

UPS Cont. & Applications

Louis Scudiero

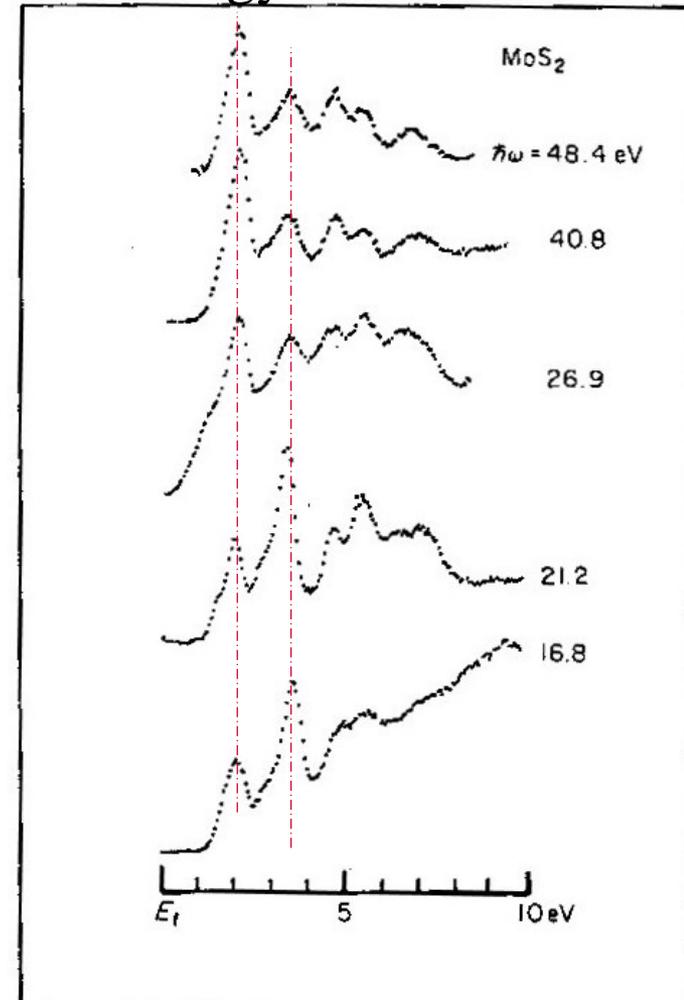
<http://www.wsu.edu/~pchemlab>; 5-2669

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MoS₂ (molybdenum disulfide) photoelectron energy distribution spectra intensity as a function of "binding" energy and photon energy.

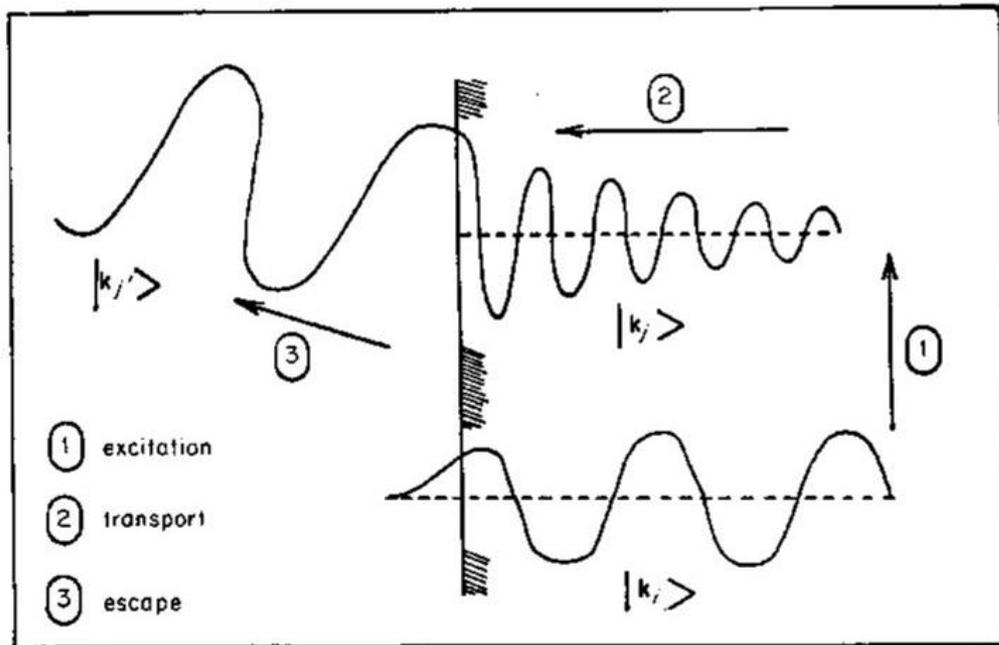
Photon energies: Ne (I) 16.8 eV, He (I) 21.2 eV, Ne(II) 26.9 eV, He (II) 40.8 eV, and He (II β) 48.4 eV.

Note that the **relative intensity of the peaks changes** in the distributions with photon energy. This is due to cross-section σ changes for the "d" and "p" region of the VB.



How is this related to the electronic structure of the material, what is the significance of the intensity variations?

To answer these questions, let us again look at the 3-step model that was first proposed by Berglund and Spicer (*C. N. Berglund and W. E. Spicer, Phys. Rev. A136, 1030, 1964*).



Initial Block state $|k_i\rangle$ with energy E_i (allowed state with a periodicity determined by the periodic potential of the crystal lattice). These electrons are then excited (1) by the photon into a conduction band state $|k_j\rangle$ at E_j (2). The excited electrons finally escape from the surface (matching at the vacuum interface between the excited state $|k_j\rangle$ and some free electron state in vacuum). This state can be represented by a single plan wave $e^{i\mathbf{p}\cdot\mathbf{r}} \approx |k_j\rangle$ (3).

The contribution to the photocurrent $I(h\nu, \varepsilon)$ with some initial state energy $E_i = \varepsilon$ (analyzer set to ε) can be expressed as follows:

$$I(h\nu, \varepsilon) \propto \int T(\mathbf{k}) \left| \langle \mathbf{k}_i | \mathbf{A} \cdot \nabla | \mathbf{k}_f \rangle \right|^2 \delta((E_j - E_i) - h\nu) \delta(\varepsilon - E_i) d\mathbf{k}$$

Where $T(\mathbf{k})$ is some function expressing the probability of transport and escape (steps 2 and 3) and where $\left| \langle \mathbf{k}_j | \mathbf{A} \cdot \nabla | \mathbf{k}_i \rangle \right|^2$ is the dipole matrix element

expressing the optical excitation (step 1).

[\mathbf{A} is the vector potential, ∇ gradient and the δ functions express the fact that 1) E_i and E_j are separated by $h\nu$ and 2) that the energy analyzer is “tuned “ to pick out the initial state E_i .]. If these conditions are met the δ s are equal to 1.

Illustration of three important effects:

1. Density of states
2. Matrix elements
3. Transport effects

Density of States

Theoretical calculations versus photoemission spectrum

Let us assume that we are slowly varying transport functions and matrix elements so that it can be given by:

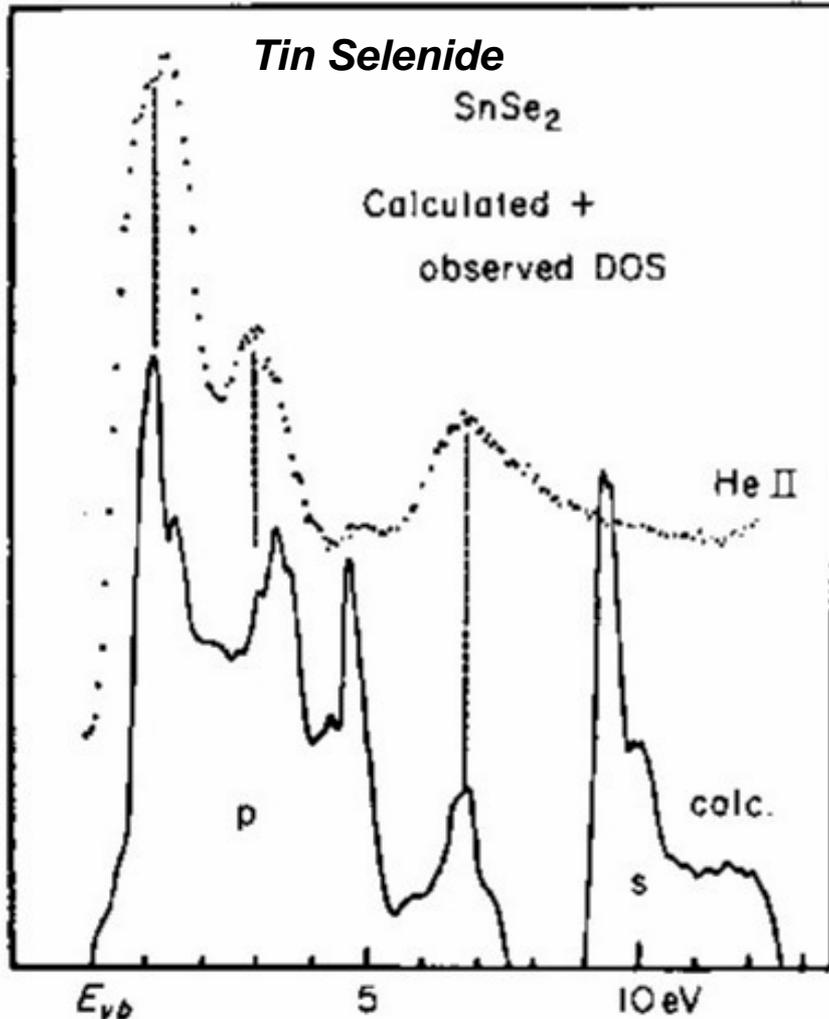
$$I \propto \int \delta(E_j - E_i - h\nu) \delta(\varepsilon - E_i) dk$$

The two δ functions define 2 intersecting surfaces in reciprocal space and if the integral is transformed to a line integral around the line of intersection the photocurrent is expressed as:

$$I \propto \int \frac{dl}{\nabla_k(E_j) \nabla_k(E_i)}$$

The integral diverges when both gradient terms go to zero (band becomes essentially “flat”). But $(1/\nabla(E)) dE$ is the density of states in an energy interval dE .

So, if we neglect the singularities, *the photoemission measures the overall density of states in the valence band of the solid and can be compared directly with calculated band diagram.*



Very good agreement between theory and experiment in the “p” region. No contribution of the “s” states is seen in the He II data. This is due to a very small value of the dipole matrix element.

