combined Angular Resolved Inverse Photoemission and Photoemission in the Vacuum Ultraviolet”, J Phys E Sci Instrum 18 (2), pp.158-160 (1985).

[3]I. G. Hill and A. B. McLean: “A comparison of two high performance inverse photoemission bandpass detectors”, Rev Sci Instrum 69 (1), pp.261-264 (1998).