No “s” contribution because

$$\left| \langle k_j | A \cdot \nabla | k_i \rangle \right|^2 \approx 0$$

Dipole Matrix Elements

Photoionization Cross-section

The absence of the 's' state in the SnSe₂ He (II) spectrum can be explained by looking at the matrix element $\left| \langle k_j | A \cdot \nabla | k_i \rangle \right|^2$

At a given photon energy $h\nu$ and for a fixed final state $|k_f\rangle$

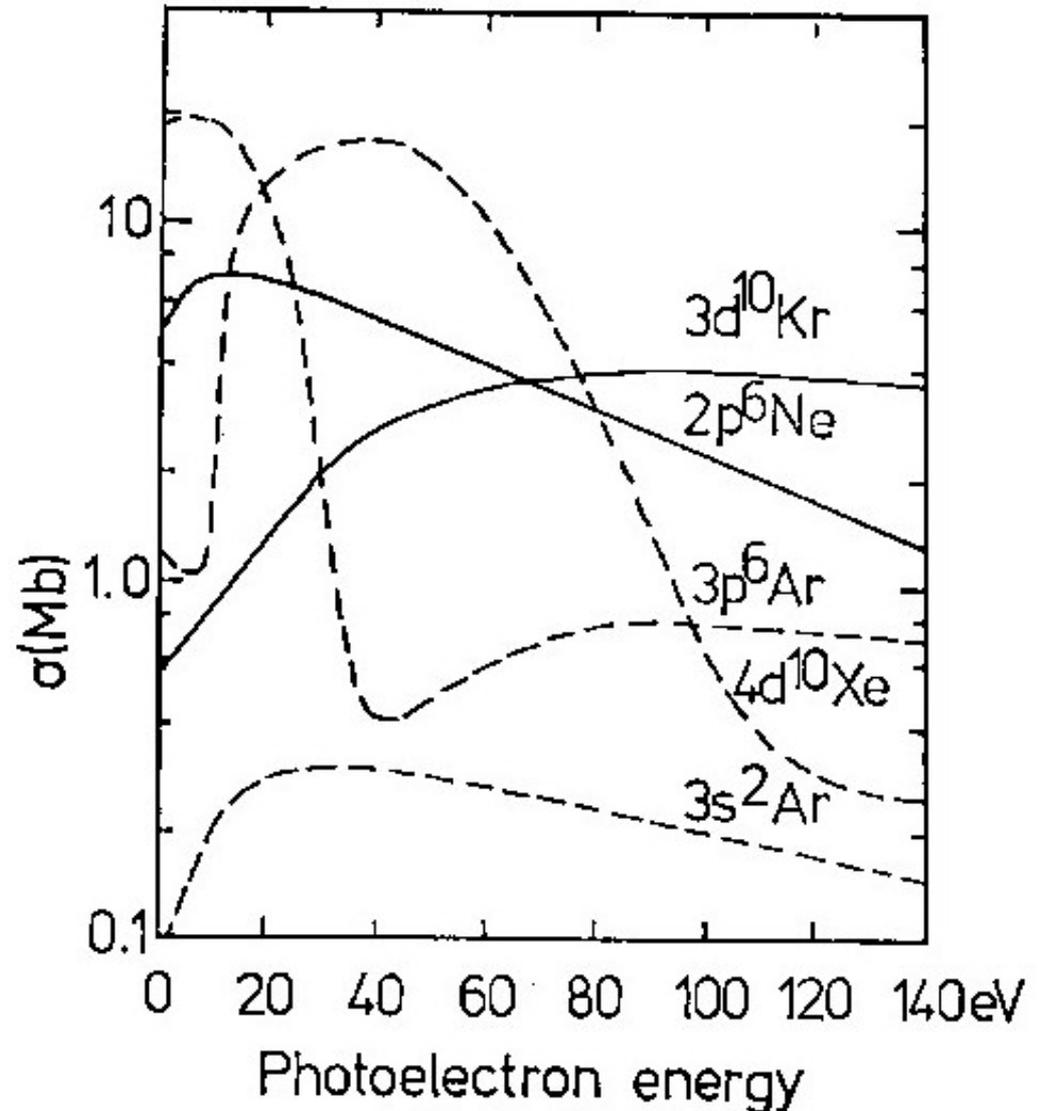
the matrix element will vary depending on whether $|k_i\rangle$ is s, p, d or f like.

In practice, the 's' cross-section is extremely low above about 10 eV until we reach soft x-ray energies. Therefore only p, d and f electrons will be detected in the energy range of 0 - 50 eV (UPS).

Calculated cross-section for certain rare-gas shells

Simplest definition of the cross-section is the probability of interaction between small particles.

Units: barn = 10^{-28} m²



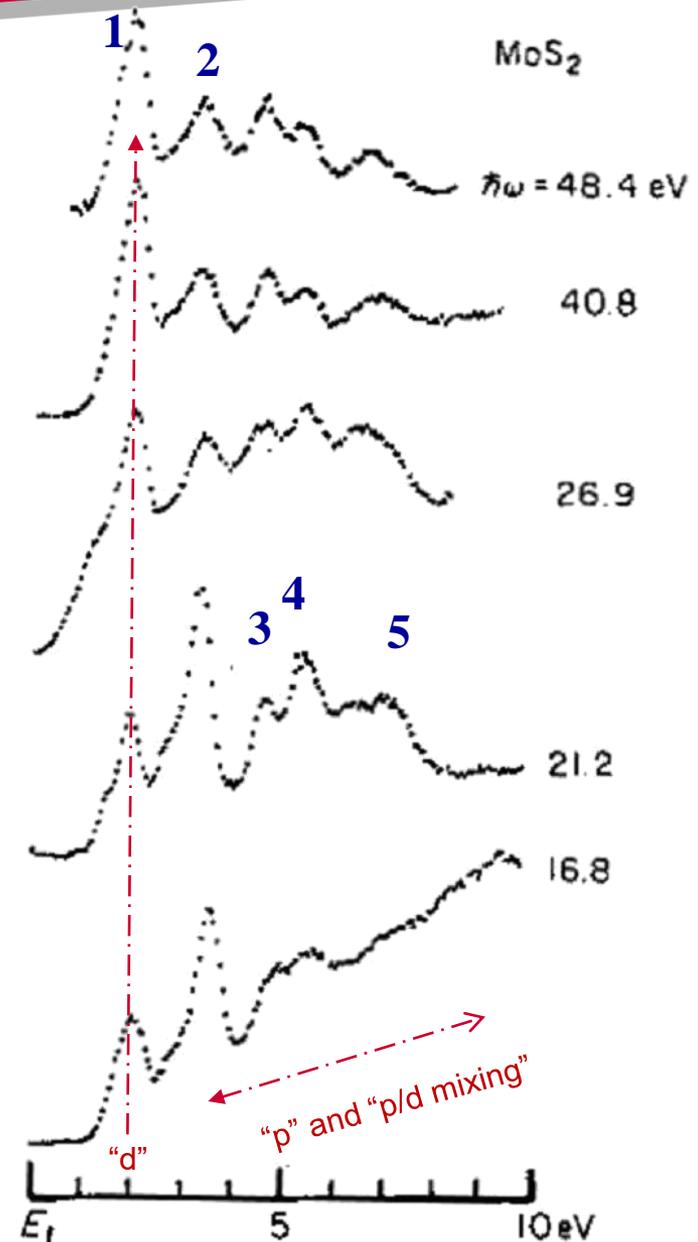
So, back to molybdenum disulfide, the VB states are formed from Mo 4d and S 3p electrons. The band near the E_F is purely 'd' like and the remaining structure comes from covalent bonding band based on the S 3p electrons. Some mixing p/d character is also expected.

Spectra measured between $h\nu = 16$ and 48 eV

Based on the plot cross-section vs. PE energy shown in the previous slide the 3p (2) states dominates below 25 eV and the 4d (1) states above 25 eV.

Bands 2 and 4 are purely S 3p and finally bands 3 and 5 are expected to have a mixed character p/d.

—————> *Atomic character of the states cause intensity changes*

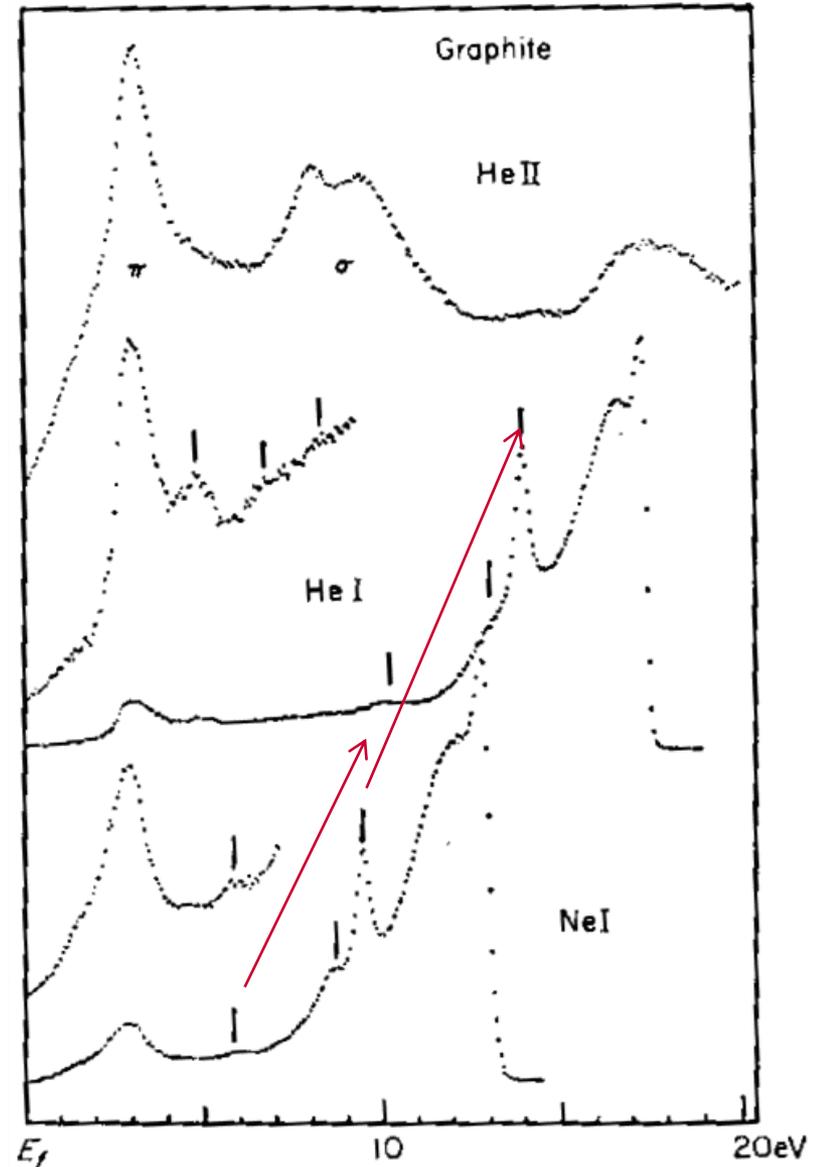


Transport Effects

This effect is mostly due to energy loss introduced by electron-electron interactions (scattering and secondary emission).

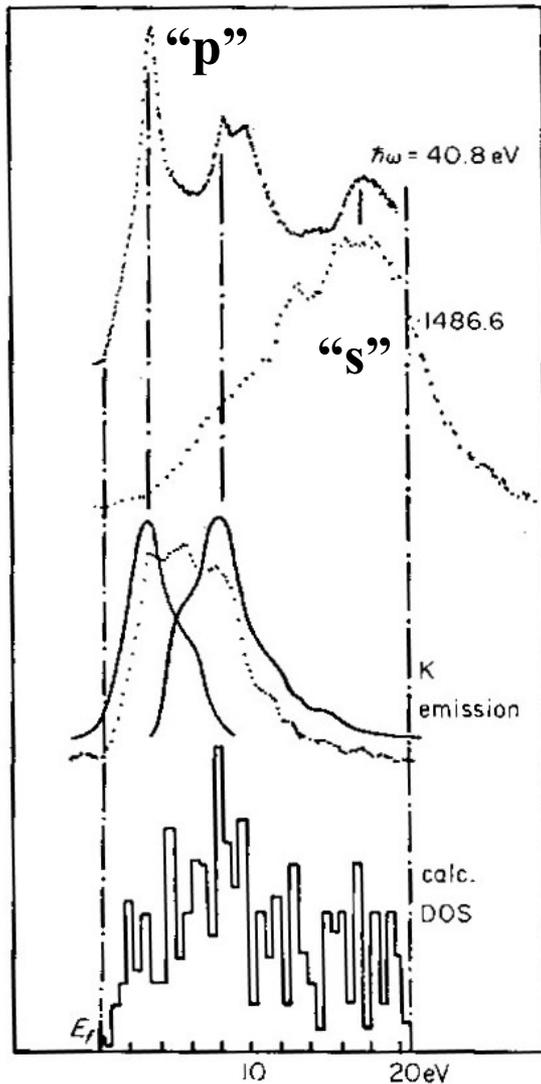
If these electrons escape the spectrum will display peaks that will move as the photon energy is changed.

Structure which ‘moves’ between NeI and HeI spectra is assigned to secondary electron emission (identified by bars)



Band Theory and PE Spectrum

(electron energy distributions)



He II

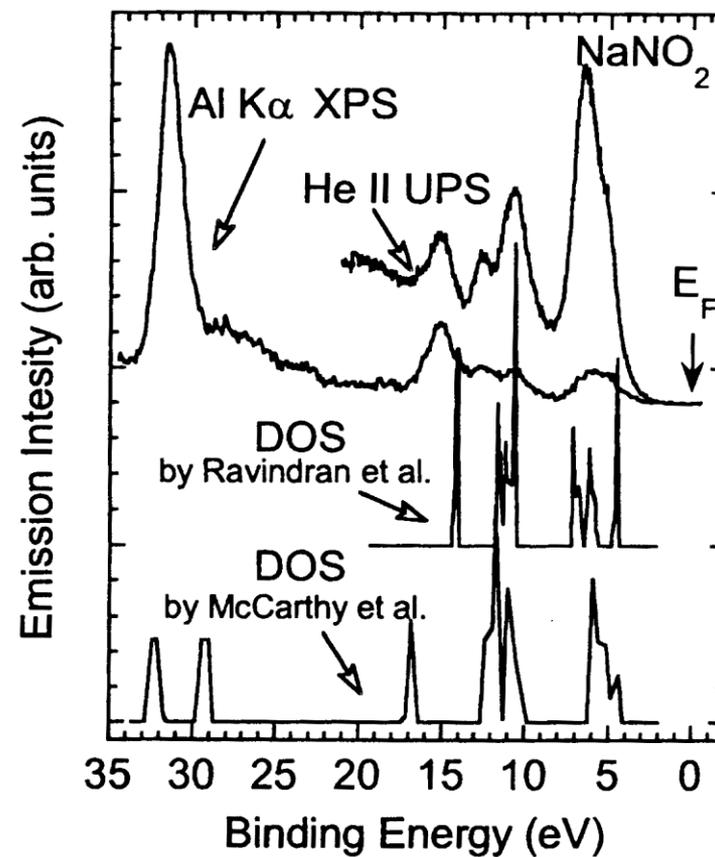
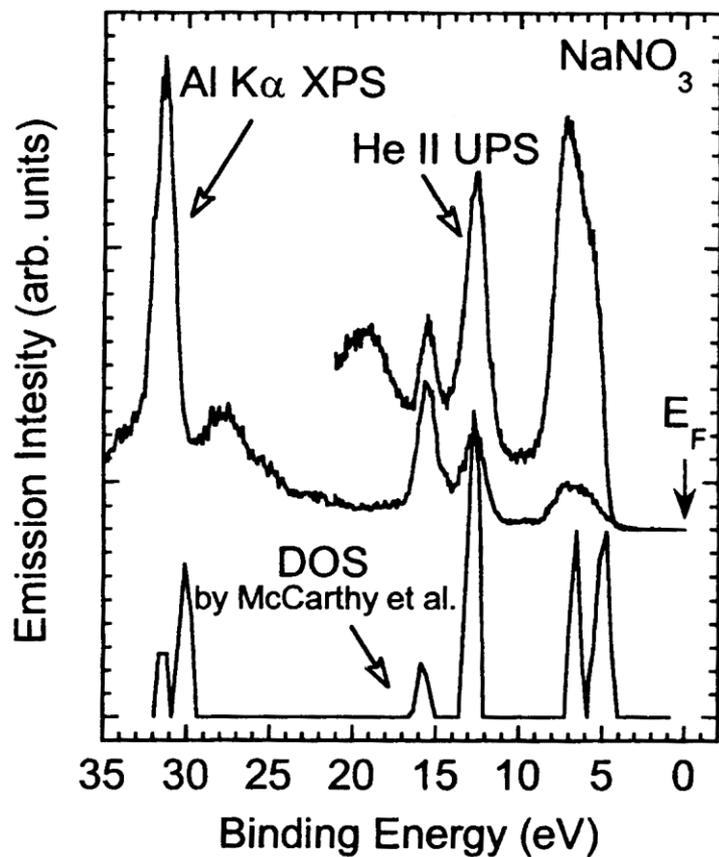
XPS

Because the C – C bond distance in graphite $\sim 1.4 \text{ \AA}$ \rightarrow strong interatomic interactions $>$ than in diamond. The VB electron distribution is important theoretically and experimentally.

$2s \rightarrow 1s$ forbidden
but $2p \rightarrow 1s$ allowed

UPS spectrum reassembles the DOS calculated

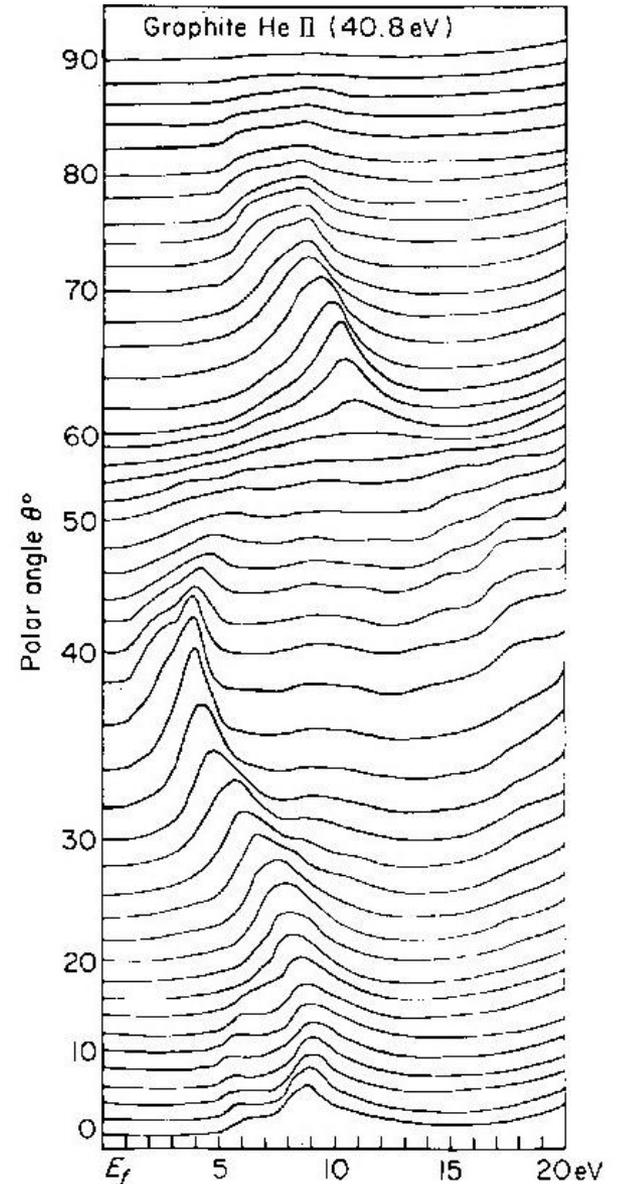
P. M. Williams, *Handbook of x-ray and ultraviolet photoelectron spectroscopy*, edited by D. Briggs, Heyden&Son Ltd, 1977.



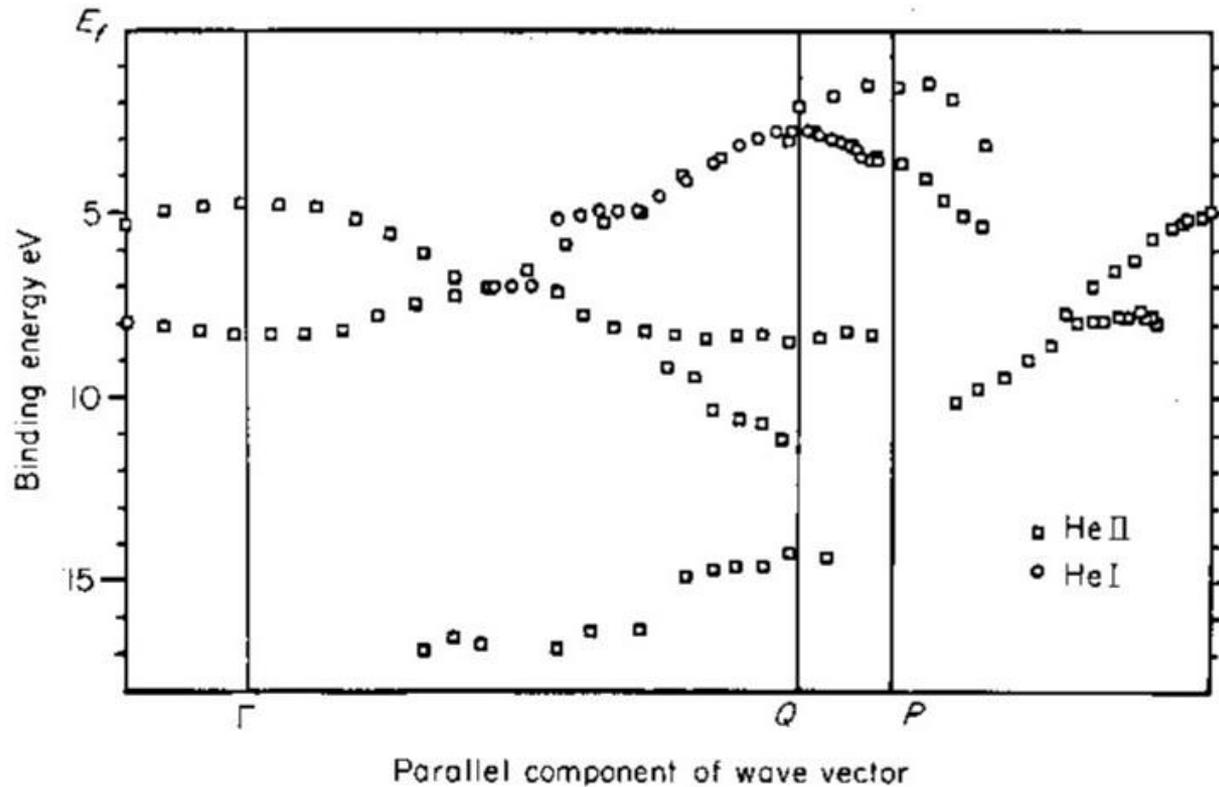
C. Bandis, L. Scudiero et al, Surface Science, 442 (1999) 413-419

Dispersion Measurements

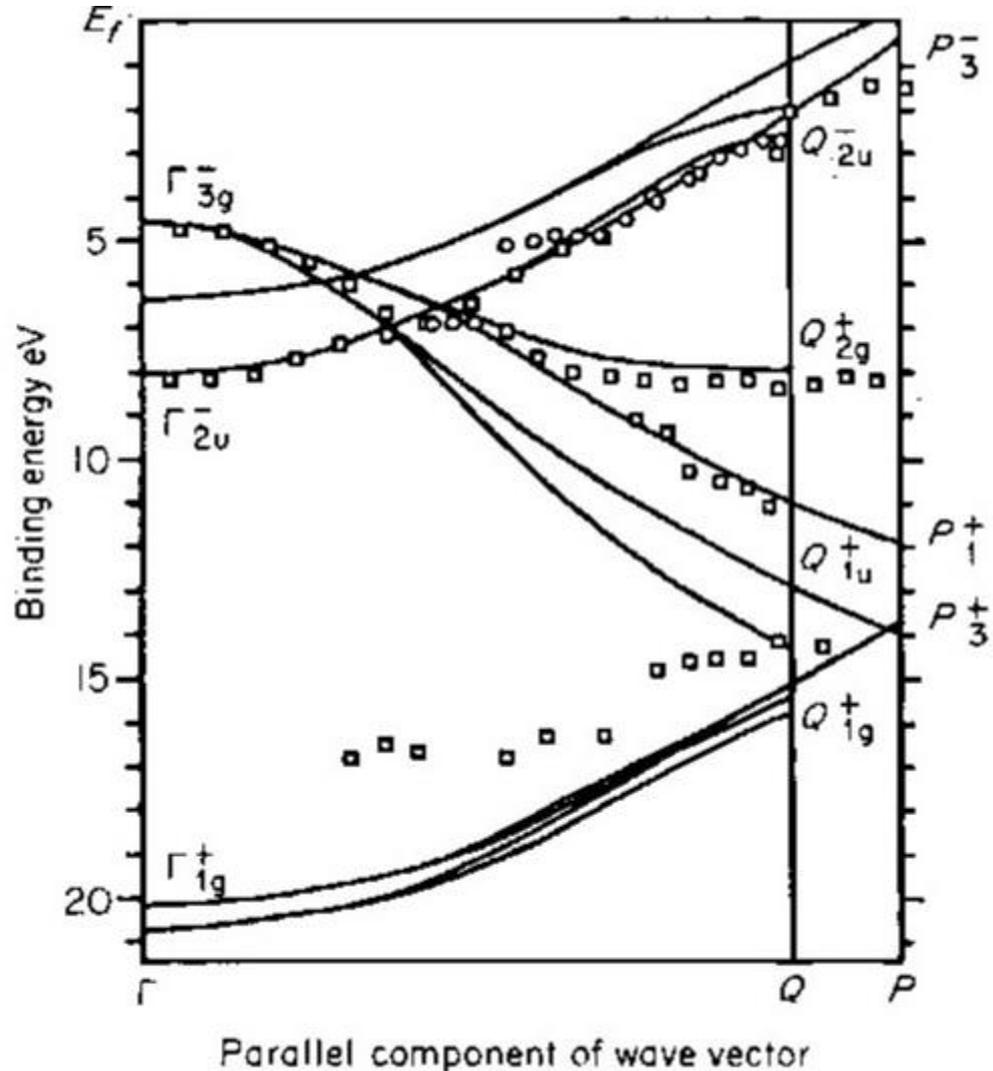
Far more useful is the direct $E \rightarrow \mathbf{k}$
(dispersion) measurement obtained
by angular photoemission studies.



By measuring the energy of the peak position with respect to the angle θ and using the expression $k_{//} \propto E \sin\theta$. The dispersion relation graph that plots the binding energy-wave vector dependence for graphite can be obtained.



The data obtained here (BE vs k_{\parallel}) for the first Brillouin zone agrees well with the calculated bands of Painter and Ellis (*G.S. Painter and D. E. Ellis, Phys. Rev. B1, 4747, 1970*) shown here.

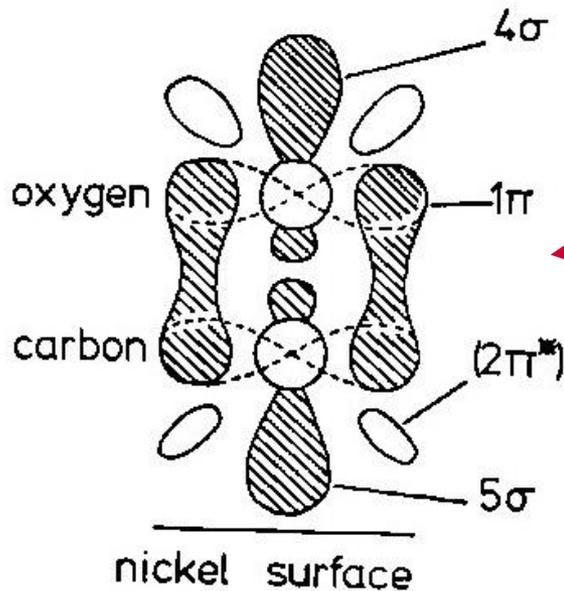




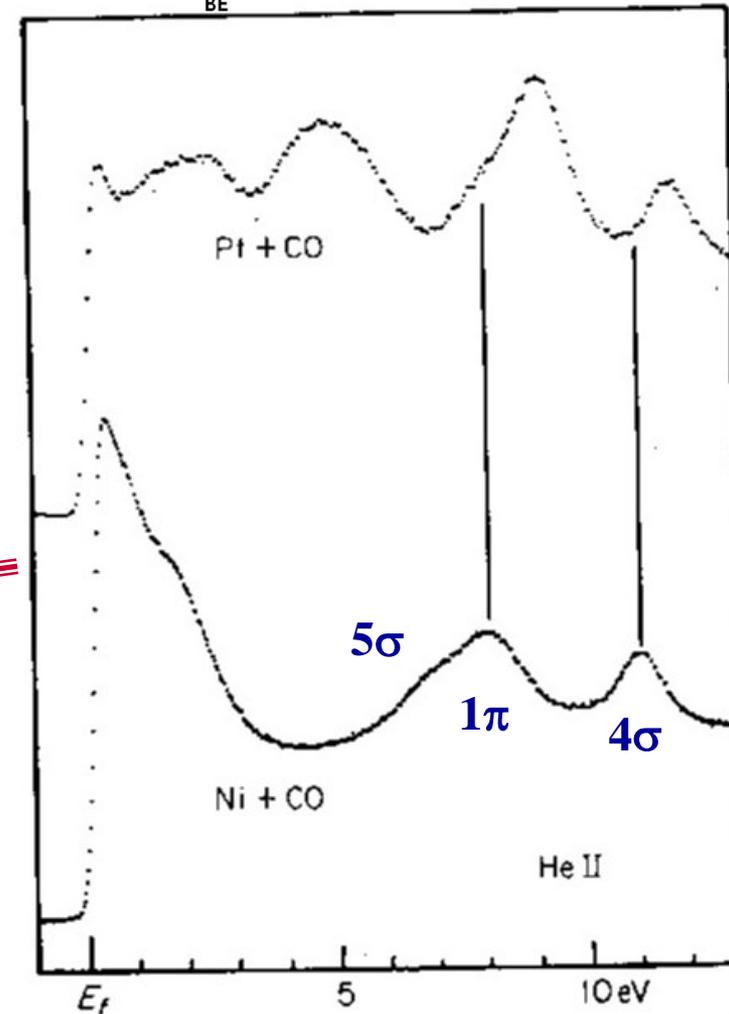
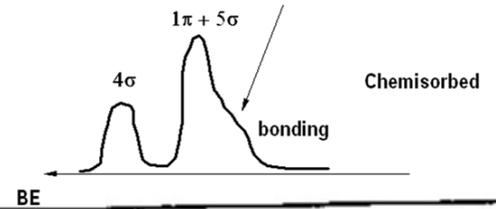
Adsorption on solids

Adsorption of a monolayer of CO on polycrystalline Pt and Ni.

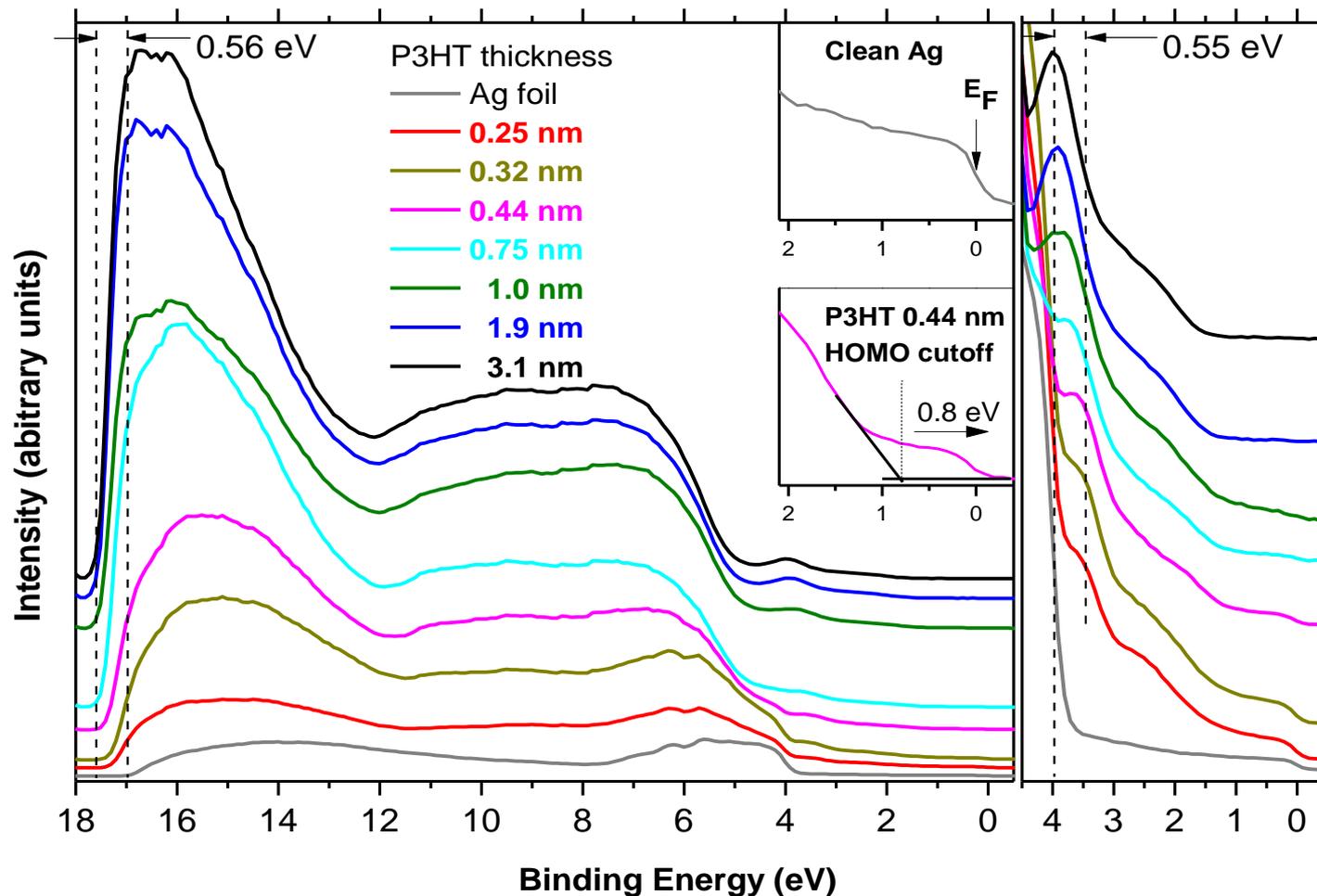
From this kind of data the following schematic of molecular orbitals could be obtained:



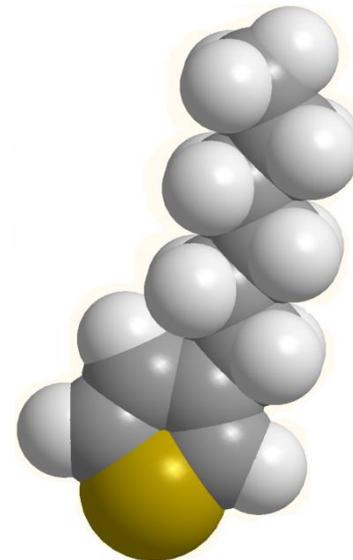
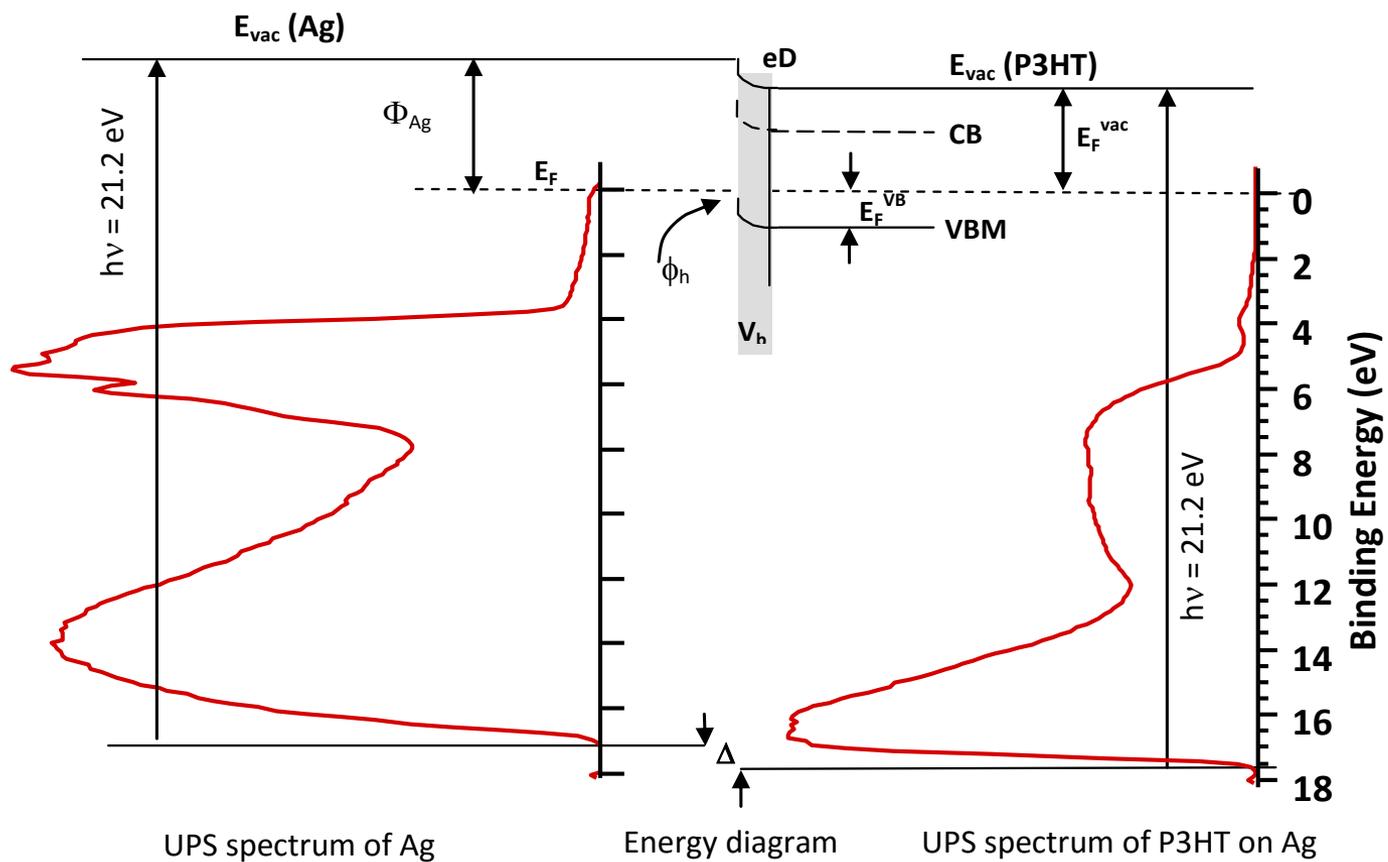
5σ , 1π and 4σ contribute to the PE spectrum



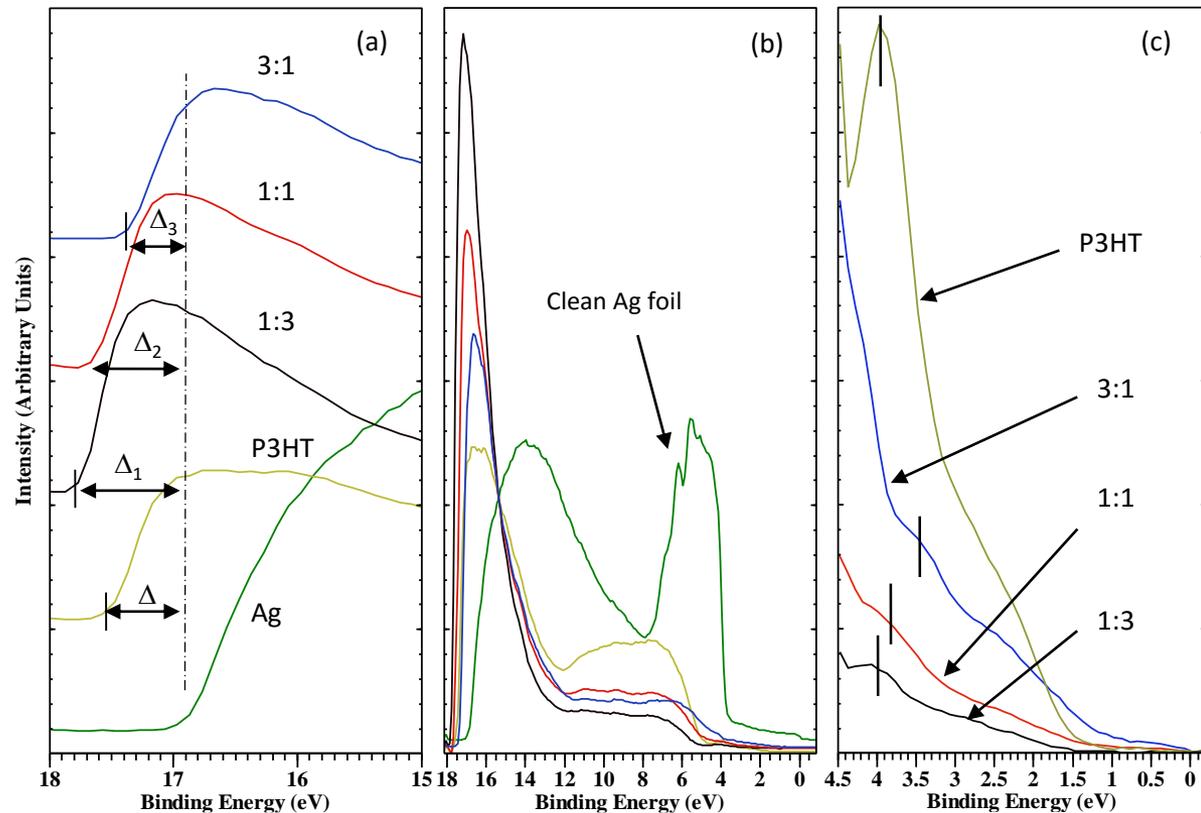
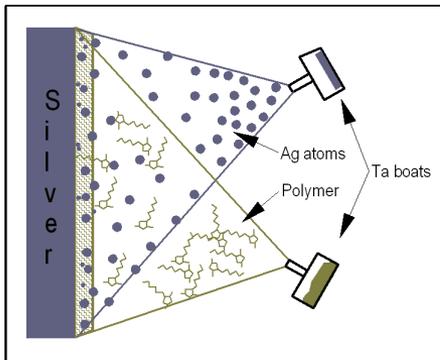
Polymer (P3HT) thermally deposited on clean Ag



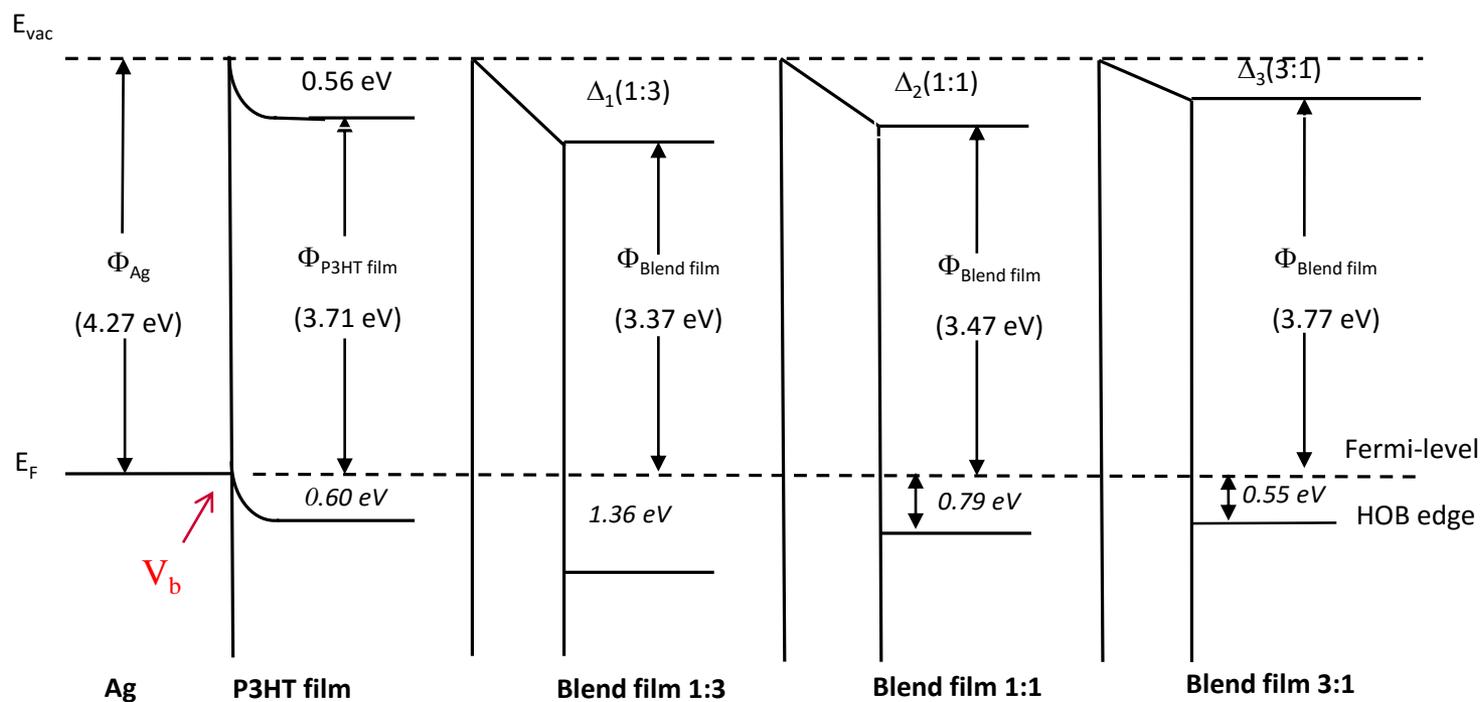
$\Delta = 0.56$ eV (interface dipole moment) and HOMO (VBM) = 0.55 eV



Hybrid Nanocomposites for Electronics Applications (P3HT-Ag nanoparticles)



It is possible to tune the value of the barrier height (hole injection) from 0.55 to 1.36 eV by simply varying the composition of the blend film (P3HT/Ag ratio ranging from 3:1 to 1:3) and changing the electronic properties of nanocomposite materials.

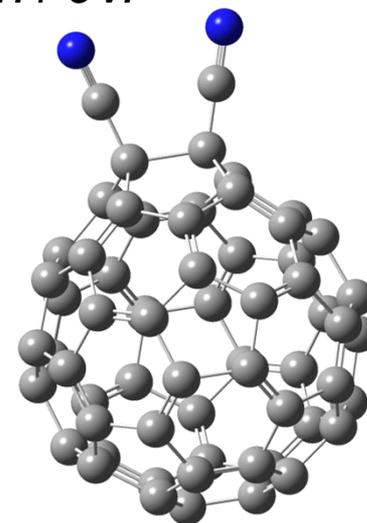
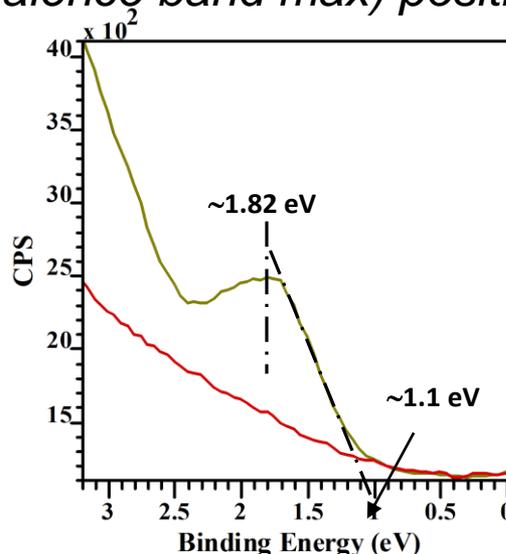
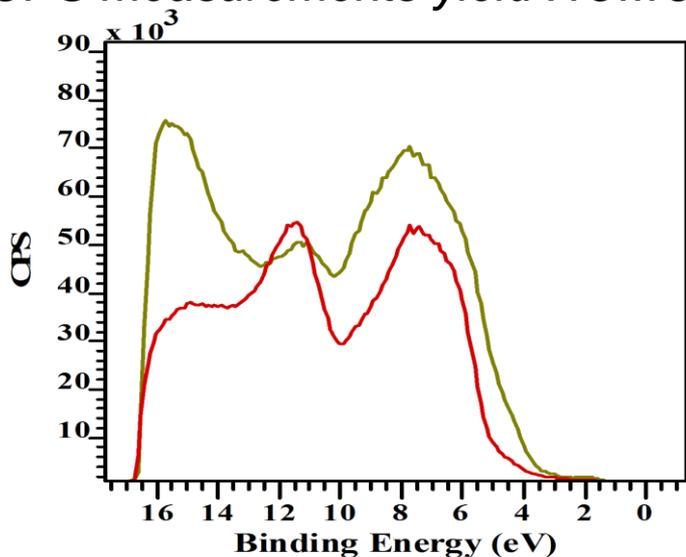


Combining UV-Vis measurements and/or computational chemistry to measure or calculate band gap of materials and UPS measurements of the HOMO (VB energy) a energy diagram can be easily drawn.

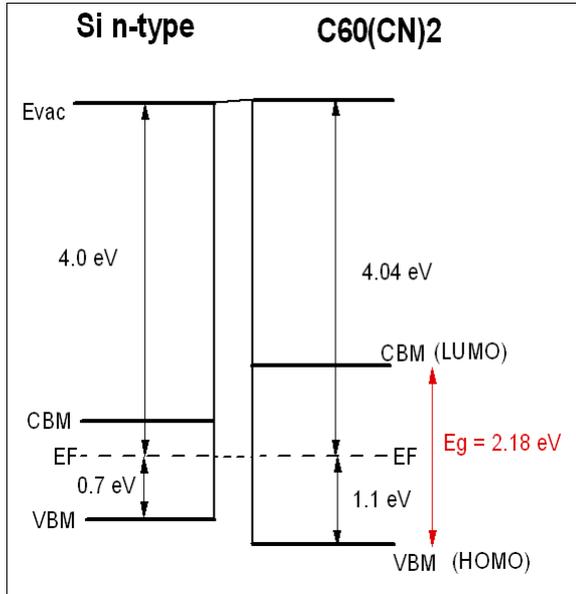
Example: $C_{60}(CN)_2$ deposited on semiconductor by spin coating for photovoltaic applications.

UV-Vis measurements give a band gap energy = 2.18 eV, Calculation (TD-DFT) gives 1.99 eV (isolated molecule, energy difference between HOMO-LUMO).

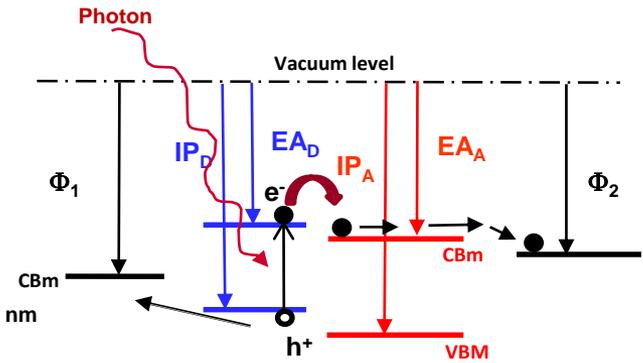
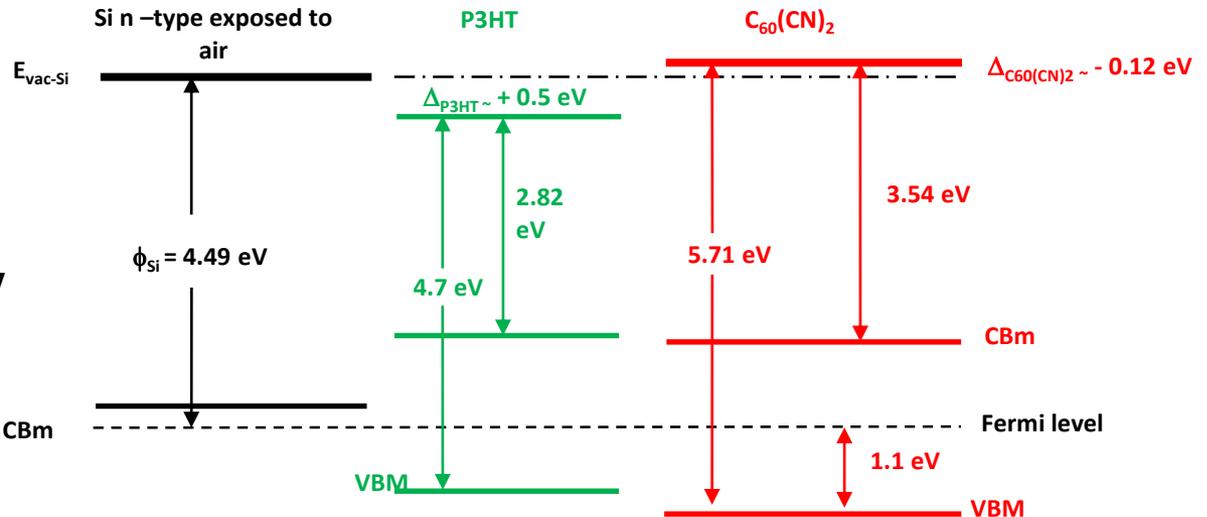
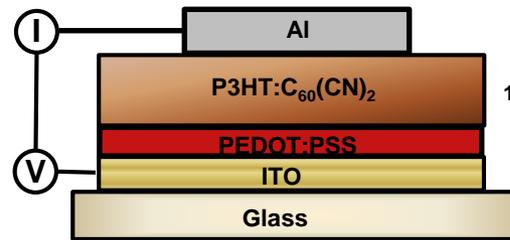
UPS measurements yield HOMO (valence band max) position at 1.1 eV.



Photovoltaic effect (PV)

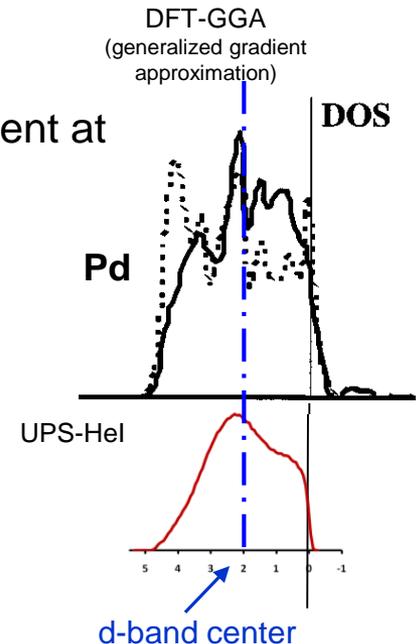


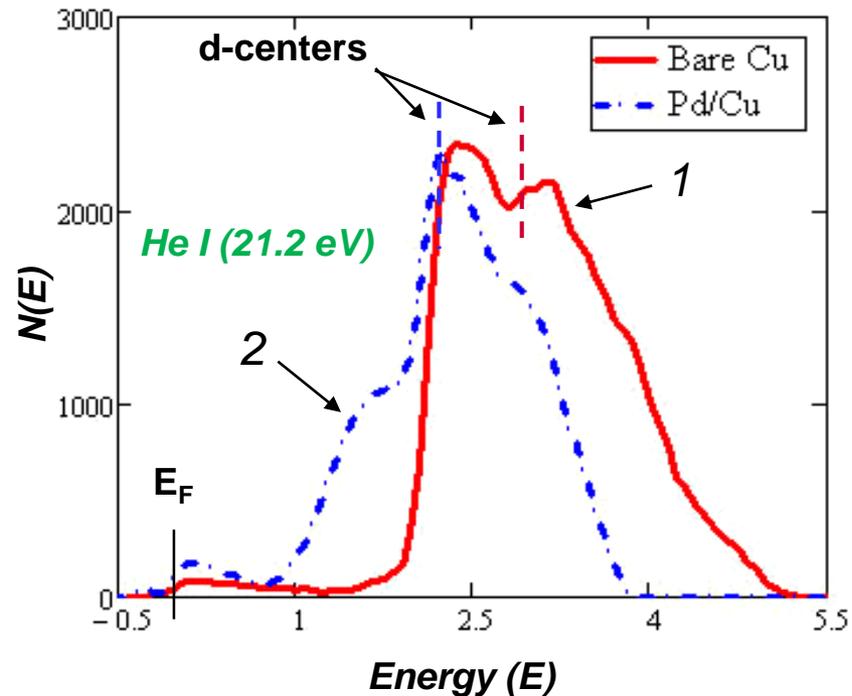
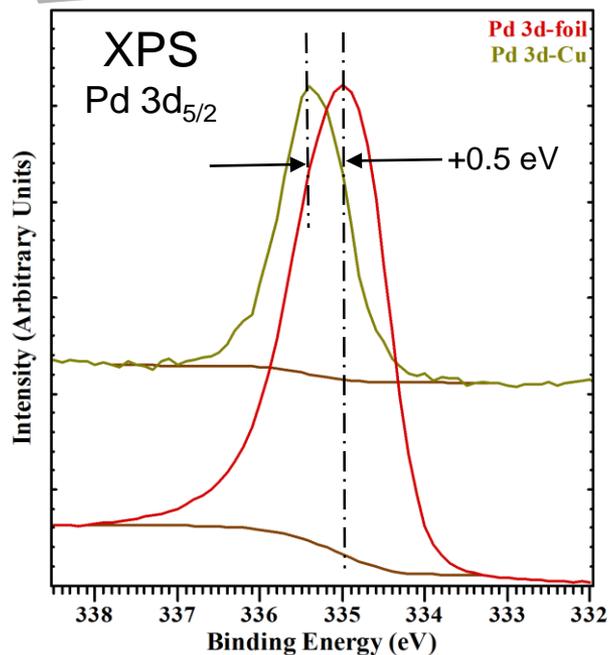
$HOMO_a = 1.1 \text{ eV} \Rightarrow IP = 5.54 \text{ eV}$
 $LUMO_a = 3.54 \text{ eV} \Rightarrow EA = 3.42 \text{ eV}$



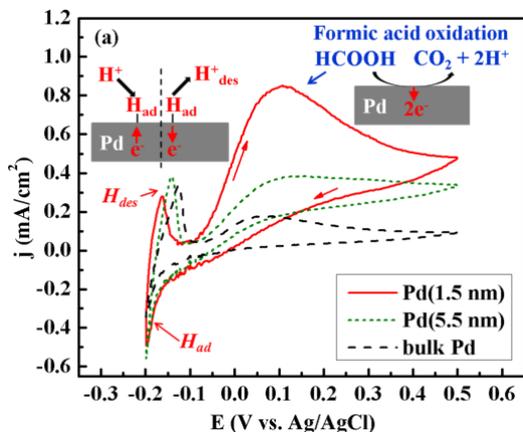
Catalysis applications (bimetallic systems) : XPS and UPS combined

1. Bonding between different materials leads to charge transfer, from surface and bulk atoms to maintain a common Fermi level. (e.g. *energy shift of d peak (XPS) and d-band center of substrate shift (UPS)*).
2. Typically elements having initially the larger fraction of empty states in their valence band gain electrons (Goodman et al. *Science* 257 (1992) 897). Behavior different than bulk alloys. (eg. For monolayer film of Pd (4d band: electron population 0.974—empty =0.026, Ni substrate 3d band filled 0.888 and empty= 0.112 → electrons will transfer from Pd to Ni)
3. Electronic perturbation => electron deficiency in surface atoms (less efficient at backdonation to adsorbate) => alters chemical properties. (e.g. *reduction of CO desorption temperature*)
4. Typically scales with the binding energy shift of overlayer Pd (XPS). *The larger the BE shift is, the greater is the decrease in temperature.*
5. d-band center shift predict or contradict the directionality of the charge Transfer (XPS data).





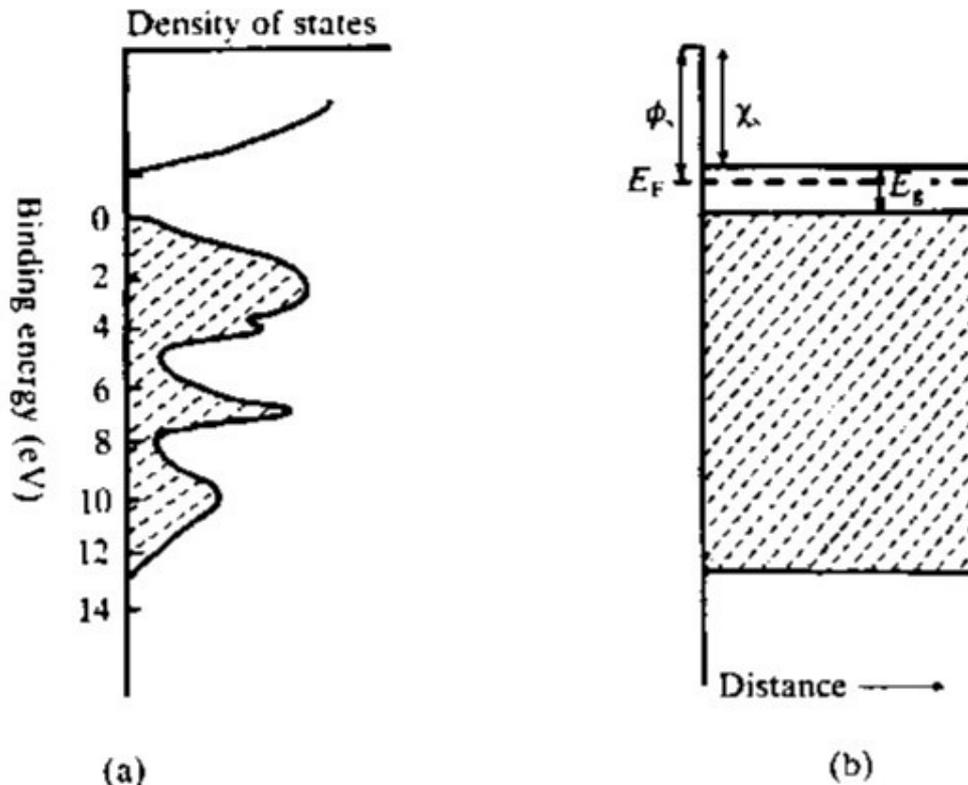
Resulting in a d-band center downshift of 0.7eV for the CuPd (blue dashed line) w.r.t. the Fermi level.



Metal- Semiconductor Contacts

2nd Edition E. H. Rhoderick and
R. H. Williams Oxford Science
Publications

Electron states in solids and at surfaces



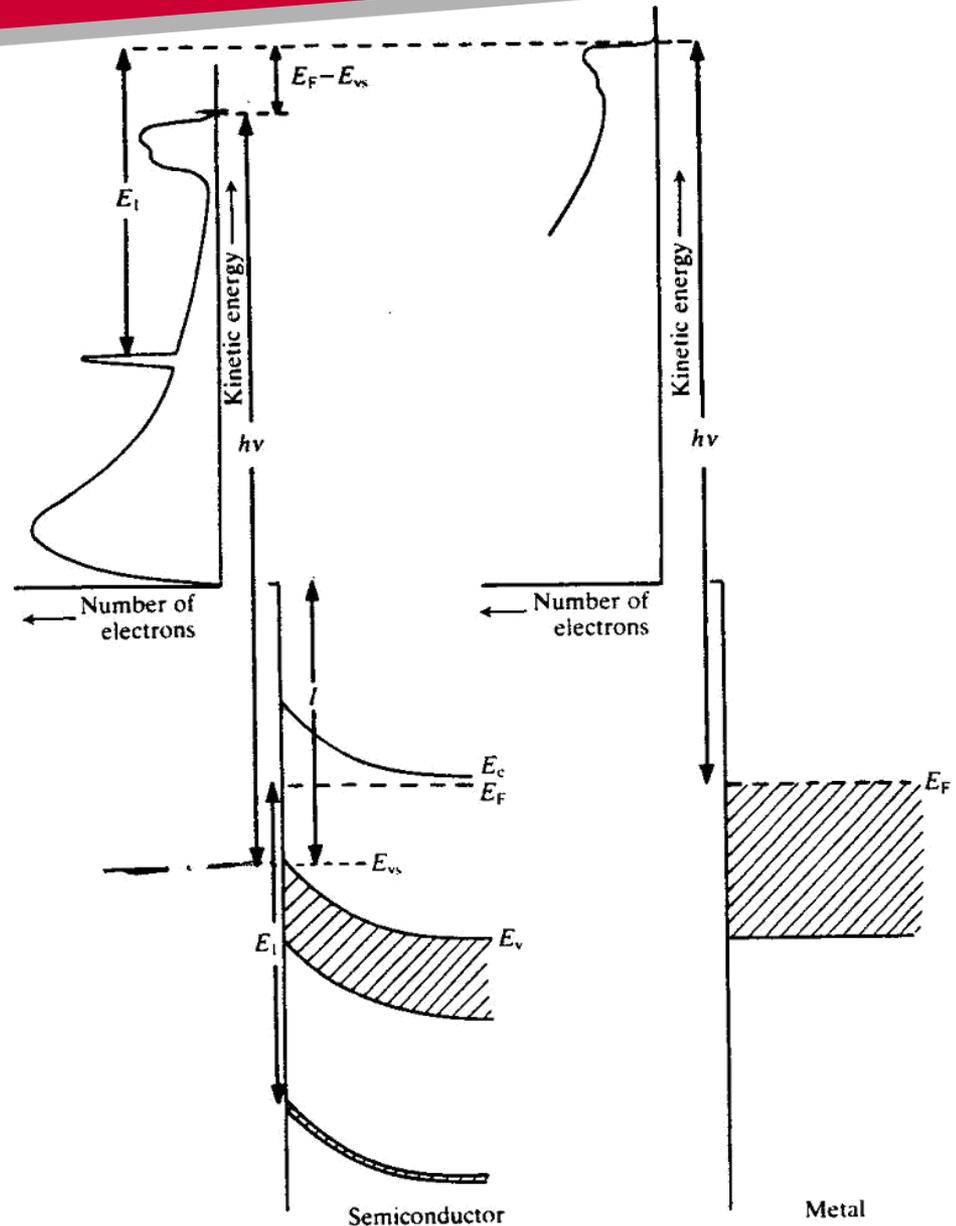
Density of states for n-type Si (a)
and band structure as a function of
distance (b).

The important surface parameter for semi-conductor is the electron affinity χ_s defined as the difference in energy between an electron at rest outside the surface and an electron at the bottom of the conduction band just inside the surface

I is the minimum energy needed to remove an electron from the VB. $I = \chi_s + E_g$

Typical PE spectrum for *n*-type SC

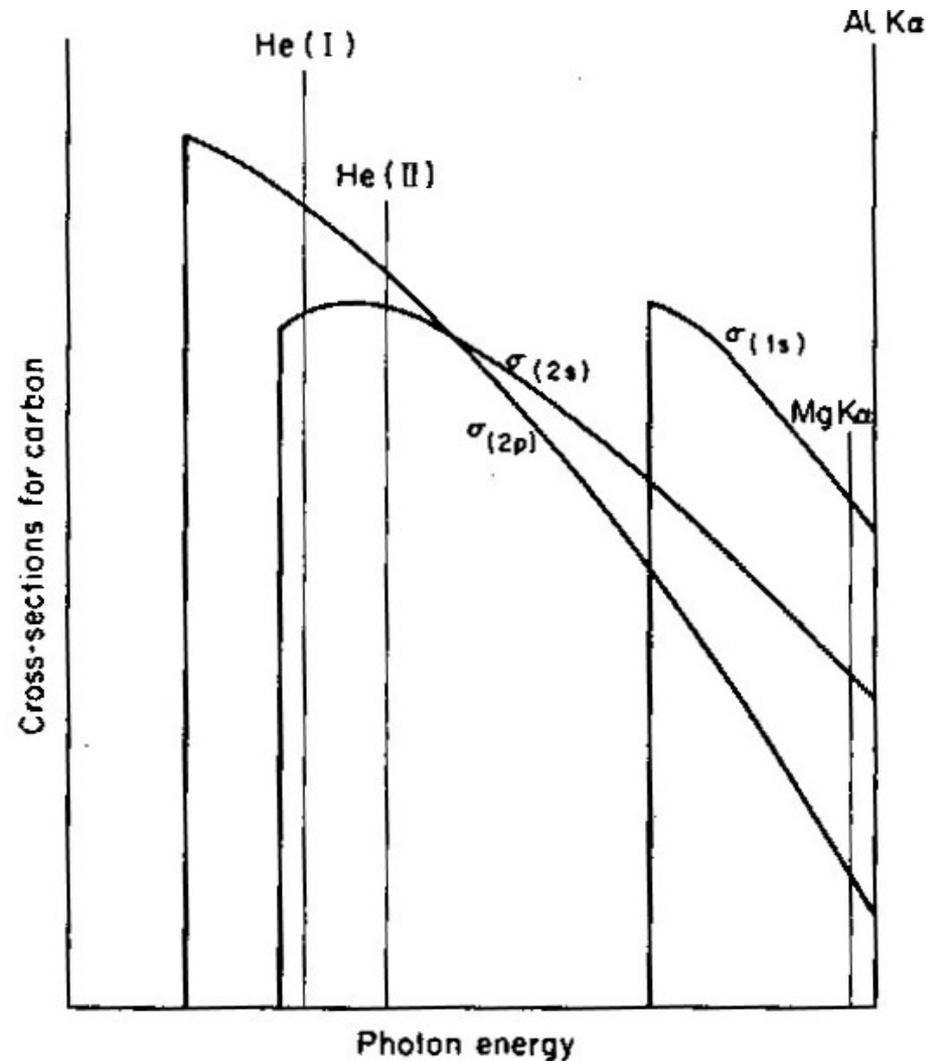
Band bending near the surface could be caused by either surface states on a free surface or a metal overlayer.



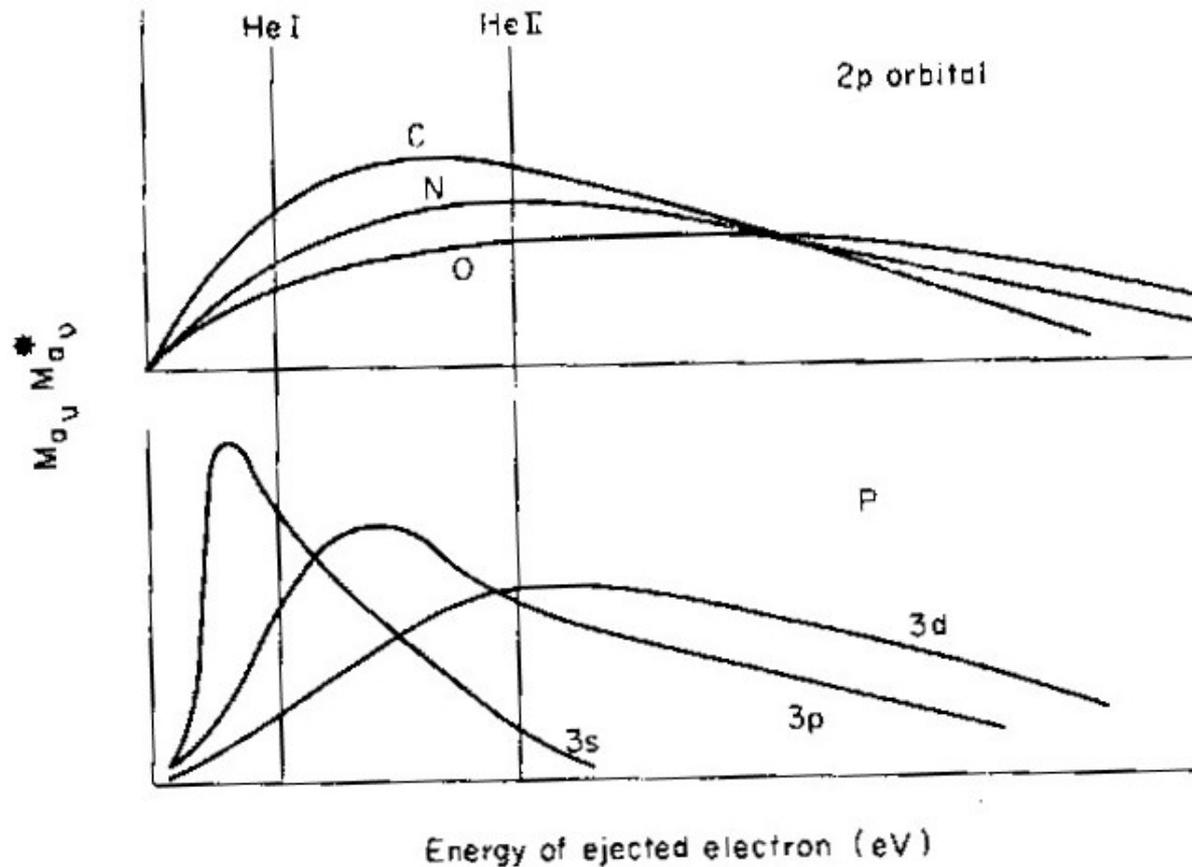
Photoionization Cross-section of C

(Theoretical variation of cross-section).

Likelihood of ionization of an electron from a given orbital in an atom.



1. Elemental dependency of the cross-section on photon energy for C, N and O.
2. Difference in cross-section for different orbitals for Phosphorus.



References

- Handbook of x-ray and ultraviolet photoelectron spectroscopy, edited by D. Briggs, Heyden&Son Ltd, 1977.
- P.M. Williams *same Handbook*. p.313 – 340
- M. Thompson, P.A. Hewitt and D. S. Wooliscroft *same Handbook*, p341 -379
- B. L. Sharma, Plenum Press, New York